Principles and Applications of Powder Diffraction

Edited by Abraham Clearfield, Joseph Reibenspies and Nattamai Bhuvanesh



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Dedication

As the saying goes, we all stand on the shoulders of the giants who preceded us.

I, Abraham Clearfield, remember the first lecture I heard where Linus Pauling described the structure of silicates and how it would be possible to understand life processes through solving the structures of biological molecules. I then had the good luck of working with one of Pauling's students, Philip A. Vaugan, for my doctorate. We learned our crystallography from books by Martin J. Buerger and solved structures using Patterson's method. I had the good fortune to hear the first presentation of Hauptman and Karle's direct methods at the ACA meeting held at the University of Michigan. To these and other leaders in the field I am grateful. Of course I would be remiss to not similarly dedicate this book to my wife Ruth who urged me to go on to earn a PhD and has always been my advisor and steadfast supporter.

I, Joseph H. Reibenspies, wish to dedicate this book to my parents, John and Claire, who gave me life and taught me to love learning. I also dedicate this book to my advisor and friend Oren Anderson, who taught me to love science. Finally I dedicate this book to my wife Lisa, who taught me the meaning of love and will always be the love of my life.

I, Nattamai Bhuvanesh, would like to dedicate this book to my parents, my brothers, my wife and kids, my teachers, and to all those who presented me with interesting challenges in science.

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Preface

Powder diffraction has been the staple analytical tool for chemists and materials scientists for more than 50 years. Powder diffraction is a tool to identify and characterize materials by analyzing the radiation scattering produced when the materials are illuminated with X-rays or neutrons. The patterns formed by the scattered radiation provide an abundance of information from simple fingerprinting to complex structural analysis. This work will introduce the reader to the world of powder diffraction, why it works and how it works and in the end what you can and cannot do with it. Some of the top researchers in the field of powder diffraction have collaborated on this work to bring the reader the most comprehensive source on the subject. The following paragraphs describe some of the information the reader may find in this work as well as a guide to how to best use the material that is presented.

Chapter 1 contains a short overview of the information obtainable using modern powder diffraction methods to stimulate the reader's interest. The main topics of later chapters (phase identification, structure solution, Rietveld refinement and non-ambient methods) will be introduced in outline using examples from the world of pharmaceuticals, organic and inorganic materials. The limitations of powder diffraction will be detailed as well as comparisons to single-crystal diffraction methods.

Chapter 2 contains all the theory required to understand later chapters and is written at a level suitable for readers following or with an undergraduate science degree. The basic phenomenon of diffraction from a periodic array leading to Bragg's law is developed. The more rigorous derivation of the Laue equations and their visualization via the Ewald sphere will then be introduced to help "demystify" the concept of the reciprocal lattice and its use in crystallography. The chapter describes the basic elements of symmetry and space groups in the solid state and the use of International Tables in powder diffraction problems.

Chapter 3 contains the practical information needed to perform successful powder diffraction measurements using laboratory, synchrotron and neutron sources. The generation of X-rays by typical laboratory sources such as sealed tubes and rotating anodes is discussed. Modern X-ray detectors including scintillation, solid-state, linear position-sensitive detectors and area detectors are highlighted. The general X-ray diffraction experimental setups, such as the Bragg–Brentano and transmission geometry which are of utmost importance is discussed. Focused, para-focusing and pinhole X-ray beams and their applications to normal and micro-diffraction is included. Sample mounting and measuring procedures are described. Chapter 4 discusses the general area of powder diffraction profile analysis, which includes factors, which affect peak intensity, position and shape. The resolution of the profiles along with a discussion of the various profile analysis functions, including the fundamental parameters approach are explained.

Chapter 5 introduces the reader to "non-laboratory" radiation sources. The chapter highlights the advantages of high brilliance synchrotron X-ray sources. A brief description of the state-of-the-art neutron instrumentation winds up the chapter and finally a discussion on the general uses of neutron powder diffraction concludes the chapter.

Chapter 6 describes some of the "classical" applications of powder X-ray diffraction to sample identification and determination of phase mixtures. Specialized fields such as high-throughput screening and combinatorial analysis are discussed. The use of whole profile analysis, including cell refinement and indices assignment is integrated with search-match methodology. Finally, an overview of the methods for quantitative analysis of crystalline and amorphous containing phases is given.

Chapter 7 describes the topics of structure solution from powder diffraction data. Each stage of the structure solution process is described using examples from both organic and inorganic systems. Both the potential power of the method and its inherent limitations are described. Particular examples of combined neutron and X-ray analysis are highlighted.

Chapter 8 covers topics on Rietveld refinement from powder diffraction data. Each stage of the refinement process is described using examples from both organic and inorganic systems. Both the potential power of the method and its inherent limitations are presented. Particular examples of combined neutron and X-ray analysis will be highlighted. Quantitative analysis by the Rietveld method is outlined.

Chapter 9 presents a number of more specialized/advanced topics not considered in detail elsewhere in the book. These include methods for size/strain analysis using powder diffraction, methods that have become more widely used in nano-technologies and non-ambient methods for studying materials as a function of temperature, pressure, humidity or chemical environment; *in situ* methods for studying phase transitions or chemical reactions by powder diffraction; and the opportunities for structural insight given by pair distribution function analysis.

The editors trust that the reader will find in this book, the elements of X-ray and neutron powder diffraction that are relevant to his or her particular needs.

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Chapter 1 An Overview of Powder Diffraction

Lachlan M.D. Cranswick

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1.1 Introduction

1.1.1 Paths of most resistance and paths of least resistance in pure and applied science

Much of the practicalities of scientific research, and the applied use of science, is in finding the most appropriate paths to reach a desired endpoint (Figure 1.1). The required judgment to discover and differentiate the paths and solutions in a timely manner that lead to a successful research program or industrial initiative can be quite subtle and extensive. Cliffs and walls are many, clear pathways few; constrained by "good, quick, cheap – pick any two." Thus, the aim of this text is to provide the reader with insight on where powder diffraction might provide possible pathways to assist the materials scientist: pathways rocky and smooth, cheaper and more expensive, quick, or on icy routes where haste is best made slowly. Every technique has inconvenient details and pitfalls. So that an inaccurate optimism or inappropriate gloss does not occur, pitfalls and limitations are emphasized in the text.



Figure 1.1 "The path of most resistance." (Image courtesy of Stephen Notley, creator of Bob the Angry Flower, http://www.angryflower.com/.)

1.1.2 The usefulness of powder diffraction to materials science

Depending on the intricacies within a program of research, or the requirements of an industrial process, a materials researcher will require access to a variety of scientific techniques. Each technique will have varying degrees of usefulness and importance depending on the research's requirements. Each technique will require a suitable knowledge, learning and expertise to operate at dexterity commensurate with the difficulty of the scientific objectives. Each technique has the potential to provide useful pathways to help reach a successful conclusion.

A major emphasis of materials science is in understanding the elemental compositions and corresponding atomic structures present in materials of interest. This knowledge confirms a material's purity and suitability for use, and allows explanation for its properties and performance. Just as chemical elements form a plethora of compounds, so a compound may pack in different arrays to form a variety of distinct crystal structures (known as polymorphs or phases). An example is carbon, which forms a variety of phases, where the two most commonly known phases are graphite and diamond (Figure 1.2). Elemental composition and physical characteristics such as color and hardness might differentiate phases when encountered in pure form. When in mixtures or reacted with other materials, identification of phases based on physical characteristics or elemental composition can quickly become impossible.

Powder X-ray diffraction (PXRD) offers a convenient method to characterize materials via their constituent crystal structures. When a crystal containing regular repeating arrays of atoms is irradiated by a monochromated X-ray beam, it generates a unique fingerprint in the form of diffraction peaks. By this diffraction process, a powder diffractogram is used to identify crystalline components of a sample. Figure 1.3 shows an example where powder diffraction can easily and unambiguously identify the two crystalline forms of titanium



Figure 1.2 Crystal structures for two phases of carbon, (a) diamond with polyhedra showing the 3D tetrahedral co-ordination of the carbon and (b) graphite with unit cell displayed and a plane highlighting the 2D sheets of carbon. (Crystal structures drawn by lan Swainson using the CrystalMaker software.)



Figure 1.3 (a) Crystal structure of anatase (TiO₂) with unit cell shown using dotted lines, (b) corresponding simulated powder X-ray diffractogram of anatase at Cu X-rays wavelength (1.54056 Å), (c) crystal structure of rutile (TiO₂) with unit cell shown using dotted lines, (d) corresponding simulated powder X-ray diffractogram of rutile at Cu X-rays wavelength, (e) corresponding simulated powder X-ray diffractogram of 50:50 by volume mixture of rutile and anatase at Cu X-rays wavelength. The crystalline phase responsible for each peak in the diffractogram is marked as "A" (anatase) or "R" (rutile). (Crystal structures drawn by Ian Swainson using the CrystalMaker software, patterns calculated using PowderCell.)



Figure 1.3 Continued.

dioxide, rutile and anatase, despite them being of identical elemental composition (TiO₂). With modern, optimized diffraction hardware and analysis software, phase identification of a routine sample, starting from grinding it to a powder to complete analysis, can be performed in the order of 5–15 min, where the actual data collection may take in the order of a minute or two depending on the diffractometer configuration and detector. Figure 1.4a shows an example of a modern commercial powder X-ray diffractometer goniometer in Bragg–Bretano reflection geometry mode, with X-ray tube housing on the left, single sample



Figure 1.4 (a) Goniometer of modern commercial powder X-ray diffractometer in Bragg–Bretano reflection geometry mode and multi-element detector. (Photograph courtesy of PANalytical.) (b) A modern commercial microdiffractometer with 2D detector, including computer-controlled translators for 2D phase mapping. (Photograph courtesy of Bruker AXS.)

stage in the rotation center of the goniometer and multielement detector on the right. An installed system would include an X-ray generator, and a fully interlocked radiation enclosure consistent with radiation protection regulations. Figure 1.4b shows a commercial microdiffractometer with 2D detector, which can non-destructively obtain powder diffraction patterns of small targeted areas and 2D phase maps from samples such as mineralogical thin sections, metals, artworks, forensic materials, corrosion layers, deposits, and so on (see Sections 1.3.2, 1.6.2, 1.7.3, 1.7.10 and 1.7.16).

The above describes a routine and common usage of PXRD for phase identification and is elaborated in Chapter 6. Specialized use of powder diffraction can quantify phase amounts (Chapters 6 and 8); solve crystal structures (Chapter 7); and refine crystal structures (Chapter 8); determine micro-structural characteristics such as crystallite size, shape and strain (Chapter 9); identify the spatial distribution of phases down to the micron level using mapping microdiffraction (Chapter 3); and investigate phase stability and reactions under a range of different conditions such as time, temperature, pressure and atmosphere (Chapter 9). Laboratory based X-ray diffractometers are most commonly used for diffraction analysis, but electrons, and non-laboratory sources such as synchrotron X-rays and neutrons can also be applied in cases where they offer distinct advantages (Chapter 5).

Modern powder diffraction is computer intensive and requires a data analysis capability. A variety of general and specialist diffraction analysis software is available from commercial vendors, or freely available via the Internet. As is re-emphasized below, much of this software incorporates the expertise of their authors to an extent where a new user of diffraction can apply it to many nontrivial problems at the push of a button. A list of X-ray powder diffraction software is described in Appendix A.1.

1.2 Range of fields using powder diffraction

The usefulness of powder diffraction ranges throughout all areas where materials occur in the crystalline solid state. Uses for powder diffraction are found within the following fields and beyond:

- 1 Natural Sciences
- 2 Materials Science
- 3 Pharmaceuticals
- 4 Geology and Petrochemicals
- 5 Engineering
- 6 Metallurgy
- 7 Forensics
- 8 Conservation and Archaeology

Applications are elaborated in Section 1.7.

1.3 Advantages of powder diffraction

Potential users of powder diffraction are not immune from being busy in their working hours. Therefore, any technique wishing their attention must quickly justify itself and its

potential. Some of powder diffraction's advantages are described below, with other applications in Section 1.7. The two advantages first listed (Sections 1.3.1 and 1.3.2), may be putting the cart before the horse of more simpler and common usage of PXRD. The justification for this is that many readers may be more familiar with the laboratory powder diffraction technology of ten to twenty years ago. The technology has changed greatly, and the first two stated advantages reflect this.

1.3.1 Continuous on-line XRD analysis (COXA) for initial and exploratory laboratory solid-state synthesis

Full fathom five thy father lies, Of his bones are coral made: Those are pearls that were his eyes, Nothing of him that doth fade, But doth suffer a sea-change Into something rich & strange

Ariel sings, from The Tempest by William Shakespeare (1564–1616)

With the above verse, Shakespeare's Ariel could just as well be reciting an incantation for a solid-state synthesis undergoing a sea-change into new things rich and strange. Similar to an incantation, much of what occurs within the furnace or vessel of modern solidstate synthesis may be poorly characterized or unknown. The starting materials are mixed together, reaction conditions selected, reaction started, continued, stopped and the product analyzed. Most often the analysis uses a powder X-ray diffractometer to identify desired or undesired, crystalline reaction products. The scientific richness occurring within, that could guide the materials scientist, is obscured from view. Many of the methods used to follow a solid-state synthesis (i.e., thermal gravimetric analysis), can provide information that an event of some sort is occurring, but few details as to the state of the phases present, whether an impurity or a desired product can be ascertained. Therefore, a consideration for the materials scientist is how to obtain a clearer picture of phase formation during solid-state synthesis. The following suggests such a method.

As diffraction methods provide a direct measure of crystalline phases present, it can prove powerful when routinely integrated into the initial exploratory mode of solid-state synthesis. For solid-state synthesis with the aid of modern diffraction technology, combined with appropriate *in situ* apparatus, reactions can be continuously followed and tweaked on-line to gain a clear view of any intermediate phases being formed, and conditions required to achieve the final crystalline product. Reactions competing with desired reaction pathways can be identified at the point they interfere and parameters manipulated to gain an indication if a clean synthesis is possible. Continuous on-line XRD analysis (COXA) can also be applied to control industrial processes as shown in Section 1.7.2.

This application is practical due to the ability of modern commercial powder diffractometers to collect quality diffraction data for phase identification in seconds to minutes. Figure 1.5 displays this, using an example provided by Mario Bieringer of the University of Manitoba, of performing the synthesis of ScVO₄ in air from NH₄VO₃ + Sc₂O₃ in the XRD in a continuous on-line mode. Figure 1.5a shows the diffractometer hardware with a multi-element detector (that can collect data up to 2 orders of magnitude faster than a



Figure 1.5 (a,b) PANalytical X'Pert Pro diffractometer with X'Celerator multi-element detector, with Anton Paar HTK2000 high-temperature furnace attachment used at the University of Manitoba to characterize solid-state synthesis. (c) Two intermediate reactions described in the text at 175°C (labeled "1"), 250°C (labeled "2") are evident with the final product produced at 700°C (labeled "3"). (Photographs and figure courtesy of Mario Bieringer.)

traditional point counter) and an attached furnace. Figure 1.5b shows the furnace at temperature. In this example, data are collected using 10 min scans collected from 10° to 90° 2θ , with 25° temperature intervals, where Figure 1.5c shows the resulting diffraction data.

At 175°C ammonium metavanadate decomposes into vanadium pentoxide hydrate and ammonia gas is released.

$$2NH_4VO_3 \xrightarrow{175^{\circ}C} V_2O_5 \cdot H_2O + 2NH_3$$
(1.1)

At 250°C vanadium pentoxide hydrate forms vanadium pentoxide and releases water

$$V_2O_5 \cdot H_2O \xrightarrow{250^{\circ}C} V_2O_5 + H_2O \tag{1.2}$$

At 700°C vanadium pentoxide reacts with scandium oxide resulting in the formation of scandium vanadium oxide.

$$V_2O_5 + Sc_2O_3 \xrightarrow{700^\circ C} 2ScVO_4 \tag{1.3}$$

More complicated syntheses can be studied including those involving gases flowing over the sample (Lundgren *et al.*, 2006). Other *in situ* stages are available commercially. For non-ambient stages that cannot be purchased commercially, custom equipment (unique or described in the literature) can be constructed in-house where the capability exists. Where it might not be obvious how a solid-state synthesis method can be integrated with continuous on-line XRD, the art would be to work out how.

As the above example by itself might appear contrived, Figure 1.6a,b shows the XRD data of a COXA run where thermal gravimetric analysis (TGA) and diffraction data was used to reveal the existence of an InVO₃ phase (a bixbyite structure type, Figure 1.6c) via a reaction of In_2O_3 with NH_4VO_3 in a CO/CO₂ buffer gas (Lundgren *et al.*, 2006). This also displays the sweet-spot to achieve a pure InVO₃ synthesis under these gas conditions at 550°C. Using this information, multiple gram batches of the InVO₃ can be produced with 100% reliability in the laboratory, on demand, for other experimental purposes.

A COXA enabled solid-state synthesis laboratory would involve installation of at least one powder X-ray diffractometer optimized for COXA. Whether the advantage of COXA analysis finds favor with the great mass of materials scientists involved in solid-state synthesis remains to be seen. Nevertheless, it is one of the major modern advantages of powder diffraction for materials science.

1.3.2 Microdiffraction of small sample areas and 2D spatial diffraction mapping of samples

A common assumption for powder diffraction is that samples are ground before running in the diffractometer. This is not the case for tiny microsamples. Traditionally, for obtaining powder diffraction data of tiny samples, a grain would be extracted from the total sample matrix, and mounted on equipment such as a film-based Gandolfi camera. However, if it is important that non-destructive analyses occur, or that spatial arrangements of phases within the sample are important, the above methods are inadequate. These include samples involving corrosion layers (Figure 1.7a,b), grain boundaries (Figure 1.7c,d) and some types of deposits found within industrial plants, where just knowing the phases present is not that useful unless it is also known where the phases are located in the sample matrix. In other cases, the analysis of artwork or forensic samples may result in part of the object being destroyed if the sample is extracted, thus providing incentive for non-destructive analysis of tiny, targeted areas.

Laboratory X-ray microdiffractometers allow the analysis of sample volumes in the 10s of micron length scale. Figure 1.8a,b shows a microdiffractometer produced by the Rigaku Corporation installed at the Smithsonian Institution in Washington DC. The diffraction



Figure 1.6 (a,b) Contour plots of powder X-ray diffractograms from 25°C to 1000°C using 25°C increments showing the synthesis of InVO₃. Contour levels are plotted using constant increments. Diffraction peaks are labeled as follows: $InVO_4$ = open circles, $InVO_3$ = solid circles, In_2O_3 = open squares, V_2O_3 = open diamonds. The In_2O_3 impurity in the starting material is indicated with a star and (c) $InVO_3$ bixbyite structure of (In/V)– O_6 octahedra determined from powder diffraction data. (Figure courtesy of Mario Bieringer.)

setup includes a wide-angle image plate detector and X–Y sample stage mounted on an oscillation stage. Combined with a rotation of the sample by the oscillation stage, the large area of the image plate allows good powder diffraction data to be collected, even on a single crystallite embedded in the larger sample matrix (Figure 1.8c,d). Where optical microscopy, SEM or microprobe has identified areas of interest in a sectioned sample, the sample can be transferred to the microdiffractometer for phase identification. Using a



Figure 1.7 (a) Optical micrograph of a corrosion layer in a heavily cycled positive lead-acid battery plate and (b) SEM micrograph of two corrosion layers in a heavily cycled positive lead-acid battery plate. A 0.1 mm scale is visible. Phases present in the corrosion layer can potentially include several forms of PbO₂ (including scrutinyite and plattnerite), of PbO (litharge or massicot), and a variety of intermediate lead oxides. (Micrographs courtesy of Tony Hollenkamp.) (c) MgO refractory brick showing a number of grains and grain boundaries. A 100 μ m bar is visible (Micrograph courtesy of Robert Flann.) and (d) high calcium silicate MgO refractor brick. The calcium silicate appears as bright regions between MgO grains. Dark areas are air-filled pores. (Micrograph courtesy of Steven Tassios.)

computer-controlled X–Y stage, 2D phase maps can be generated and overlaid with elemental composition maps. Such functionality is useful for studying a range of problems where chemical information provided by SEM or microprobe does not resolve phase ambiguity. Unpolished uneven samples can be mounted and particles on the surface analyzed. As described in Sections 1.6.2 and 1.7.16, a modern single-crystal system with 2D detector can be used as a microdiffractometer of sorts.

One caveat of collecting 2D maps, is that it can be more efficient to generate an elemental map using an SEM or microprobe. The microdiffractometer is then used to focus only on points of interest identified by the chemistry map. Another caveat, where diffraction mapping appears justified, 2D maps can generate such large amounts of diffraction data, that



Figure 1.8 (a,b) Rigaku Corporation microdiffractometer with wide-angle image plate detector installed at the Smithsonian Institute in Washington, DC, (c) example of raw 2D image plate data with spotty diffraction rings – an effect of poor particle statistics, typical of much microdiffraction data. Oscillation or spinning of the sample in combination with a wide area 2D detector allows (d) the integrated 1D data to have overall representative intensities. (Photographs and data courtesy of Jeffrey Post, Smithsonian Institution.)



Figure 1.9 Data from 2D microprobe mapping as displayed in the Chimage software. (a) Mg/Ca/Si composite Electron Probe MicroAnalysis (EPMA) map of a magnesia refractory sample, (b) Ca–Si scatter plot for all the data points in the composite map. The two distinct clusters are identified and labeled as C2S (dicalcium silicate) and C3S (tricalcium silicate) and (c) a "phase" map constructed from the composite EPMA map and elemental scatter plots. While elemental microanalysis identifies the presence of C2S and C3S in the grain boundaries, there are a variety of possible crystal structures consistent with these chemical compositions that would affect suitability and performance of the refractory. (Figure courtesy of Steven Tassios.)

conventional analysis software may have difficulty in presenting the hundreds to thousands of diffraction datasets to the analyst in usable manner. The users may therefore need to develop their own custom software to display the data in a way they find optimal, especially if combining 2D phase maps with maps generated by other spatial mapping analysis (e.g., microprobe, qualitative elemental maps using an SEM, cathodoluminescence, etc.). Many of these analysis packages tend to be internal to research institutes, and focused on visualizing data from techniques that can use 2D mapping, not specifically diffraction.

An example of an internal 2D mapping program is the Chimage software developed within the CSIRO Division of Minerals Products (now CSIRO Minerals) in Melbourne, Australia (Macrae *et al.*, 2005; Harrowfield *et al.*, 1993). Figure 1.9a shows a chemical 2D

map within Chimage of a magnesia refractory sample (Tassios, 2000). A variety of phases including calcium silicates can occur within the grain boundaries that affect refractory performance. Two possible phases are monticellite (CaO·MgO·SiO₂) and merwinite (3CaO·MgO·2SiO₂), which melt at 1495°C and 1575°C, respectively. This has implications for magnesia refractories lining iron steelmaking vessels operating at about 1600°C. Figure 1.9b shows a chemical cluster map where two distinct clusters due to the presence of C2S (dicalcium silicate) and C3S (tricalcium silicate) are evident, which is applied to the map in Figure 1.9c. However, there are different crystal structures/polymorphs of C2S and C3S, which diffraction methods would need to establish. There is no corresponding diffraction analysis due to a very common reason: mapping microdiffractometers are rare compared to microprobes and SEMs. Thus, the potential of mapping microdiffraction for much industrially relevant research is currently not well utilized.

Most laboratories would more urgently need a standard Bragg–Brentano PXRD to run bulk samples than a microdiffractometer. A microdiffractometer can be a larger capital purchase compared to a standard Bragg–Brentano PXRD. However, if the purchase case is successful, a microdiffractometer can generate considerable amounts of warm appreciation from its users. Much of this is due to the apparatus being able to handle research and industrial problem-solving situations that can only be dreamt of without it (see Sections 1.6.2, 1.7.3, 1.7.9, 1.7.10 and 1.7.16).

An alternative to an X-ray microdiffractometer is the use of a scanning electron microscope (SEM) with a backscatter diffraction camera performing phase identification using electron backscatter diffraction (EBSD) (Michael, 2002; Maitland, 2004; Michael and Goldstein, 2005). This technique is also termed backscatter Kikuchi diffraction (BKD). This instrument can perform phase identification involving multiple phases and 2D mapping down to micron and sub-micron sample areas. Knowledge of chemistry, obtained from the SEM, and effective databases can be required as part of phase identification. EBSD is stated as being more commonly used for automated pole figure/texture mapping. Personal communications indicate EBSD is not as commonly available as would be expected, but is continuously improving and getting better appreciated in the electron microscopy community. For readers who may need phase identification of microsamples, besides evaluating any available microdiffractometers, they are also advised to call or visit the local microscopy laboratories to check out the facilities. At present where EBSD does not exist, it may be worth the time to collaborate with local microscopy personnel to get it implemented.

1.3.3 Fast phase identification of crystalline phases

With minimal training to the operator, a newly installed powder diffractometer can be used for routine phase identification. Usually, a sample is ground into a powder in a mortar and pestle, placed into a diffractometer sample holder, inserted into the diffractometer, and followed by an appropriate data collection optimized for phase identification. On completion, a phase identification ("search-match") program is run with which the user interacts to identify the phases present in the sample. Figure 1.10 shows a phase identification result for a sample of calcium fluoride (CaF₂/fluorite). Phase ID of pure materials can be



Figure 1.10 Phase identification of calcium fluoride (CaF₂/fluorite) using the XPLOT for Windows searchmatch program with the ICDD PDF-2 powder diffraction database.

trivial to perform on a modern diffractometer equipped with search-match software for phase identification. Qualitative elemental analysis using scanning electron microscopy (SEM) or X-ray fluorescence (XRF) should still be considered, even for samples considered trivial, as unwanted elements might have been incorporated into the crystal structures, or be present as a small amorphous phase insensitive to diffraction measurement. It is not unknown for components within fluxes (Cranswick *et al.*, 2003), solvents (Harlow *et al.*, 1999) or reaction vessels to be incorporated into crystalline phases, with the consequent potential for confusing a phase identification and crystallographic analysis if an elemental analysis of the reaction or crystallization products is lacking.

1.3.4 Can handle multi-component samples

As each crystal structure generates a unique fingerprint in the form of a diffraction pattern, mixtures of crystalline materials can be identified. The more complicated the mixture of phases, the more time and effort that may be required for phase identification. Different combinations of phases might provide an acceptable accounting of the diffraction peaks. To narrow down the range of possible phases, techniques such as *SEM* or *XRF* can be used to provide chemical information. Figure 1.11 shows a phase identification result for a powdered sample containing three phases: calcium fluoride (CaF₂/fluorite), aluminum oxide (Al₂O₃/corundum) and zinc oxide (ZnO/zincite). Refer to Chapter 6 for more detailed information on phase identification.



Figure 1.11 Phase identification of a multiphase sample containing roughly equal proportions of corundum, fluorite and zincite. The phases responsible for each peak is in the diffractogram are marked as "C" (Al₂O₃/corundum), "F" (CaF₂/fluorite) and "Z" (ZnO/zincite).

1.3.5 Study behavior of materials under a wide variety of conditions

Traditionally, and unlike the setup described in Section 1.3.1, users of powder diffraction often regard a non-ambient experiment as a special undertaking. As elaborated in Chapter 9, powder diffraction can study materials under a variety of conditions combining varying temperature, pressure and atmosphere including relative humidity, as well as wet-cell stages where fluid can flow through the solid phase material (Warr and Hofmann, 2003). Figure 1.12 shows a commercially available attachment for low-temperature laboratory PXRD that can take a sample from room temperature down to 11 K, while Figure 1.13 shows a commercial PXRD furnace stage for taking samples from room temperature up to 2300°C. Non-ambient diffraction is covered further in Chapter 9. The use of in situ methods removes the uncertainties associated with quenching, where the quenched phases may not be representative of the phases occurring at conditions of interest. Where required in situ apparatus is not commercially available or not described in the literature, the art is to create it. Examples of other styles of *in situ* stage are described further in the text, including: high magnetic fields in Section 1.7.8, applications of energy dispersive diffraction in Section 1.7.9, in situ acid leaching in Section 1.7.13, combined with a differential scanning calorimeter (DSC) in Section 1.7.14 and an in situ welding stage in Section 1.7.17.

1.3.6 Do more things with powder diffraction than you can poke a stick at

The point for this entry is that potential applications and uses of powder diffraction may only be limited by the creativity and needs of the materials scientist with a problem to



Figure 1.12 Low-temperature attachment for laboratory powder X-ray diffractometry with a range of 11–315 K (–251°C to 42°C). (Photograph courtesy of Oxford Cryosystems.)

solve. Advantages of powder diffraction can also be discerned from Section 1.7, dealing with applications of powder diffraction.

1.4 Limitations of powder diffraction

There is an aphorism which states that "you should learn to seize things not by the blade, which cuts, but by the handle, which saves you from harm" and continues that "a wise man gets more use from his enemies than a fool from his friends" (Gracian, 1647). Every technique has limitations, pitfalls and advantages (its blades and handles, enemies and friends). It is important to understand these before undertaking a program of materials research, so that a technique's controls may be grasped and used to productive effect; rather than it being mishandled where the research risks (figuratively) becoming a bit of a trainwreck. The advantages of a technique tend to explain themselves. However, limitations and pitfalls, when first encountered, unexpected or unappreciated, can result in a range of human emotions: befuddlement, confusion and frustration. Descriptions of friends, fools, enemies and angels not of our better nature, might seem rather melodramatic. Allegedly from a U.S. Army training notice, "when the pin is pulled, Mr. Grenade is not our friend." Similarly,



Figure 1.13 Furnace attachment for powder X-ray diffractometer with range from 298 to 2573 K (room temperature to 2300°C). (Photograph courtesy of Anton Paar GmbH.)

a mishandled piece of scientific apparatus is also not our friend, but to a trusting user, a machine's undesirable side might not easily show. Some of the more general limitations and pitfalls are given below, with more detailed information provided within the following chapters.

1.4.1 Requires appropriate diffraction equipment

Powder diffraction apparatus might all claim equality, but some are more equal than others. Undertaking a program of research involving powder diffraction may only be feasible in a desired timeframe if the appropriate equipment is available. While perseverance, time and diligence can potentially surface with old film or point detector-based diffraction equipment, diffraction technology has undergone radical changes within the last five to ten years. Multi-element detectors allow the fast collection of high-quality diffraction data at one to two orders of magnitude faster than a traditional single point detector. Prior to the commercial availability of two-dimensional area detectors and image plates, hours to days may have been required for obtaining a quality powder diffractogram on small grains and micro-samples. However, with this large area detector technology, now seconds to minutes may be adequate. With modern X-ray focusing elements and detectors, laboratory data collection previously considered impossible due to time expenditure or time required, sample and detector limitations may now require a day or a weekend of data collection time to



Figure 1.14 (a) Goniometer of a modern laboratory powder X-ray diffractometer set to collect data on a powder protein sample within a capillary and (b) the resulting diffraction data profiled using a whole pattern Le Bail fit. (Photograph and plot courtesy of PANalytical.)

be feasible. Figure 1.14a shows a laboratory goniometer setup to collect powder diffraction data on protein samples, where Figure 1.14b shows the resulting data (Prugovecki *et al.*, 2005). A few years ago, to analyze this type of sample in the laboratory would have been derided as ludicrous, but it is now feasible with modern laboratory diffractometers. Reproducible placement of ancillary equipment and optics allow the quick-change into other experimental configurations without the need for an expert diffractionist performing a tedious realignment of the instrument. An example of a commercial system optimized for fast phase analysis and handling a batch of samples via an automatic sample changer is shown in Figure 1.15a. Figure 1.15b,c show the modularity of these systems to other modes using different attachments without the need for realignment (also refer to the XRD systems within Sections 1.3, 1.7 and Chapter 3).



Figure 1.15 (a) Goniometer of a modern laboratory powder X-ray diffractometer with sample spinner, 45-position sample changer and multi-element detector. Modern diffraction systems of this type have the ability to exchange a series of attachments without the need for realignment. With the configuration shown, a typical high-quality dataset for phase identification can be obtained in less than a minute of data collection, (b) sample spinner, 15-position sample changer and detector, placed in transmission geometry and (c) system set for capillary measurements with capillary cooler/heater attached. (Photographs courtesy of PANalytical.)

1.4.2 Requires a critical mass of expertise commensurate to the difficulty of the research

The more complex a powder diffraction problem, the more specialized the scientific expertise is required to fully solve it. When default procedures fail to provide a fully adequate result, this may signal that a non-routine diffraction problem has been encountered, and that an original pathway to find a solution is required. If required human expertise is unavailable, there is little chance that work will progress in a timely manner as specialist scientific expertise can be difficult to quickly bootstrap from zero. This lack of expertise can be obtained over time by hiring in the expertise, collaboration, sending staff on sabbatical, and internal career development programs. Above all, there needs to be a work atmosphere of un-panicked consistency, so that an area of scientific expertise of real and significant depth and substance can be developed. As with other areas of science, a useful, in-depth expertise in powder diffraction cannot be picked up in short flurries of hand waving enthusiasm and manic dancing frenzies.

Figure 1.16 shows a simplified flow diagram of what the author believes differentiates a (i) trivial, (ii) nontrivial and (iii) difficult powder diffraction problem. Such designations are a moving goalpost, where the difficult problems of yesterday are considered the trivial problems of today; and where problems of yesterday thought easy or solved, can turn out to be more involved. As is discussed in Section 1.6.1 in comparing single crystal vs. powder methods on solving the crystal structure of tetracycline hydrochloride (see Chapter 7), what is considered trivial and impossible varies greatly as to the expertise of the diffraction analyst. Trivial problems can be completed easily. There is judgment required to ensure a trivial problem is in reality trivial. The appearance of triviality can be due to the analyst having delegated the scientific thought and decisions to the authors of the analysis software, whose expertise and judgment have been programmed within. Non-trivial diffraction problems may hit hurdles that require the creative application of available equipment, knowledge and experience. As suggested above, much expertise is incorporated within modern analysis software, such that a hurdle for a nontrivial problem may be overcome by knowing which button to press on a piece of analysis software, or another method of sample preparation, or using other equipment. However, difficult problems cannot be solved by button pressing or the application of rote learning. For these, original thought and original scientific creativity is required. Many of the applications in Section 1.7 describe difficult problems that were solved via original, custom solutions. Difficult powder diffraction problems can sometimes be made easier by redoing laboratory XRD experiments at a synchrotron or neutron diffraction facility. Indexing, structure solution and refinement can be made far easier by the growing of single crystals for analysis by single-crystal diffraction methods. Much quantitative phase analysis, structure solution and structure refinement using powder diffraction data are still difficult problems. While this description oversimplifies a more complex reality, it gives a feel for what a new diffraction user can expect.

Part of the expertise required in powder diffraction is recognizing when a problem originally considered easily solvable or routine is actually more complicated. Another part of the expertise required in powder diffraction is recognizing when in some instances, the analysis is signaling to all useful purposes its completion, or in others that a scientific hurdle has been encountered. The more difficult or demanding the scientific problem, then subtle might be these signals. To know when a good model and corresponding fit to the data is



Figure 1.16 A flow diagram illustrating what differentiates a (i) trivial, (ii) nontrivial and (iii) difficult scientific problem.

good, but not good enough, can be difficult. Figure 1.17 provides an example during structure solution of a complex inorganic phase ZrP_2O_7 (Stinton *et al.*, 2006), where different structure models are being tested to see which provides the best fit to the raw data. "Good enough is the enemy of better." For those needing to see a good fit, the structure model based on space group Pa3) (Figure 1.17a) could be interpreted as good. However, the model based on Pbca (Figure 1.17b) is better and also supported by solid-state NMR analysis. For complex structures considered essentially correct, there is always the possibility that newer research or analysis may find a better fitting model.

Some text, quoted with permission, within the Tmacle software manual by Armel Le Bail (Gao *et al.*, 1992) (author of Chapter 7 on structure solution) is worth considering:

GOOD LUCK IT'S VERY HARD! DON'T YOU THINK SO? ONLY THE BOSS SAID THAT IT IS EASY, BUT HE NEVER TRIED! TO HAVE THE SOLUTION DEPENDS ON YOU, NOT ON THIS PROGRAM WHICH IS JUST ABLE TO TEST YOUR HYPOTHESIS ...

1.4.3 May need the use of other complementary methods

The effective use of scientific techniques can require that they do not sit in isolation. Depending on the type of powder diffraction analysis, other complementary methods may be routinely required for validating results or constraining a model to be within physically reasonable parameters. For phase identification and quantitative phase analysis, qualitative and quantitative chemical analysis using SEM and XRF is useful. Table 1.1 shows part of the SR5 Rietveld program's output (Madsen and Hill, 1990) where the quantitative phase analysis results include elemental percentages and XRF style oxide elemental abundances. This enables a level of validation of the PXRD results by comparing it with independent chemical analysis.

The use of powder diffraction for structure solution and refinement may encounter difficulties inherent to the technique. Depending on the phases under study, these difficulties can include ambiguities in determining the spacegroup, number of independent formula units in the unit cell and tautomeric form. Other techniques such as solid-state NMR may provide important information for providing an initial starting model and correctness of the final structure solution and refinement. Figure 1.18 provides such an example for an organic co-crystal of benzoic acid (BA) and pentafluorobenzoic acid (PBFA) (Albesa-Jové *et al.*, 2004). High-resolution solid-state ¹³C NMR was used to provide independent information on the number of crystallographically independent molecules in the unit cell. In conjunction with the good calculated fit to the observed powder diffraction data, the NMR data helps validate the solved structure as being reasonable and correct. NMR is now more commonly used in structure solution from powder diffraction data. Section 1.7.11 mentions the use of electron microscopy to aid in structure solutions found difficult from powder diffraction alone.



Figure 1.17 Rietveld fit comparing refinements of neutron data for ZrP_2O_7 in space groups (a) $Pa\bar{3}$ and (b) Pbca. (Figure courtesy of John Evans.)

Powder diffraction cannot assign absolute configuration of solved structures due to the inherent inability to distinguish Bijvoet pairs (they have identical 2θ peak positions). If this is an issue with a structure solved by the powder method, discussion with local organic chemists or crystal growers may be beneficial. If confined to powder diffraction data, one preparative strategy would be to synthesize a salt or co-crystal of the chiral molecule of interest with a chiral component of a single known enantiomer. Since the two possible salts/co-crystals are diastereoisomeric, they should be distinguishable through normal structure determination.

Quantitative analysis	ZMV	Wt%	MAC	Density
Anatase TiO ₂	43537	2.67 (0.16)	125.12	3.90
Boehmite AlO(OH)	31136	22.19 (0.55)	28.20	3.07
Gibbsite Al(OH) ₃	265821	40.40 (0.95)	23.98	2.43
Goethite FeO(OH)	49267	11.35 (0.33)	196.42	4.26
Hematite Fe ₂ O ₃	289288	12.44 (0.32)	217.46	5.27
Quartz SiO ₂	20369	8.03 (0.32)	35.76	2.65
Kaolinite $Al_2(Si_2O_5)(OH)_4$	167635	2.93 (0.34)	30.93	2.56
Sum		100.00		
Sample			72.40	3.19
Atom abundances (wt%)			Oxide abu	Indances (wt%)
Н	2.07			
0	51.52			
Al	24.58		Al_2O_3	46.44
Si	4.40		SiO ₂	9.41
Ті	1.60		TiO ₂	2.67
Fe	15.83		Fe_2O_3	22.64
Sum	100.00		Sum	81.15

Table 1.1 Extracted output from the SR5 Rietveld software of a bauxite sample, where the quantitative phase abundances are followed by their elemental equivalents. This eases the time required to validate the phase results using chemical analysis



Figure 1.18 (a) High-resolution solid-state ¹³C NMR of BA/PFBA co-crystal which provides independent information on the number of crystallographically equivalent molecules in the unit cell, and (b) a view of the atomic structure of BA/PFBA co-crystal using the Crystals suite. (Figure courtesy of Kenneth D.M. Harris.)
1.4.4 May only give an averaged or simplified answer

Conventional XRD methods project an average representation of the electron density of the crystalline phase under study into what the diffraction analyst has considered the most appropriate common repeating unit (the unit cell). As the important "phase" information is lost in diffraction measurements, indirect mathematical reconstructions are used to place a crystal structure model into the unit cell, as justified by the fit to the diffraction data. Figure 1.19a shows part of a Fourier electron density map of an organic crystal generated using single-crystal data, and Figure 1.19b with an overlaid structure model to explain this electron density. Figure 1.19c shows a difference Fourier electron density map whereby more subtle features can be discovered; in this case showing the positions of hydrogen atoms (marked by arrows). For many classes of crystallographically ordered materials, these methods work well and provide an accurate representation of the atomic arrangements within the crystal.

Owing to structural disorder and local disorder, diffraction data may lead the analyst to an overly simplified view of the material's atomic structure. "Band aids" that model the disorder, including using enlarged Debye–Waller "thermal" factors or partial occupation of



Figure 1.19 (a) Fourier electron density map for part of the unit cell of an organic crystal generated using single-crystal XRD data, (b) overlaid structure model to explain this electron density and (c) difference Fourier map revealing presence of possible hydrogen positions.

lattice sites (Egami and Billinge, 2003a), can lead to a "wrong" view of a solved structure (Egami and Billinge, 2003b). Figure 1.20 shows two $50 \times 50 \times 50$ model crystals containing 70% black atoms and 30% vacancies, where one is randomly ordered (Figure 1.20a) and the other has short range order (SRO) (Figure 1.20b). The resulting peaks of the diffraction patterns are essentially identical (Figure 1.20c). Structure refinements will produce an identical average crystal structure model for both samples. Only subtle differences in the background due to diffuse scattering effects shown in Figure 1.20d (likely to be hidden in the noise of real diffraction data) indicate that a form of short-range order exists in the



Figure 1.20 $50 \times 50 \times 50$ model crystals containing 70% black atoms and 30% vacancies where (a) is randomly ordered, (b) has short range order and (c) overlaid powder patterns from the two crystal structures showing no significant difference in the diffraction peaks, (d) overlaid powder patterns from the two crystal structures showing a weak difference in the background where the local short-range order causes weak diffuse scattering effects in the background. (Figure courtesy of Dr Thomas Proffen, Lujan Neutron Scattering Center.)

second structure. This displays how local atomic order may be impossible to model using only conventional diffraction methods. Other analytical methods; very careful analysis of the powder diffraction data; and the use of crystal chemical knowledge, may assist in cases where a crystallographically averaged structure model is not considered adequate. Chapter 9 introduces a developing method for modeling crystallographic local order in the form of pair distribution function (PDF) total scattering analysis, where the monograph by Egami and Billinge provides a rigorous overview (Egami and Billinge, 2003a).

1.4.5 Not a quick cure-all for complicated problems and questions

When a process or material unexpectedly fails, an instinctive response can be to rely on a series of quick analytical techniques in the hope they will "provide the answers." As powder diffraction is usually the only available technique that can determine the crystalline components within the materials failure, much is expected of it. While it will probably identify the phases, in a larger context, all it may show is that the material or process has failed in ways mysterious, indicating a lack of needed fundamental knowledge. The need for expending resources and time on more fundamental research, such as phase equilibria studies ("road maps for materials processing" (Wong-Ng *et al.*, 2001)), modeling and *in situ* studies, may be an unwelcome but unavoidable conclusion.

1.5 Pitfalls, misconceptions and requirements

1.5.1 Inappropriate to treat as a black box or turn-key method

Over time, powder diffraction can be unreliable if continually and unthinkingly used as a black box or turn-key method. If the underlying basis of an analytical method, and its results, are not validated and continually checked, then an analytical method can drift over time to provide inaccurate (but still reasonable looking) numbers. Sample preparation, hardware, software defaults or analysis logic can be accidentally changed; easy to occur when moving the analysis to a different computer or diffractometer. Applying an analytical method to "identical" materials produced by a different process should be checked carefully. Aberrations in routine samples might only be evident from close examination of the data. Where possible, spot-checking of results using independent validation should occur.

1.5.2 Easy for over optimism, over-interpretation and mis-interpretation of diffraction data

Combined with an over-eager eye, an enthusiastic heart, and a lack of scientific knowledge or experience, it can be easy to over-interpret and mis-interpret powder diffraction data. Examples of mis-interpreting the data include: not recognizing spurious peaks as artifacts of the instrument and assigning them as trace phases; explaining away all poor intensity matching as preferred orientation; explaining away misfits in the Rietveld refinement goodness-of-fit plot due to whatever reason seems most convenient; ignoring errant bond lengths in a structure refinement. A lack of experience may result in not being able to recognize when a result is "strange" or somehow "not right" and needs further clarification or checking. Figure 1.21 shows an example of phase identification where parasitic radiation passed through the diffracted beam monochromator of an older style of diffractometer into the detector, thus complicating the analysis. Without knowledge of the potential for spurious peaks, it can be easy to incorrectly assign crystalline phases to these peaks. A 1992 paper by Rod Hill describes many types of unwelcome peaks and effects that can enter into a diffraction pattern (Hill, 1992). Identifying and dealing with the types of situations described above, as well as others, are discussed in the relevant chapters.

1.5.3 The legal requirements for performing all diffraction experiments safely

I ought to have known . . . the possibility of Singapore having no landward defences, no more entered my mind than that of a battleship being launched without a bottom.

(Winston Churchill, 1942; Kletz, 2001b)

In the modern workplace and literature, it can be typical for the employee and reader to be on the receiving end of some stern words relating to safety, if they welcome it or not, and this text is no exception. Legal requirements, safety regulations and regulators, make it unambiguous that workplaces must know their obligations to ensure employees and public are defended from harm. While the International Tables volume C (2006) of the International Union of Crystallography has a section on "Precautions against radiation injury" (Creagh and Martinez-Carrera, 2006), the following aims more on the principles of modern workplace safety that might get overlooked during eagerness to make use of diffraction. Detailed safety aspects of ionizing radiation and safety cabinet design are also provided in Chapter 3. As the author is not an OH&S professional, the following has the weight of a single person's opinions. Therefore it is advisable that local OH&S representatives and resources are used for queries, clarification or extra information. Legislation relevant to federal Canadian legislation is cited, and text quoted as an example of what can be expected in other jurisdictions. Other jurisdictions are not mentioned, as regulatory and OH&S compliance may require detailed local knowledge.

The quid-pro-quo that society demands of facilities whereby they are allowed to perform modern pure science or applied modern industry, is that hazards are controlled, with employees, public and environment protected from harm. Society enforces this expectation of protection from harm by enshrining it in laws and regulations, whereby a safe workplace is a legal requirement (Canada, 1985a). The laws and regulations relating to Occupational Health and Safety are all derivatives in fine detail of a single overall directive, "First, do no harm," the Doctor's Credo. Whatever work is done, must be done without harming employees and the public, to the expectations of employees, the public, the law, the regulators and any extra workplace site policies. Facilities have found to their cost that failure to satisfy regulator or public expectations on safety have resulted in grounds for closure: temporary, partial or permanent.

In Canada, the safe operation of analytical X-ray equipment is subject to a strict set of legal requirements known as the Radiation Emitting Devices (RED) Regulations



Figure 1.21 (a) Phase identification of zincite (zinc oxide/ZnO) using data collected on an older generation powder diffractometer using CuK α X-rays and curved graphite diffracted beam monochromator. Two trace unassigned peaks are evident at *d*-spacings of 3.115 and 2.740 Å; (b) changing the wavelength in the search-match software to that of CuK β (1.39225 Å) shows that the trace peaks are due to this parasitic radiation getting through the diffracted beam monochromator. In aging X-ray tubes, parasitic radiation of Tungsten (1.476 Å) can become significant and also leak through into the detector.

(Canada, 1981), enabled by the Radiation Emitting Devices Act (Canada, 1985b); part XIV of the RED regulations deals with analytical X-ray equipment. "Safety Requirements and Guidance for Analytical X-ray Equipment - Safety Code 32 (Canada, 2004d)" provides requirements and regulator guidance as to the RED regulations. This includes under "3.4.1 Equipment Owner Responsibilities" to "ensure that all users and maintenance personnel have received adequate training, and have read and understood the relevant parts of this [Radiation Emitting Devices Regulations] Safety Code (Canada, 2004b)." A number of issues relating to safe operation of X-ray analytical apparatus are elaborated, including "3.4.2 User Responsibilities," for apparatus users to "stop the operation of the analytical X-ray equipment if any unsafe operational conditions arise, and immediately notify the equipment owner or designee of such conditions (Canada, 2004c)." For acquiring X-ray analytical apparatus, regulator guidance states, "When selecting or procuring analytical X-ray equipment, the equipment owner is well advised to obtain a copy of the most recent regulations to familiarize oneself with the requirements, and to enquire of the intended manufacturer or importer if the product complies with those current regulations. (These actions may eliminate or minimize the need for modifications to the equipment. Such modifications may be costly and cause considerable inconvenience because of disruption in service.) (Canada, 2004a)" Modern commercial XRD equipment is in general exceptionally and so well engineered with respect to safety, that no significant radiation dose or radiation incident can be expected from a lifetime of correct use and proper maintenance. It is in part from high expectations on X-ray safety, routinely achieved and exceeded by modern commercial apparatus, that if an incident does occur (most likely due to the improper disabling of safety interlocks, or unqualified equipment maintenance), it can generate a serious and (for the laboratory) debilitating safety investigation.

There is always potential when performing experiments, especially involving aging or "grandfathered" equipment, where unsafe workplace situations may develop. Unsafe situations involving diffractometers and ancillary equipment can include running apparatus with disabled safety interlocks; running experiments contrary to good practise as required by the regulations; ignoring regulatory or qualified advice on safety; unqualified "make it work" electrical by-passes and other unqualified ad-hoc quick fixes; or working with a lack of personal protective equipment (PPE) considered appropriate for the experiment. It is generally new staff most at risk, as they might not fully understand potentially unsafe situations; that work considered potentially unsafe should be halted until issues are resolved; that any supervisory directives considered unsafe should be refused. With adequate training, most unsafe situations can be recognized and appropriately acted upon (refer to Canada Labour Code, Part II: "Internal Complaint Resolution Process" (Canada, 1985c) and the "Refusal to work if danger" procedure (Canada, 1985d)).

For general OH&S reading, industrial safety literature written by Trevor Kletz is excellent, highly readable and makes points using a plethora of well-illustrated and topical examples (Kletz, 1993, 1999a, 1999b, 2001a, 2003). The Columbia Accident Investigation Board report (CAIB) on the NASA space shuttle disaster, especially Chapters 1 (The Evolution of the Space Shuttle Program), 6 (Decision Making at NASA) and 7 (The Accident's Organizational Causes), is enlightening as to the principles of maintaining aging experimental equipment where failures can have severe consequences (Columbia Accident Investigation Board, 2003).

1.6 Comparison to single-crystal diffraction

1.6.1 The obvious superiority of single-crystal methods over powder for indexing, solving and refining crystal structures

While the frontiers of crystal structure solution using single-crystal diffraction are still a challenging area, generic solving of small molecule crystal structures using single-crystal data is considered "routine." The word "Routine," in this case, being defined with respect to the expectations of single-crystal diffraction users. Structures of the complexity commonly encountered with powder diffraction generally solve "on demand" using single-crystal methods to near completeness at the press of a button in seconds to minutes. Fine features such as tautomeric form can also be unambiguously determined purely from the single-crystal diffraction data. Providing the crystals can be grown, modern single-crystal diffraction methods provide an unambiguous direct measure of molecular connectivity by showing the electron density. Since the mid-1990s, single-crystal diffraction apparatus has undergone a revolution, by the replacement of point detectors with 2D detectors in the form of CCDs, and image plates. This has allowed the improved detection of twinned crystals, and consequent analysis of data. When optimized for speed, complete single-crystal data collection can be 5-30 min. Although, for reasons including quantity of samples and conservatism on quality of data, data collection of hours is more typical. Depending on elemental composition and unit cell size, if a micro-single-crystal can be grown in the tens of microns length range, there is a good chance it can be successfully run on a modern laboratory single-crystal diffractometer. Where microcrystals have failed to solve on laboratory systems due to inadequate intensity, a synchrotron-based single-crystal XRD system may succeed. The non-routine structure solution of ZrP_2O_7 (Birkedal *et al.*, 2006) using a $20 \times 20 \times 20 \ \mu m$ crystal (Figure 1.22) and the routine structure solution of tetracycline hydrochloride (Clegg and Teat, 2000) using a $40 \times 30 \times 20 \,\mu\text{m}$ crystal (Figure 1.23) were solved and refined using single-crystal data collected at synchrotron beamlines. It should be noted that laboratory apparatus continues to develop, with the latest commercial singlecrystal systems using higher flux laboratory sources and higher sensitivity 2D detectors. These laboratory systems are capable of handling microcrystals that a few years previously were the exclusive remit of the X-ray synchrotron (refer Figure 1.24).

With the expectations of single-crystal diffraction users as a benchmark, solving structures from powder diffraction data should be considered non-routine, not easy and not "on demand." As is mentioned by Armel Le Bail, in his Chapter 7 on structure solution, solving structures from powder diffraction is a small crystallographic niche compared to the numbers of structures solved with single-crystal data. Structure solving techniques are improving, but structures that can be solved from powder data routinely are often done already, with non-routine samples remaining. Solving crystal structures from powder diffraction data should be considered as a method of last resort, and only when the growing of a suitable single crystal is found impossible. As some materials will refuse to form suitable single crystals, undertaking a structure solution by powder diffraction methods must then be considered. Many scientists value the thrill of undertaking structure solution using powder methods due to it being an interesting and challenging intellectual endeavor. Background and methods of solving structures from powder diffraction data are given in Chapter 7.



Figure 1.22 SEM image of ZrP_2O_7 single crystals with linear dimensions of $\sim 20 \,\mu$ m, suitable for structure solution and refinement using single-crystal diffraction. (Photograph courtesy of Henrik Birkedal.)

To elaborate on the above statements, Figure 1.23 shows the antibiotic, tetracycline hydrochloride, as solved by single-crystal methods, including hydrogen positions and revealing an unexpected tautomeric form (Clegg and Teat, 2000). This contrasts with the tetracycline hydrochloride solved using powder methods (no hydrogens) by "Participant 4" as part of the first structure solution from powder diffraction data Round Robin in 1998 (Le Bail and Cranswick, 2001). Hydrogens are normally calculated for structures solved by powder methods. The single-crystal data could solve at the press of the button in a few minutes using a PC computer and all commonly available software of the time. However, only a fraction of Round Robin participants who downloaded the powder diffraction data solved the structure in the required time frame. The use of Patterson methods followed by Fourier recycling by Participant 4 to solve the structure from powder data is of particular interest, as it shows the importance of skill, experience and intuition in nonroutine structure solution. Most powder crystallographers, including the Round Robin organizers, would not have considered the use of these methods due to pre-conceived ideas that it would be a fruitless strategy, but not Participant 4. Despite such a method appearing simple in hindsight, it is not straightforward, as many of the peaks in the initial electron density map, phased on the chlorine heavy atom, were spurious (Le Bail and Cranswick, 2001).

Another example of importance of skill and experience relates to the US1000 DuPont Challenge, awarded to the first person to provide a satisfactory solution of the structure of HAlF₄ (an intermediate product in the industrial synthesis of AlF3 catalysts)



Figure 1.23 Crystal structure of tetracycline hydrochloride as displayed in a chemist friendly form via the crystals single-crystal analysis package. Using singlecrystal data, all non-hydrogen atoms are freely refineable for position and anisotropic displacement parameters; all hydrogens are observed in the Fourier difference map.



Figure 1.24 Bruker APEX II ULTRA laboratory single-crystal X-ray diffraction system. (Photograph courtesy of Bruker AXS Inc.)

with powder diffraction data provided by the DuPont Corporation (The DuPont Powder Challenge, 1997). The successful result was published in 1999 titled, "The DuPont Powder Challenge: The Crystal Structure of $[C_5NH_6][Al_3F_{10}] - A$ Cautionary Tale" (Harlow *et al.*, 1999). The cautionary tale being that the composition DuPont considered correct, $HAlF_4$, was incorrect, and the structure contained a pyridinium molecule. The solved crystal structure was also found to contain some unusual edge-sharing AlF₆ octahedra. A message sent by Armel Le Bail in France, to an Internet bulletin board, titled "Chemical analysis of the year" (Le Bail, 1998) commented on the supplied chemistry being incorrect. This message was followed-on by the challenge winner (Solovyov, 1999), Leonid Solovyov in Krasnoyarsk, Russia, describing the methodology used to solve the structure, including obtaining a portion of the sample, and psychological factors of dealing with a sample personally analyzed, and diffraction data personally collected. This reinforces the encouragement to routinely characterize materials using a suite of analytical techniques, including elemental and NMR analysis. As well as re-emphasizing that skill, expertise and canniness may be routinely required in the solving of structures using powder methods.

A set of structure solutions published in 2006 that allow a further comparison of single crystal and powder methods is that of the 136-Atom crystal structure of ZrP_2O_7 shown in Figure 1.25a (powder solved) (Stinton *et al.*, 2006) and Figure 1.25b (single crystal solved) (Birkedal *et al.*, 2006). The powder crystallographers in Durham University, UK, solved the structure using ³¹P NMR, laboratory powder X-ray and time-of-flight neutron powder diffraction data, and the Topas Academic software (Coelho, 2006). To solve such a large



Figure 1.25 Structure of ZrP_2O_7 solved (a) by powder diffraction (figure courtesy of John Evans), (b) by single crystal diffraction (figure courtesy of Henrik Birkedal) and (c) superposition of atoms from a typical P_2O_7 group from powder (light) and single crystal (dark) refinements (figure courtesy of John Evans).

inorganic structure using powder methods currently requires a high level of crystallographic expertise and ability. Literature relating to ZrO_6 octahedra and P_2O_7 groups was used to provide restraints during the structure solution, with an excellent final fit to the powder data. The pan-European group that solved and refined the ZrP_2O_7 structure using single-crystal methods included specialist expertise in crystal growing. As with many complex inorganic structures, the structure solution and refinement using single-crystal data is nonroutine. The information from the ³¹P NMR was similarly used, but the structure solution could proceed without the need to include detailed chemical information such as restraints on local coordination. As shown in Figure 1.25c, the atomic positions of both the powder and single-crystal structures are essentially identical, but the single-crystal result includes anisotropic displacement parameters (ADPs); often called "thermal" factors. Depending on the material applications, knowing accurate APDs for each atom may or may not be important, but they can assist in validating the correctness of the structure. As this example indicates, the preferred and successful pathway to solve a crystal structure can depend on whether the available expertise is in crystal growing, or in powder diffraction.

A powder diffraction problem might only reveal itself as being difficult when an attempt is made to tackle it. Problems might not solve on demand, and may require a number of years before a model can be developed that is considered essentially correct. In many areas of materials research, this can be the norm, not the exception. In the research areas of mineralogy, archaeology and cultural heritage, aerinite, the "blue mineral," a naturally occurring fibrous silicate of interesting history, was a crystal structure of note which for many years resisted being solved by a variety of groups until achieved by researchers in Spain (Rius *et al.*, 2004).

1.6.2 Use of modern single-crystal diffractometers for powder diffraction

Modern single-crystal diffraction apparatus containing 2D detectors have the capability for use in a wide range of flexible powder diffraction applications unavailable to a conventional

Bragg–Bretano PXRD. For powder diffraction of microgram to nanogram amounts of material, Figure 1.26 shows the mounting of a sample onto a 10 μ m nylon loop, then onto a single-crystal diffractometer, through to a Rietveld fit of the resulting data (Bhuvanesh and Reibenspies, 2003). Section 1.7.16 shows further applications, reinforcing that a modern single-crystal system should also be considered as a flexible low to medium resolution powder microdiffractometer.

1.6.3 Both methods best mixed into a single diffraction laboratory

Traditionally, single-crystal diffractometers and powder diffraction systems were placed in different laboratories, more often in different departments, where rarely the twain did meet. Powder diffraction was seen more as a technique of industry or applied science, single-crystal methods for pure science. Single crystallographers and powder diffractionists had little interaction with each other, moving in different circles and more often attending different conferences. So that researchers can benefit from both methods, modern practise is to attempt inclusion of both single crystal and powder diffraction equipment into a single laboratory. A further trend is to link the diffraction facilities with other analytical and synthesis laboratories so materials scientists can benefit from a suite of interconnected facilities. With modern apparatus, what was thought a powder might now be considered a collection of microcrystals, suitable for single-crystal methods. The ability of modern powder diffraction to perform a wide variety of analysis on bulk samples can make it too valuable a technique to ignore because of arbitrary boundaries of olden times.

1.7 Applications using powder diffraction

In this section, a number of applications displaying advantages and features of powder diffraction are elaborated. The applications are not in any particular order, as the reader would benefit considering how the applications might be used for other situations. By default, the literature publishes successes, not failures, thus giving a skewed impression of 100% success rates. It is a pity there cannot be an emphasis on somehow publishing research failures: there can be benefits of lighthouses also showing location of rocks and reefs. As modern powder diffraction covers such a wide range of actual and possible applications, and is published in such disparate corners, the author finds it necessary to apologize in advance if illustrations, that might have found favor with the reader, are missing. There are many notable achievements scattered over the field of science using powder diffraction, but limited space to describe them here.

1.7.1 Routine checking of starting materials prior to chemical synthesis

While this application may seem pedestrian, not checking starting materials prior to use can make for much mayhem and potential futility in attempting a chemical synthesis. Elemental analysis to check for chemical purity will be inadequate where crystal form can



Figure 1.26 Pictographic example of using single-crystal diffraction apparatus to collect powder diffraction data on microgram to nanograms of material: (a) 10 μ m loop loaded with powder sample, (b) mounted on a single-crystal diffractometer, (c) Rietveld fit to 1D data. (Photographs and figures courtesy of Nattamai Bhuvanesh and Joseph Reibenspies.)



Figure 1.27 Example of phase identification of lime (calcium oxide; CaO) containing a small amount of portlandite (calcium hydroxide; Ca(OH)₂) impurity, using calculated data. Diffraction peaks due to lime are labeled L, peaks due to portlandite labeled P. For starting materials used in synthesis, powder X-ray powder diffraction can easily check phase purity. Calculated data such as this (e.g., 5 wt% portlandite in lime) can be used to determine the estimated counting time required to see the potential impurity phase at the desired level.

affect reactivity. Chemicals can be incorrectly labeled, be impure, or degrade over time: for example, hydroxylation from crystalline oxide to crystalline hydroxide. These crystal forms can be detected routinely by powder diffraction. For instance, lime (calcium oxide; CaO), a common starting material in much solid-state synthesis, might contain a small amount of portlandite impurity (calcium hydroxide; Ca(OH)₂), affecting its suitability for use. To determine the estimated counting time required to observe potential impurity phases at desired levels, powder patterns can be calculated. This is shown in Figure 1.27 where a powder pattern of 5 wt% portlandite in lime is calculated using the GSAS Rietveld software (Larson and Von Dreele, 2004).

1.7.2 COXA and control of Portland cement manufacture

Continuous measurement of process streams allows optimum control on industrial plants to keep products within specification. The use of on-line XRD analysis is advantageous where there is chemical ambiguity, and process phases can only be distinguished by diffraction methods. Figure 1.28a shows an industrial on-line XRD from FCT ACTech Pty Ltd optimized for control of process control on Portland cement plants (Scarlett *et al.*, 2002). Traditionally, a cement plant would rely on intermittent XRF results for plant control, and



Figure 1.28 (a) Industrial on-line XRD from FCT ACTech Pty Ltd and (b) example phase analysis results for alite, belite and free lime from on-line XRD used for Portland cement plant control. (Photograph and figure courtesy of FCT ACTech Pty Ltd.)

estimate a phase composition from the chemistry. XRD allows a direct measure of phase composition. With the FCT on-line XRD, a continuous flow of sample is extracted from the production stream and moved through the diffraction position of the diffractometer. The XRD detector is a stationary INEL position sensitive detector (PSD) that simultaneously collects a 120° wide aperture of diffraction data. A quantitative phase result is reported every minute via an automated Rietveld analysis. Figure 1.28b shows part of the quantitative phase analysis results of the on-line XRD: alite (tricalcium silicate/Ca₃O·SiO₄), belite (dicalcium silicate/Ca₂SiO₄) and free lime (calcium oxide/CaO).

1.7.3 High-throughput polymorph screening of pharmaceutical systems

Research, product usage and patent protection of pharmaceuticals can involve high importance being placed on polymorph screening and the use of powder diffraction. For polymorph mapping, Figure 1.29 shows a Bruker-AXS microdiffractometer with 2D area detector optimized for high-throughput screening (HTS) using combinatorial libraries. Chapter 6 describes the use of PolySnap software to analyze the large amounts of diffraction data that are produced (Barr *et al.*, 2004).



Figure 1.29 Bruker D8 DISCOVER with GADDS HTS (High-Throughput Screening) microdiffractometer in transmission mode with crystallization plate for mapping of polymorphs using combinatorial libraries. (Photograph courtesy of Bruker AXS Inc.)

1.7.4 Solving of pharmaceutical and organic crystal structures from powder diffraction data using the Dash software

Dash is a program for MS-Windows optimized for solving of organic, organometallic and pharmaceutical crystal structures from powder data (David *et al.*, 1998, 2006; Florence *et al.*, 2005). The range of structures solved by Dash, some indicated in Figure 1.30, speaks for itself.

1.7.5 Standards based on whole profile quantitative phase analysis of pharmaceuticals

Reliable quantitative phase analysis of pharmaceutical systems can be difficult due to the presence of poorly crystalline or amorphous filler materials, and crystalline phases with high degrees of peak overlap. A whole profile fitting method by use of external standards for complex mineral assemblages has been developed at the Mineralogy Department of the Natural History Museum in London, UK (Cressey and Schofield, 1996; Batchelder and Cressey, 1998). It also shows great promise for reliable quantitative phase analysis of pharmaceutical materials (British Crystallographic Association Industrial Group, 2004). This application is based around an INEL 120° position-sensitive detector (PSD), with Microsource® X-ray generator and microwell sample holder (Figure 1.31a,b). An example of the least-squares fit of the standards to the sample is shown in Figure 1.31c, and resulting quantitative phase results in Table 1.2.

1.7.6 Effective quantitative phase analysis of complex mineral ores via single peak analysis method

Commercial process plants and mining sites are environments where best compromises in available resources may need to be determined and continually redetermined to keep the facility viable and profitable in the face of changing competition and regulatory requirements. If a specification requires an accuracy of "X," it may be considered a waste of time, cost and resources to go further and provide an improved accuracy of "Y." If required by a specification, this can still involve analytical techniques working at their most demanding levels of accuracy and precision. Depending on plant necessities, staff may have to work up an analysis regime that provides the best compromise of machine usage, workload, cost, speed, accuracy, precision and reproducibility.

Quantitative analysis of XRD data using single peak methods of complex phase assemblages are usually of lower accuracy, precision and reproducibility than whole profile methods. However for a mining site, Karsten Winter in Western Australia describes development of a single peak methodology for quantitative analysis of complex mineral assemblies that satisfied requirements (Winter, 2002). There was a restricted analysis database of ~600 different minerals relevant to the mine site and company exploration geologists. Using a Bragg–Brentano diffractometer with solid-state point detector and 42 position sample changer, Karsten noted: "using the combination of highly skilled people, dedicated machine and simple technique, the laboratory was able to analyse more than 35,000 samples in 2001." Single peak methods for quantitative phase analysis are elaborated in Chapter 6.



Figure 1.30 A collage of some phases, including pharmaceuticals, solved by users of the Dash software. (Figure courtesy of Norman Shankland, Alastair Florence and Kenneth Shankland.)

1.7.7 Quantitative phase analysis of mine tailings for acid mine drainage research using the Rietveld method

Regulatory bodies can require the modeling and prediction of mine-based acid rock drainage from the oxidation of sulfide-bearing wastes, where effluents enriched in potentially toxic metals may result. For such modeling, it is important for accurate quantitative phase



Figure 1.31 (a) Single-crystal ("zero background") micro-well sample holder for containing ~100 μ g of pharmaceutical sample for quantitative analysis (about 1/1000 of the issued 100 mg mixture sample "pill"). (b) INEL 120 deg position-sensitive detector (PSD) with an 80 Watt Microsource® X-ray generator (used to generate high brightness copper K α radiation) and incident beam monochromator. Photograph is shown with a high-temperature stage mounted in the sample position, and (c) plot with diffraction data of pharmaceutical and standards, showing the sequential quantitative phase analysis fits. (Photographs and figure courtesy of Gordon Cressey.)

Phase	Least-squares pattern fit %	Mass absorption coefficient	Weight %	Actual weight %
Lactose	86.8	7.47	83.2	84.92
Paracetamol	13.2	5.63	16.8	15.08

Table 1.2 Quantitative phase analysis results of a pharmaceutical sample using the standards based on whole pattern method developed by the team led by Gordon Cressey at the Natural History Museum in London, UK. (Table courtesy of Gordon Cressey)



Figure 1.32 A goodness-of-fit (GoF) plot for quantitative phase analysis of mine wastes using the Rietveld method. (Figure courtesy of Mati Raudsepp, University of British Columbia.)

analysis of the mineral assemblages. The Rietveld method is often considered the best method for quantitative phase analysis, combining flexibility and accuracy where the crystal structures of phases are known. Showing the results of work performed at the University of British Columbia (Raudsepp *et al.*, 2002), Figure 1.32 displays a goodness-of-fit plot of mine tailings using the Rietveld method via the Fundamental Parameters based Topas software. Table 1.3 displays the quantitative analysis results.

1.7.8 In situ powder diffraction using high magnetic fields to study new high technology materials

To properly understand the fundamental science of new materials can be a difficult undertaking, but necessary if seeking to create optimized high technology materials. New hardware

Phase	Chemical formula	Wt%
Calcite	(CaCO ₃)	8.7 (0.2)
Siderite	(FeCO ₃)	2.5 (0.2)
Ankerite	$(Ca(Fe_{0.73}Mg_{0.27})(CO_3)_2)$	5.2 (0.2)
Quartz	(SiO ₂)	57.4 (0.4)
Muscovite	$(K_{0.94} AI_{1.96}(AI_{0.95}Si_{2.85}O_{10})((OH)_{1.74} F_{0.26}))$	2.6 (0.3)
Pyrite	(FeS ₂)	0.4 (0.1)
Kaolinite	$(Al_2Si_2O_5(OH)_4)$	20.4 (0.4)
Hematite	(Fe_2O_3)	2.3 (0.2)
Barite	(BaSO ₄)	0.5 (0.1)
Total		100.0

Table 1.3Quantitative phase analysis results of a mine tailing waste sampleusing the Rietveld method via the Fundamental Parameters based Topassoftware. (Table courtesy of Mati Raudsepp)

or software may need development of which Figure 1.33a,b shows an exemplary laboratory example of equipment installed at the Ames Laboratory, Iowa, USA. This diffraction apparatus was optimized to study the crystallographic changes of new intermetallics under high magnetic fields (0–4 T) and variable temperature (2.5–315 K). Powder diffraction data showing a magnetic field induced structure change in Gd₅Ge₄ is displayed in Figure 1.33c with structural changes displayed in Figure 1.33d (Pecharsky *et al.*, 2003).

1.7.9 Depth profiling of cement using synchrotron-based energy dispersive powder diffraction

The synchrotron-based energy dispersive XRD technique allows the user to probe defined volumes within a sample or sample environment using a high energy, multi-wavelength white X-ray beam and an energy-sensitive detector at a fixed angle (Figure 1.34a). Where phase formation can change as a function of position, energy dispersive XRD can be used to obtain phase information as a function of depth. It can also probe inside samples and ancillary apparatus during *in situ* experiments, such as hydrothermal synthesis, samples at high pressure and setting materials such as cement. In a cement sample exposed to sulfate solution, Figure 1.34b shows the change of phases as a function of depth using 50 μ m steps (Jupe *et al.*, 2004).

1.7.10 Using microdiffractometers for non-destructive phase analysis of works of art

For preservation of artworks, phase analysis may be required so that an appropriate conservation strategy can be determined. In other cases, identification of phases can provide information on provenance or the methods used in the creation of the artwork. Modern



Figure 1.33 (a) Powder diffractometer at the Ames Laboratory for *in situ* experiments involving magnetic fields (0–4 T) under variable temperature (2.5–315 K), (b) closeup of diffractometer with labels describing the diffractometer hardware, (c) changes to the Gd_5Ge_4 diffraction data induced by changing magnetic field strength at 25 K and (d) the antiferromagnetic low field Gd_5Ge_4 (left) and ferromagnetic high field Gd_5Ge_4 crystal structures (right) refined by powder diffraction data, and viewed along the *z* axes showing the crystallographic changes induced by changes in the magnetic field. (Photographs and figures courtesy of Vitalij Pecharsky, Ames Laboratory, Iowa State University.)

microdiffractometers allow the mounting of large samples, including complete paintings so that non-destructive phase composition can be determined. Figure 1.35a shows a painting mounted on a Bruker GADDS microdiffractometer, and a diffractogram with phase identification given in Figure 1.35b (Hay *et al.*, 2005).

1.7.11 New algorithms and methods for solving zeolite and other crystal structures from powder diffraction data

When new complex materials of technological importance require their structures to be solved, the limitations of known structure-solving methods might make such an endeavor impossible. In such cases, the bounds of the possible must be pushed further out. Zeolites,



Figure 1.34 (a) Schematic showing the principles by which spatially resolved energy dispersive X-ray diffraction works, moving the sample relative to the "gage" volume and (b) example of energy dispersive X-ray diffraction (EDXRD) showing the change of phases as a function of depth in a cement sample exposed to sulfate solution. Plot was constructed from 81 EDXRD patterns recorded at 50 μ m intervals. (Figure courtesy of Angus Wilkinson.)

used as exchangers, adsorbents, and catalysts, are materials of high industrial importance, including the petrochemical industry. Nearly all of the world's petrol (gasoline) is produced or upgraded using zeolites. However zeolites can be difficult to grow as single crystals, evidenced by NASA's Zeolite Crystal Growth Furnace (ZCG) (National Aeronautics and Space Administration, 2007) which is taken on space-shuttle missions and the International Space Station to try to produce enhanced crystal growth of zeolites using microgravity conditions. Figure 1.36 shows two difficult zeolite structures solved from powder diffraction data with new methods and algorithms developed by the Laboratorium f. Kristallographie of ETHZ, Zurich, Switzerland. When a new zeolite has shown the limitations of current powder-based structure-solving methods, it has been a strength of the Laboratorium f. Kristallographie of ETHZ to develop or adapt new strategies for solving difficult structures. These developments include, using preferred orientation via texture-based methods (McCusker *et al.*, 2001); structure envelopes (Brenner *et al.*, 2002); complementary use of electron microscopy (Gramm *et al.*, 2006); and using the new charge flipping algorithm, enhanced for application to powder diffraction data (Baerlocher *et al.*, 2007a,b).



Figure 1.35 (a) Charles Conder's painting "Sketch Portrait" (c.1889) from the collection of the National Gallery of Victoria, Melbourne, mounted on a Bruker microdiffractometer (Photograph by: Mark Fergus, CSIRO, 2005) and (b) powder diffraction data of a "red streak on the right shoulder" of the painting showing the phases hydrocerussite (lead carbonate hydroxide/Pb₃(CO₃)₂(OH)₂), strontium chromium oxide (SrCrO₄) and cinnabar (mercury sulfide/HgS). (Photograph and data courtesy of David Hay, CSIRO Australia and John Payne and Jennie Moloney of the National Gallery of Victoria, Melbourne, Australia.)

1.7.12 Understanding sintering of iron ore fines as used in blast furnaces for steel making

Significant parts of industrial processes can be unambiguously analyzed using *in situ* methods as shown in Figure 1.37, where powder diffraction is used to understand the phase changes used to agglomerate iron ore fines in blast furnaces (sintering) (Scarlett *et al.*, 2004).



Figure 1.36 (a) Pole figure for the 102 reflection of the textured UTD-1F zeolite sample, (b) small sections of five diffraction patterns of UTD-1F collected at the sample orientations indicated in the pole figure (a–e), (c) structure of the 117-atom high-silica zeolite UTD-1F determined from the textured data, (d) structure envelope of ITQ-1 zeolite generated using just four reflections ({002}, {101}, {002} and {102}) and (e) an isosurface (80% of maximum Fourier peak) of ITQ-1 zeolite generated using 72 reflections. (Figure courtesy of Lynne McCusker and Christian Baerlocher.)



Figure 1.37 (a) INEL CPS-120 position-sensitive detector fitted with Anton-Paar high-temperature stage and (b) accumulated XRD patterns showing *in situ* formation of SFCA (a silicoferrite of calcium and aluminum). The data are represented as a three-dimensional plot viewed down the *z*-axis (intensity) with diffraction angle (2 θ) along the *x*-axis and temperature (°C) along the *y*-axis. Significant phase changes are indicated on the plot. Quantitative phase analysis performed using the Rietveld method. (Photograph and figure courtesy of Nicola Scarlett.)

1.7.13 Pressure acid leaching of nickel laterite ores

As stated in Section 1.3.1, the art for *in situ* study of solid-state synthesis may be used in determining a method compatible with the XRD apparatus. Figure 1.38 shows the use of a capillary system (Madsen *et al.*, 2004), in this application for studying acid leaching of nickel laterite ores. Originally performed on a laboratory system, the figures show its upgraded use on a synchrotron powder XRD beamline to obtain faster collection of higher resolution diffraction data.

1.7.14 Combining PXRD with DSC under controlled humidity conditions

Similar to the themes of Section 1.7.13, Figure 1.39 shows a commercial PXRD with an *in situ* differential scanning calorimeter (DSC) attachment stage under controlled humidity conditions (Kishi and Toraya, 2004). Reactions shown occurring by the DSC, such as involving pharmaceutical compounds, can be directly and unambiguously correlated with the diffraction data.

1.7.15 Use of powder diffraction in forensic investigations

As with other analytical appropriate techniques, powder diffraction can be used to identify and match the provenance of samples involved in criminal investigations (Fitzpatrick and Raven, 2005). The following example, from CSIRO Land and Water/Centre for Australian Forensic Soil Science (CAFSS) in South Australia, is of a double murder case started when a mother and son were reported missing in September 2000. A muddy and bloodstained shovel was recovered from the mother's car found abandoned the next day (Figure 1.40a). A suspect was arrested but refused to answer questions and it was unknown where the two bodies were located. CSIRO Australia soil expert, Rod Fitzpatrick's mineralogical and soil analysis indicated the mud on the shovel was most likely from an industrial gravel quarry in an acidic/low salt region of the Adelaide Hills. Use of soil and geology maps, including other evidence, led to the Oakbank Quarry in the Adelaide Hills. PXRD by Dr Fitzpatrick and CSIRO analytical X-ray specialist Mark Raven, matched the mud to the Oakbank Quarry (Figure 1.40b). This eventually led to the recovery of the two bodies in the quarry. As a consequence, the suspect confessed and was convicted of the double murder.

1.7.16 Fast quantitative phase analysis of steel and film texture analysis using a single-crystal diffractometer

In Section 1.3.2, it was mentioned that a modern single-crystal diffractometer could be applied to a range of powder diffraction applications. Such an example is shown in Figure 1.41a,b, where a TRIP steel sample is mounted on a Bruker single-crystal diffractometer with APEX 2D detector for routine quantitative phase analysis involving a 5 min data collection. The same apparatus is also used for texture measurements. (b)

A

B

(a)





Figure 1.38 (a) View of capillary sample stage pieces for *in situ* acid leaching experiments showing: A, the capillary reaction vessel filled with slurry; B, the graphite ferrule providing the pressure seal to the reaction vessel; C, the pressure line; and D, the Swagelock fittings comprising the stage itself. (b) Sample environment in place on the goniometer at Station 6.2, Daresbury SRS, showing: A, the oscillation device for the sample stage; B, the pressure line; C, the Swagelock sample stage; D, the goniometer head holding the sample stage; E, the capillary reaction vessel; F, the thermocouple; and G, the hot air blower and (c) results of Rietveld-based quantitative analysis of the major phases present during the pressure acid leaching of saprolite ore at 220°C and 2413 kPa in the low acid environments. The temperature was reduced to ambient at about 190 min resulting in the dissolution of kieserite on cooling. (Photographs and figures courtesy of Nicola Scarlett.)



Figure 1.39 (a) Rigaku XRD-DSC (differential scanning calorimetry) system. A, X-ray sealed tube, B, goniometer (ULTIMA), C, scintillation counter, D, DSC unit, E, DSC control unit and F, humidity control unit. (b) Powder diffraction patterns observed during the dehydration process of trehalose dihydrate plotted as a function of temperature. Numbers represent (I) dihydrate, (II) anhydrate, (III) liquid and (c) variations of integrated intensities of some selected diffraction reflections and the DSC curve plotted as a function of temperature. (Photograph and figures reproduced from *The Rigaku Journal*, Vol. 21, no. 1, 25–30. Copyright 2004 with permission of the Rigaku Corporation.)



Figure 1.40 (a) Blood stained and muddy shovel found in abandoned car boot, (b) overlaid PXRD patterns showing a match from the mud on the shovel and quarry. (Photographs and figure courtesy of Mark Raven/CSIRO Australia.)

1.7.17 In situ welding rig for time-resolved and spatially resolved phase mapping of welds by powder diffraction

For better understanding of welding processes (Figure 1.42a), a synchrotron-based *in situ* welding stage has been developed which allows the combination of time-resolved and spatially resolved X-ray diffraction (Lawrence Livermore National Laboratory, 2001; Zhang *et al.*, 2002; Elmer *et al.*, 2002; International Union of Crystallography, 2007b). Figure 1.42b shows a rendering of the weld rig. Using the high intensity synchrotron X-ray beam, datasets were collected at 20 diffraction patterns per second. Figure 1.42c shows the phase transformations during weld solidification of a flux-cored arc-welding electrode.



Figure 1.41 TRIP steel sample mounted for routine quantitative phase analysis on a Bruker single-crystal X-ray diffractometer containing an APEX CCD 2D detector, (a) 2D raw diffraction using a 5 min data collection and (b) resulting Rietveld fit of the three phases present, ferrite, austenite and martensite. (Photograph and figures courtesy of James Britten.)

1.7.18 And much more

There is much more to powder diffraction, but the above examples give a flavor of available applications, and what can be achieved. Two useful resources that report developments are the IUCr Journal of Applied Crystallography (International Union of Crystallography,



Figure 1.42 (a) Illustration of a fusion weld, (b) rendering of the *in situ* weld station, (c) time-resolved X-ray diffraction results show phase transformations during weld solidification and cooling of a flux-cored arc-welding electrode. (Photograph and figures courtesy of John Elmer and Todd Palmer.)

2007b) and IUCr Commission on Powder Diffraction Newsletters (freely available on-line) (International Union of Crystallography, 2007a).

1.8 Conclusion

Down the scientific gold mines, the ore does not extract itself, let alone the rare fines of precious metal within. Thus, solid-state materials researchers need both an awareness of powder diffraction, but also the ability to use it. Using powder diffraction requires a diligence, intelligence and imagination commensurate with the difficulty of the research being undertaken. The following chapters provide information on the fundamental and practical information for applying powder diffraction to materials science.

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Appendix A.1 List of available software relevant to powder diffraction

Software can often move to different webpages or different websites. Thus if any of the following links are broken, try the following: use a search engine such as Google at http://www.google.com/; browse the CCP14 website at http://www.ccp14.ac.uk/ or the IUCr Crystallography News site at http://www.iucr.org/cww-top/crystal.index.html

Software with search-match/phase identification capability

AXES: http://www.physic.ut.ee/~hugo/axes/ CMPR: http://www.ncnr.nist.gov/xtal/software/cmpr/ Crystallographica Search-Match: http://www.crystallographica.co.uk/ DIFFRAC^{plus} SEARCH: http://www.bruker-axs.de/index.php?id=search Jade:http://www.materialsdata.com/products.htm MacDiff: http://www.esm-software.com/macpdf/ MATCH: http://www.crystalimpact.com/match/ Pulwin: http://users.uniud.it/bruckner/pulwin.html RayfleX: http://www.geinspectiontechnologies.com/en/products/x-ray/analytical_x-ray/ software/overview.html

Sieve: http://www.icdd.com/products/pdf2.htm#software Traces: http://www.gbcsci.com/products/xrd/software.asp TXRDWIN: http://www.omniinstruments.com/txrd.html WinDust32: http://www.italstructures.com/softwares.htm X'Pert HighScore: http://www.panalytical.com/index.cfm?pid=160 Xplot for Windows: http://www.clw.csiro.au/services/mineral/xplot.html XSPEX: http://www.dianocorp.com/software.htm ZDS System: http://krystal.karlov.mff.cuni.cz/xray/zds/zdscore.htm

Databases relevant to search-match/phase identification

COD (Crystallography Open Database): http://www.crystallography.net/ ICDD PDF2: http://www.icdd.com/ MacDiff: http://servermac.geologie.uni-frankfurt.de/Staff/Homepages/Petschick/ RainerE.html Mineral Database: http://www.materialsdata.com/MINERALS.htm Pauling File: http://www.asminternational.org/ (then perform a search on "Pauling File")

Crystal Structure Databases

American Mineralogist Crystal Structure Database: http://rruff.geo.arizona.edu/AMS/ amcsd.php CCDC (Cambridge Structure Database) (organics & organometallics): http://www.ccdc.cam.ac.uk/ COD (Crystallography Open Database) (general database): http://www.crystallography.net/ CRYSTMET (metals, alloys & intermetallics): http://www.tothcanada.com/databases.htm ICDD PDF-4+: http://www.icdd.com/products/pdf4.htm ICSD (Inorganic Crystal Structure Database) (inorganics, elements, minerals & intermetallics): http://icsd.ill.fr/ Incommensurate phases database: http://www.mapr.ucl.ac.be/~crystal/ LAMA Incommensurate Structures Database: http://www.cryst.ehu.es/icsdb/ MINCRYST (minerals): http://database.iem.ac.ru/mincryst/ Pauling File (elements and binary compounds): http://www.asminternational.org/ (then do search for "Pauling File") Pearson's Crystal Data (inorganics): http://www.crystalimpact.com/pcd/Default.htm PDB (Protein Data Bank): http://www.rcsb.org/pdb/ Zeolite Structures Database: http://www.iza-structure.org/databases/

Integration of 2D data to 1D

Datasqueeze: http://www.datasqueezesoftware.com/ FIT2D: http://www.esrf.eu/computing/scientific/FIT2D/ MAUD: http://www.ing.unitn.it/~maud/ NIH-Image: http://rsb.info.nih.gov/nih-image/ Powder3D: http://www.fkf.mpg.de/xray/html/powder3d.html XRD2Dscan: http://www.ugr.es/~anava/xrd2dscan.htm

Conversion of powder data to different formats

AXES: http://www.physic.ut.ee/~hugo/axes/ CMPR: http://www.ncnr.nist.gov/xtal/software/cmpr/ ConTEXT: http://www.context.cx/ ConvX: http://www.ccp14.ac.uk/ccp/web-mirrors/convx/ Fullprof Suite: http://www.ill.fr/sites/fullprof/ MacDiff: http://www.esm-software.com/macpdf/ Powder3D: http://www.fkf.mpg.de/xray/html/powder3d.html Powder Cell: http://www.ccp14.ac.uk/ccp/web-mirrors/powdcell/a v/v 1/powder/ e cell.html Powder v4: http://www.ccp14.ac.uk/ccp/web-mirrors/ndragoe/html/software.html PowderX: http://www.ccp14.ac.uk/ccp/web-mirrors/powderx/Powder/ PowDLL: http://users.uoi.gr/nkourkou/ POWF: http://www.crystal.vt.edu/crystal/powf.html Pulwin: http://users.uniud.it/bruckner/pulwin.html VCTCONV: http://www.ccp14.ac.uk/ccp/web-mirrors/convx/ WinFIT: http://www.geol.uni-erlangen.de/index.php?id=58&L=3

Conversion of crystal structures to different formats

AXES: http://www.physic.ut.ee/~hugo/axes/ Cryscon: http://www.shapesoftware.com/#anchor_cryscon Crystals: http://www.shapesoftware.com/#anchor_cryscon Crystals: http://www.shapesoftware.com/#anchor_cryscon Gretep: http://www.ccp14.ac.uk/tutorial/lmgp/ MolXtl: http://www.ccp14.ac.uk/tutorial/lmgp/ MolXtl: http://www.uwm.edu/Dept/Chemistry/molxtl/ Open Babel: http://openbabel.sourceforge.net/ GUI Ortep III for Windows: http://www.chem.gla.ac.uk/~louis/software/ Platon: http://www.cryst.chem.uu.nl/platon/ Platon (MS-windows port): http://www.chem.gla.ac.uk/~louis/software/ Powder Cell: http://www.ccp14.ac.uk/ccp/web-mirrors/powdcell/a_v/v_1/powder/ e_cell.html Structure Tidy: (within Platon) WinGX: http://www.chem.gla.ac.uk/~louis/software/

Powder pattern viewing and processing

AXES: http://www.physic.ut.ee/~hugo/axes/ CMPR: http://www.ncnr.nist.gov/xtal/software/cmpr/ Fityk: http://www.unipress.waw.pl/fityk/ Fullprof Suite: http://www.ill.fr/sites/fullprof/ OpenGenie: http://www.isis.rl.ac.uk/OpenGENIE/ Powder3D: http://www.fkf.mpg.de/xray/html/powder3d.html Powder Cell: http://www.ccp14.ac.uk/ccp/web-mirrors/powdcell/a_v/v_1/powder/ e_cell.html Powder v4: http://www.ccp14.ac.uk/ccp/web-mirrors/ndragoe/html/software.html PowderX: http://www.ccp14.ac.uk/ccp/web-mirrors/powderx/Powder/ Pulwin: http://users.uniud.it/bruckner/pulwin.html WinFIT: http://www.geol.uni-erlangen.de/index.php?id=58&L=3 XFIT: http://www.ccp14.ac.uk/tutorial/xfit-95/xfit.htm

Software packages which can perform peak finding and peak profiling

AXES: http://www.physic.ut.ee/~hugo/axes/ CMPR: http://www.ncnr.nist.gov/xtal/software/cmpr/ Fityk: http://www.unipress.waw.pl/fityk/ Fullprof Suite: http://www.ill.fr/sites/fullprof/ GSAS RawPlot: http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/gsas/public/gsas/ Powder3D: http://www.fkf.mpg.de/xray/html/powder3d.html Powder v4: http://www.ccp14.ac.uk/ccp/web-mirrors/ndragoe/html/software.html PowderX: http://www.ccp14.ac.uk/ccp/web-mirrors/powderx/Powder/ PRO-FIT: http://www.crl.nitech.ac.jp/~toraya/software/ PULWIN: http://users.uniud.it/bruckner/pulwin.html SHADOW: http://www.du.edu/~balzar/breadth.htm SHADOW-Commercial: http://www.materialsdata.com/ WinFIT: http://www.geol.uni-erlangen.de/index.php?id=58&L=3 XFIT: http://www.ccp14.ac.uk/tutorial/xfit-95/xfit.htm

Powder indexing

Dicvol 91: http://sdpd.univ-lemans.fr/ftp/dicvol91.zip Dicvol 2004 / Dicvol 2006: http://www.ccp14.ac.uk/ccp/web-mirrors/dicvol/ Eflect/Index: http://www.bgmn.de/related.html Fjzn: http://www.ccp14.ac.uk/tutorial/crys/ Ito: http://sdpd.univ-lemans.fr/ftp/ito13.zip Kohl/TMO: http://www.ccp14.ac.uk/ccp/web-mirrors/kohl-tmo/ Lzon: http://www.ccp14.ac.uk/tutorial/crys/ MAUD: http://www.ing.unitn.it/~maud/ McMaille: http://sdpd.univ-lemans.fr/McMaille/ Supercell: http://sdpd.univ-lemans.fr/McMaille/ Supercell: http://www.ill.fr/dif/Soft/fp/ Taup/Powder: http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/taupin-indexing/pub/ powder/ Topas-Academic: http://members.optusnet.com.au/~alancoelho/ Topas: http://www.bruker-axs.de/index.php?id=topas Treor90: http://sdpd.univ-lemans.fr/ftp/treor90.zip Treor 2000: http://www.ic.cnr.it/ VMRIA/AUTOX: http://www.ccp14.ac.uk/ccp/web-mirrors/vmria/ XCell: http://accelrys.com/products/materials-studio/modules/xcell.html

Powder indexing suites

AXES: http://www.physic.ut.ee/~hugo/axes/ CMPR: http://www.ncnr.nist.gov/xtal/software/cmpr/ Crysfire: http://www.ccp14.ac.uk/tutorial/crys/ Powder v4: http://www.ccp14.ac.uk/ccp/web-mirrors/ndragoe/html/software.html PowderX: http://www.ccp14.ac.uk/ccp/web-mirrors/powderx/Powder/ Fullprof Suite: http://www.ill.fr/dif/Soft/fp/ Chekcell: http://www.ccp14.ac.uk/tutorial/Imgp/

Spacegroup assignment

Absen: http://www.nuigalway.ie/cryst/software.html Chekcell: http://www.ccp14.ac.uk/tutorial/lmgp/ Extsym: http://www.markvardsen.net/projects/ExtSym/main.html ISOTROPY: http://stokes.byu.edu/isotropy.html IUCr International Tables for Crystallography: http://it.iucr.org/ MAUD: http://www.ing.unitn.it/~maud/ Platon: http://www.cryst.chem.uu.nl/platon/ Platon (MS-windows port): http://www.chem.gla.ac.uk/~louis/software/ Topas-Academic: http://members.optusnet.com.au/~alancoelho/ Topas: http://www.bruker-axs.de/index.php?id=topas WinGX: http://www.chem.gla.ac.uk/~louis/software/

Spacegroup information

Bilbao Crystallographic Server: http://www.cryst.ehu.es/
cctbx – sgtbx Explore symmetry: http://cci.lbl.gov/cctbx/explore_symmetry.html
GETSPEC: http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown/getspec/
Hypertext Book of Crystallographic Space Group Diagrams and Tables:
http://img.chem.ucl.ac.uk/sgp/
IUCr International Tables for Crystallography: http://it.iucr.org/
SGInfo: http://cci.lbl.gov/sginfo/
Space Group Explorer: http://www.calidris-em.com/archive.htm
Space Group Info: http://www.ill.fr/sites/fullprof/
Superspace groups for 1D and 2D Modulated Structures: http://quasi.nims.go.jp/
yamamoto/spgr.html
Wgetspec: http://www.ccp14.ac.uk/tutorial/lmgp/

Unit cell refinement

Celref: http://www.ccp14.ac.uk/tutorial/lmgp/ Eracel: http://sdpd.univ-lemans.fr/ftp/eracel.zip LAPOD: http://www.ccp14.ac.uk/ccp/web-mirrors/lapod-langford/ LAPODS: http://www.ccp14.ac.uk/ccp/web-mirrors/powderx/lapod/ Powder v4: http://www.ccp14.ac.uk/ccp/web-mirrors/ndragoe/html/software.html Refcel: http://img.chem.ucl.ac.uk/www/cockcroft/profil.htm UNITCELL: http://rock.esc.cam.ac.uk/astaff/holland/UnitCell.html UNITCELL: http://www.crl.nitech.ac.jp/~toraya/software/ XLAT: http://ruppweb.dyndns.org/new_comp/xlat_new.htm

Le Bail whole profile fitting

(available in nearly all modern Rietveld software)

Pawley whole profile fitting

GSAS: http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/gsas/public/gsas/ PRODD: http://www.ccp14.ac.uk/ccp/web-mirrors/prodd/~jpw22/ Simpro: http://www.uni-tuebingen.de/uni/pki/simref/simpro.html Topas-Academic: http://members.optusnet.com.au/~alancoelho/ Topas: http://www.bruker-axs.de/index.php?id=topas WPPF: http://www.crl.nitech.ac.jp/~toraya/software/

Pole figure and texture analysis

BEARTEX: http://eps.berkeley.edu/~wenk/TexturePage/beartex.htm GSAS: http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/gsas/public/gsas/ LABOTEX: http://www.labosoft.com.pl/ MAUD: http://www.ing.unitn.it/~maud/ POFINT: http://www.ecole.ensicaen.fr/~chateign/qta/pofint/ PopLA: http://www.lanl.gov/orgs/mst/cms/poplalapp.html STEREOPOLE: http://www.if.tugraz.at/amd/stereopole/ TexTools: http://www.resmat.com/ TexturePlus: http://www.ceramics.nist.gov/webbook/TexturePlus/texture.htm

Size/Strain analysis

BGMN: http://www.bgmn.de/ BREADTH: http://mysite.du.edu/~balzar/breadth.htm CMWP-fit: http://www.renyi.hu/cmwp/ Fullprof Suite: http://www.ill.fr/dif/Soft/fp/ GENEFP: http://crystallography.zhenjie.googlepages.com/GeneFP.html MAUD: http://www.ing.unitn.it/~maud/ MudMaster: ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/MudMaster/ Powder Cell: http://www.ccp14.ac.uk/ccp/web-mirrors/powdcell/a_v/v_1/powder/ e_cell.html Topas-Academic: http://members.optusnet.com.au/~alancoelho/ Topas: http://www.bruker-axs.de/index.php?id=topas WinFIT: http://www.geol.uni-erlangen.de/index.php?id=58&L=3

Single crystal suites

Crystals: http://www.xtl.ox.ac.uk/ DS*SYSTEM: http://www.ccp14.ac.uk/ccp/web-mirrors/okada/ LinGX: http://www.xtal.rwth-aachen.de/LinGX/ ORTEX: http://www.nuigalway.ie/cryst/software.html Platon / System S: http://www.cryst.chem.uu.nl/platon/ Sir2004: http://www.ic.cnr.it/ WinGX: http://www.chem.gla.ac.uk/~louis/software/ Xtal: http://xtal.sourceforge.net/

Powder diffraction suites

AXES: http://www.physic.ut.ee/~hugo/axes/ BRASS: http://www.brass.uni-bremen.de/ CPMR / EXPGUI / GSAS: http://www.ncnr.nist.gov/xtal/software/cmpr/ & http://www.ncnr.nist.gov/programs/crystallography/software/expgui/ Fullprof Suite: http://www.ill.fr/sites/fullprof/ Topas-Academic: http://members.optusnet.com.au/~alancoelho/ Topas: http://www.bruker-axs.de/index.php?id=topas

Quantitative phase analysis (also refer to Rietveld software)

Fullpat: http://www.ccp14.ac.uk/ccp/web-mirrors/fullpat/ MAUD: http://www.ing.unitn.it/~maud/ Quanto: http://www.ing.unitn.it/~luttero/ RiQAS: http://www.materialsdata.com/ri.htm Rockjock: ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/RockJock/ Siroquant: http://www.sietronics.com.au/siroquant.html

Solving structures from powder data

BGMN: http://www.bgmn.de/ Dash: http://www.ccdc.cam.ac.uk/products/powder_diffraction/dash/ Endeavour: http://www.crystalimpact.com/endeavour/ EXPO: http://www.ic.cnr.it/ ESPOIR: http://sdpd.univ-lemans.fr/sdpd/espoir/ Focus: http://cci.lbl.gov/~rwgk/focus/ Fox: http://objcrvst.sourceforge.net/Fox/ Fullprof Suite: http://www.ill.fr/sites/fullprof/ Gest: http://crystallography.zhenjie.googlepages.com/GEST.html GRINSP: http://sdpd.univ-lemans.fr/grinsp/ Organa: E-mail: rene@science.uva.nl Reflex: http://accelrvs.com/products/materials-studio/modules/reflex.html Ruby: http://www.materialsdata.com/products.htm SARAh: http://www.chem.ucl.ac.uk/people/wills/ Superflip: http://superspace.epfl.ch/superflip/ Topas-Academic: http://members.optusnet.com.au/~alancoelho/ Topas: http://www.bruker-axs.de/index.php?id=topas WinCSD: http://www.chem.umd.edu/facility/xray/Zavalij/CSD.html ZEFSA II: http://www.mwdeem.rice.edu/zefsaII/

Single crystal structure solution

Crisp: http://xtal.sourceforge.net/ Crunch: http://www.bfsc.leidenuniv.nl/software/crunch/ Dirdif: http://www.xtal.science.ru.nl/documents/software/dirdif.html Shake'n'Bake (SnB): http://www.hwi.buffalo.edu/SnB/ ShakePSD: http://www.ccp14.ac.uk/ccp/web-mirrors/okada/ Shelx86 to Shelxd: http://shelx.uni-ac.gwdg.de/SHELX/ Sir 92 to Sir2004: http://www.ic.cnr.it/

Structure building and single crystal refinement

Crystals: http://www.xtl.ox.ac.uk/ Platon / System S: http://www.cryst.chem.uu.nl/platon/ Shelxl97: http://shelx.uni-ac.gwdg.de/SHELX/ Sir2004: http://www.ic.cnr.it/ Xtal: http://xtal.sourceforge.net/ WinGX: http://www.chem.gla.ac.uk/~louis/software/

Free-standing Fourier map generation or display

DrawXTL: http://www.lwfinger.net/drawxtl/ FOUE: http://www.ccp14.ac.uk/ccp/web-mirrors/scott-belmonte-software/foue/ Fox: http://objcryst.sourceforge.net/Fox/ GFourier/ Fullprof Suite: http://www.ill.fr/sites/fullprof/ MCE – Marching Cubes: http://www.vscht.cz/min/mce/ OpenDX: http://www.opendx.org/

Platon: http://www.cryst.chem.uu.nl/platon/

Platon (MS-windows port): http://www.chem.gla.ac.uk/~louis/software/

VENUS: http://homepage.mac.com/fujioizumi/visualization/VENUS.html

WinGX: http://www.chem.gla.ac.uk/~louis/software/

Rietveld

ARITVE: http://sdpd.univ-lemans.fr/aritve.html BGMN: http://www.bgmn.de/ BRASS: http://www.brass.uni-bremen.de/ DBWS: http://www.physics.gatech.edu/downloads/young/DBWS.html DIFFaX+: E-mail matteo.leoni@unitn.it EXPO: http://www.ic.cnr.it/ Fullprof Suite: http://www.ill.fr/sites/fullprof/ GSAS: http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/gsas/public/gsas/ IC-POWLS: E-mail W.Kockelmann@rl.ac.uk Jana: http://www-xray.fzu.cz/jana/Jana2000/jana.html Koalariet: http://www.ccp14.ac.uk/ccp/web-mirrors/xfit-koalariet/ MAUD: http://www.ing.unitn.it/~maud/ MXD: http://perso.neel.cnrs.fr/pierre.wolfers/PW Programs/Prog Cristallo.html PFLS: http://www.crl.nitech.ac.jp/~toraya/software/ Powder Cell: http://www.ccp14.ac.uk/ccp/web-mirrors/powdcell/a_v/v_1/powder/ e cell.html PREMOS: http://quasi.nims.go.jp/yamamoto/ PRODD: http://www.ccp14.ac.uk/ccp/web-mirrors/prodd/~jpw22/ Profil: http://img.chem.ucl.ac.uk/www/cockcroft/profil.htm RIETAN: http://homepage.mac.com/fujioizumi/rietan/angle_dispersive/ angle_dispersive.html Rietica: http://www.rietica.org/ Simref: http://www.uni-tuebingen.de/uni/pki/simref/simref.html SR5/Riet7/LHPM: http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/csirominerals-anon-ftp/ pub/xtallography/sr5/ Topas-Academic: http://members.optusnet.com.au/~alancoelho/ Topas: http://www.bruker-axs.de/index.php?id=topas VMRIA: http://www.ccp14.ac.uk/ccp/web-mirrors/vmria/ XND: ftp://ftp.grenoble.cnrs.fr/xnd/ XRS-82/DLS-76: http://www.crystal.mat.ethz.ch/Software/XRS82/

Pair distribution function/total scattering

DERB and DERFFT: http://www.ccp14.ac.uk/ccp/web-mirrors/derb-derfft/ DISCUS: http://www.mineralogie.uni-wuerzburg.de/crystal/discus/ MCGRtof: E-mail m.g.tucker@rl.ac.uk PDFFIT: http://www.mineralogie.uni-wuerzburg.de/crystal/discus/ PDFgetN: http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetN/ PDFgetX2: http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/ RAD: http://www.pa.msu.edu/~petkov/software.html RMC++: http://www.szfki.hu/~nphys/rmc++/opening.html RMCprofile: http://www.isis.rl.ac.uk/RMC/ or E-mail m.g.tucker@rl.ac.uk RMCAW95: http://sdpd.univ-lemans.fr/glasses/rmca/rmcaw95.html

Hydrogen calculation and placement

Crystals: http://www.xtl.ox.ac.uk/ Hydrogen/CalcOH: http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/nardelli/pub/nardelli/ and in WinGX Platon/System S: http://www.cryst.chem.uu.nl/platon/ Shelxl97: http://shelx.uni-ac.gwdg.de/SHELX/ Sir2004: http://shelx.uni-ac.gwdg.de/SHELX/ Sir2004: http://www.ic.cnr.it/ SnB: http://www.hwi.buffalo.edu/SnB/ Xhydex: http://xray.chm.bris.ac.uk/software/XHYDEX/ & in WinGX Xtal: http://xtal.sourceforge.net/ WinGX: http://www.chem.gla.ac.uk/~louis/software/

Powder pattern calculation (also refer to Rietveld software)

Platon: http://www.cryst.chem.uu.nl/platon/ Platon (MS-windows port): http://www.chem.gla.ac.uk/~louis/software/ Powder Cell: http://www.ccp14.ac.uk/ccp/web-mirrors/powdcell/a_v/v_1/powder/ e_cell.html Powdis and Powutl: ttp://www.nuigalway.ie/cryst/software.html Poudrix: http://www.ccp14.ac.uk/tutorial/lmgp/ WinGX (using Lazy Pulverix): http://www.chem.gla.ac.uk/~louis/software/

Validation

Addsym: (within Platon) Bond Str/Fullprof Suite: http://www.ill.fr/sites/fullprof/ Bond Valence Wizard: http://orlov.ch/bondval/ CHKSYM: http://www.nuigalway.ie/cryst/software.html Crystals: http://www.xtl.ox.ac.uk/ Mogul: http://www.ccdc.cam.ac.uk/products/csd_system/mogul/ Ortex: http://www.nuigalway.ie/cryst/software.html Platon: http://www.cryst.chem.uu.nl/platon/ Platon (MS-windows port): http://www.chem.gla.ac.uk/~louis/software/ softBV: http://kristall.uni-mki.gwdg.de/softbv/ Valence: http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown/bond_valence_param/ VaList: http://www.chem.ucl.ac.uk/people/wills/ WinGX: http://www.chem.gla.ac.uk/~louis/software/

Structure plotting and drawing

ATOMS: http://www.shapesoftware.com/ Balls and Sticks: http://www.toycrate.org/ BALSAC: http://www.fhi-berlin.mpg.de/~hermann/Balsac/ Cameron: within Crystals and WinGX Carine: http://pros.orange.fr/carine.crystallography/ Crystallographica: http://www.crystallographica.co.uk/ Crystal Maker: http://www.crystalmaker.co.uk/ Crystals: http://www.xtl.ox.ac.uk/ Crystal Studio: http://www.crystalsoftcorp.com/CrystalStudio/ CrystMol: http://www.crystmol.com/ Diamond: http://www.crystalimpact.com/ DrawXTL: http://www.lwfinger.net/drawxtl/ FpStudio: http://www.ill.fr/sites/fullprof/ GRETEP: http://www.ccp14.ac.uk/tutorial/lmgp/ Mercury: http://www.ccdc.cam.ac.uk/products/mercury/ MolXtl: http://www.uwm.edu/Dept/Chemistry/molxtl/ OLEX: http://www.ccp14.ac.uk/ccp/web-mirrors/lcells/index.htm ORTEP III: http://www.ornl.gov/sci/ortep/ortep.html Ortep-III for Windows (GUI): http://www.chem.gla.ac.uk/~louis/software/ ORTEX/Oscail X: http://www.nuigalway.ie/cryst/software.html Platon: http://www.cryst.chem.uu.nl/platon/ Platon (MS-windows port): http://www.chem.gla.ac.uk/~louis/software/ PowderCell: http://www.ccp14.ac.uk/ccp/web-mirrors/powdcell/a_v/v_1/powder/ e_cell.html PRJMS: http://quasi.nims.go.jp/yamamoto/ Schakal: http://www.krist.uni-freiburg.de/ki/Mitarbeiter/Keller/ Struplo for Windows: http://www.brass.uni-bremen.de/ Struplo (old Windows port): http://www.chem.gla.ac.uk/~louis/software/ Struvir: http://sdpd.univ-lemans.fr/vrml/struvir.html Venus/PRIMA: http://homepage.mac.com/fujioizumi/visualization/VENUS.html WinGX: http://www.chem.gla.ac.uk/~louis/software/ XmLmctep: http://www.lmcp.jussieu.fr/~soyer/Lmctep_en.html X-Seed: http://x-seed.net/ Xtal-3D: http://icsd.ill.fr/icsd/help/xtal-3d.html XtalDraw: http://www.geo.arizona.edu/xtal/xtaldraw/xtaldraw.html

Chapter 2 Introduction to Diffraction

Abraham Clearfield

2.1 Introduction to X-ray diffraction

2.1.1 Brief history and Bragg's law

Following the discovery of X-rays in 1895 by Wilhelm Conrad Rontgen, Max von Laue, after discussions with P. P. Ewald, realized that crystals may act as diffraction gratings for X-rays. An experiment was set up by W. Friedrich and P. Knipping, who indeed demonstrated the validity of Von Laue's hypothesis. The year was 1912, Von Laue then developed the theory to explain X-ray diffraction that we will consider later in the text. For these achievements, Max von Laue was awarded the Nobel Prize in 1914.

X-rays are an electromagnetic radiation of small wavelengths. Crystals are threedimensional arrays of atoms or molecules with fixed positions that consist of a basic motif that is repeated in space by three non-coplanar vectors to produce the crystal. Because of this repetition and the fact that X-ray wavelengths have dimensions similar to those of bond distances, the crystal can act as a diffraction grating for the incident X-rays. The arrangement of the atoms may be considered as lying in sets of planes with varying interplanar distances *d*. This is illustrated in Figure 2.1 where the atoms have been replaced by points.

In 1914, the father and son team, William Henry Bragg and William Laurence Bragg simplified the three-dimensional theory of diffraction developed by von Laue into considering the diffracted radiation as being reflected by sets of parallel planes of atoms. The condition for diffraction from a set of parallel planes of interlayer spacing d is

$$\sin\theta = \frac{n\lambda}{2d} \tag{2.1}$$

where θ is the angle of incidence of the X-rays to the planes and λ is the X-ray wavelength as shown in Figure 2.2. When the wavelets of the X-ray beam leave the source, all the wavelets are in phase. As the wavelets enter the crystal they travel longer distances than the wavelet reflected from the surface. These distances are dependent on the interlayer spacing, *d*. The wavelets are in phase at the line *BJL* drawn parallel to *ADG*. The path length difference between the wavelets *ABC* and *DEF* is *JE* + *EK* and for the wavelet *GHI*, *LH* + *HM*. The condition for diffraction is that the wavelets be in phase at *BKM*. This requires that the distance *JE* + *EK* = $n\lambda$, that is, the path difference is an integral number of wavelengths.



Figure 2.1 A three-dimensional point lattice and some examples of a set of parallel planes of points.



Figure 2.2 Illustration of Bragg reflection from a set of parallel planes.

If $JE + EK = \lambda$, then $LH + HM = 2\lambda$, and so on and all the layers in the stack scatter in phase and the intensity of diffracted photons is recorded by the detector. If the wavelets are slightly out of phase destructive interference occurs because there are hundreds of layers with the out of phase-ness increasing by degrees, *n* is usually taken to be one, and it is understood that we are dealing with a monochromatic beam.

Applying this equation the Braggs were able to solve the crystal structures of NaCl and KCl. Subsequently, the structures of many simple inorganic compounds were solved. Single crystals are largely used for structure determination. However, upon consideration of equation (2.1) it was realized that powdered solids may also be used to provide diffraction data. In a finely divided powder containing millions of particles their orientation is normally chaotic. That is, they will statistically have large numbers of crystallites in every possible orientation to the X-ray beam. Placing such a sample in the X-ray beam generates diffraction from all the sets of planes simultaneously but at angles that depend upon the values of d. Application of the powder technique has tremendous value as not all solids can be obtained as large enough (order of tenths of millimeters) single crystals.

Powder diffraction is widely used throughout industry, academia or wherever knowledge of solids is required. With the great advances in electronics, computers and software the accuracy of the data, the ease of obtaining it and data interpretation has progressed accordingly. In the last two decades a large effort has been put forward to determine crystal structures from X-ray powder data. This effort has been largely successful to the point where a great deal of information on structure may be obtained even from solids as complex as crystalline proteins.

2.1.2 Recording an X-ray powder diffraction pattern (XRPD)

At this point you may be wondering what Bragg's equation tells us. Let us consider a powdered sample of a pure crystalline substance.

Consider a set of parallel atomic planes within the crystal to be oriented to the incident X-ray beam as in Figure 2.3a. The incident beam is at angle θ to the set of planes. The incident beam passes through the sample and strikes the detector at $\theta = 0^{\circ}$.

It is immediately apparent that the reflected beam is at angle 2θ to the zero point. If the detector were placed at the angle of reflection 2θ , it would record the diffracted intensity for this set of planes. Imagine that the set of crystal planes precesses around the incident beam while always maintaining an angle theta to it. The diffracted radiation then forms a cone of radiation about the incident beam as cone axis (Figure 2.3b). If a film is placed at the bottom of the cone, the radiation would form a black circle on the film. Since many sets of parallel planes with different d-spacings are present in the sample, a set of concentric circles would be recorded simultaneously on the film. A moment's reflection should convince you that only those cones whose base is less than the film length would be recorded. Debye and Scherrer independently developed a simple camera that would record all the data (see Chapter 3). They chose a steel hollow cylinder into which a strip of film is placed around the inside periphery. The sample is held in the center of the cylinder and is rapidly rotated to insure uniformity of distribution of the crystallites. All the concentric circles of diffracted radiation are now recorded on the 360° strip of film. The developed film appears as shown in Figure 2.3c. Portions of the base of each cone are recorded on the film as pairs of arcs that are proportional to 4θ the circle diameter. More properly we know that the angle subtended in radians is given by the arc divided by the camera radius. Cleverly, the radius of the camera was made to be 57.3 mm so that 1 mm in arc measured linearly is 1° in theta. From the measured θ values Bragg's equation allows us to determine all the recorded *d*-spacings.



Figure 2.3 (a) Bragg reflection from a set of lattice planes. (b) The cone of diffracted X-rays from a powder specimen. The cone contains all X-rays reflected from one particular family of lattice planes in all crystals which are correctly oriented. (c) The form of a powder pattern (asymmetric film mounting).

In its simplest use, the list of d-spacings serves as a fingerprint to identify the crystalline phase.

Film methods are tedious to apply. Careful measurements of all the arc-pairs may take several hours, in addition to development of the film, drying and correcting for film shrink-age. Fortunately, automated diffractometers were developed that obviate the use of film. Such instruments are able to move the detector around the focusing circle recording the X-ray intensities one at a time. One can think of it as photometering the film pattern from 0 to 90° θ to produce a pattern as shown in Figure 2.4. This powder pattern is a one-dimensional recording of the intensity of diffracted radiation from all the sets of parallel planes as a function of the angle 2θ within the angular range measured. The *d*-spacings are then calculated using equation (2.1) in the form.

$$d = \frac{n\lambda}{2\sin\theta} \tag{2.2}$$



Figure 2.4 Plot of 2θ vs X-ray intensity.

We show that from a knowledge of the d-spacings, a unit cell can be derived that contains the basic repeat motif of the crystal. The solution of the complete crystal structure involves determining the position of all the atoms in the unit cell relative to an axial system. The complete crystal structure solution requires that two problems be solved. One is geometrical in nature and requires a knowledge of the d-spacings of all the reflections or peaks in the powder pattern. In the case of a single crystal the crystal may be oriented relative to the X-ray beam such that only one set of planes at a time is in the Bragg position to diffract. Then the d-spacings for all the sets of planes may be recorded in three-dimensional space to obtain a more complete solution to the geometrical problem than is possible from a powder pattern. The solution takes the form of the unit cell dimensions, and the symmetry of the atomic or molecular arrangement in the form of a collection of symmetry elements and their position in the unit cell. This collection of symmetry elements is termed a space group.

In order to locate the individual atoms we must determine the integrated intensities of all the X-ray reflections. That is, we must measure the areas under the many peaks in the X-ray pattern. We must now consider how this is done and what use we make of these intensities. This is in the nature of a physical problem.

2.2 Solving the geometric problem

If we are to solve the geometrical problem, then we need to define the unit cell more precisely. Furthermore, if we are to locate the individual atoms within the unit cell we must have an axial system whose origin acts as the origin and along whose axes X, Y, Z we can define the unit cell. In order to do this there are certain conditions of symmetry that must be adhered to. Crystals have smooth faces and sharp edges that enclose space. In order to

System	Minimal symmetry	Axial conditions
Triclinic Monoclinic Orthorhombic Tetragonal Cubic Hexagonal (a) Rhombohedral (b) Hexagonal	1 or 1 2 or 2 222 4 or 4 Four 3s or 3s 3 or 6 (3 or 6) 3 6	$a \neq b \neq c, \alpha \neq \beta \neq \gamma$ $a \neq b \neq c, \alpha = \gamma = 90^{\circ} \neq \beta$ $a \neq b \neq c, \alpha = \beta = \gamma = 90^{\circ}$ $a = b \neq c, \alpha = \beta = \gamma = 90^{\circ}$ $a = b = c, \alpha = \beta = \gamma = 90^{\circ}$ $a = b = c, \alpha = \beta = \gamma \neq 90^{\circ}$ $a = b \neq c, \alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$

Table 2.1 Crystal axis system

fulfill the space filling requirement, the symmetry of the faces requires that the crystal shape be limited to a small number of symmetry elements. These are rotation axes that are 1-, 2-, 3-, 4- and 6-fold, mirror planes and a center of symmetry. All of these symmetry elements must pass through the center of the crystal so that the collection of symmetry elements forms a point group. There are just 32 arrangements of the symmetry elements leading to the 32 crystallographic point groups.

These symmetry elements also restrict and specify the types of axial systems to those listed in Table 2.1. It is up to the reader to convince himself or herself why non-right angle axes are required for some systems. For example, if the crystal contains a 3-fold principal axis, the symmetry operation requires a rotation of a point to an equivalent point at 120° and two additional rotations of 120° to return to point zero. Thus, three points are generated all told. In a similar manner, a 6-fold axis requires a rotation of 60°. The rhombohedral and hexagonal axial systems result from the presence of these axes within the crystal.

We can now further proceed to consider the nature of X-ray interactions with crystals.

2.2.1 Principles of X-ray diffraction: the Laue equations

X-rays form part of the electromagnetic spectrum with wavelengths ranging from 10^{-3} to several hundred Angstroms depending on the tube voltage. For X-ray diffraction purposes, characteristic radiation in the 0.5–2 Å range is used. When an X-ray beam strikes an atom, the electrons are set into periodic motion or vibration by the electric and magnetic fields of the beam. The energy absorbed is reradiated in all directions. A single electron would produce a sphere of scattered radiation about itself. Let us first consider a row or onedimensional lattice of such scattering points. A parallel beam of monochromatic X-rays is directed perpendicular to the row as shown in Figure 2.5. The rays are scattered at some angle α , which is the acute angle between the row and the scattered beam and detected (by film or Geiger counter) at some distance from the row. In order for the beam to be observed by the detector, the individual wavelets must be in phase. Since the incident wavelets were parallel, they are in phase at *FI*, but upon being scattered, travel different path lengths (*IJ* vs *FG*). *IK* is drawn perpendicular to *FG* from *I* and hence is parallel to *JG*. Then



Figure 2.5 Diffraction of X-rays from a one-dimensional lattice.

the path lengths of the scattered wavelets differ by *FK*. This distance must be an integral number of wavelengths if the waves are to be in phase at the detector. Thus, $FK = n\lambda$, where n = an integer. But $\cos \alpha = (FK/a)$ and

$$n\lambda = a\cos\alpha \tag{2.3}$$

Equation (2.3) tells us that diffraction from a one-dimensional lattice will occur at all angles α , whose cosines are $n\lambda/a$, and *a* is the distance separating the points.

When n = 0, $\alpha = 90^{\circ}$ and the rays are scattered into the path followed by the incident beam. This is termed "zeroth" order diffraction. First-order diffraction, n = 1, occurs at a smaller angle, α_1 , and so on. Now the scattered beams do not lie in a plane, as shown in Figure 2.3, but must be considered in a three-dimensional context. The line IJ (and FG) can be rotated 90° counter-clockwise while still anchored at I so that the wavelet is directed at the reader. IJ still maintains the angle α to the row of points and therefore satisfies equation (2.3). In fact, IJ and FG can act as the generator of a cone of scattered radiation, coaxial with the row of points, and of half-angle opening α (Figure 2.6a). Keeping in mind that the cones will be directed forward and backward as n can be both positive and negative. If a flat plate film is placed perpendicular to the incident X-ray beam, as shown in Figure 2.6a, then the cones will cut the film in hyperbolae and the zeroth-order circle in a straight line (Figure 2.6b).

In the general case of diffraction from a row of points, the incident beam will not be perpendicular to the row. Thus, the path length difference between the two wavelets is FK - OM (Figure 2.7) and the condition for diffraction is

$$m_1 \lambda = a \left(\cos \alpha - \cos \alpha_0 \right) \tag{2.4}$$

Let us now consider diffraction from a two-dimensional array of points in which additional rows of points identical to the first are placed at distances b apart. A series of concentric cones will form coaxial patterns with every row of points. However, only those about the a and b directions (arrows indicate vectors) need to be considered. Equation (2.4) will still hold for the cones which form along the a direction and a similar equation is required for direction b. In the general case, the incident beam will not be perpendicular to the a and b



Figure 2.6 (a) Intersection of diffraction cones from a one-dimensional lattice with a flat plate film to produce hyperbolae. (b) The appearance of the hyperbolae on the film. The values of m are equivalent to n in equation (2.3).



Figure 2.7 Diffraction from a one-dimensional row of points when the incident beam is not perpendicular to the row.

rows and then the conditions necessary for diffraction are

$$m_1 \lambda = a \left(\cos \alpha - \cos \alpha_0 \right) \tag{2.5a}$$

$$m_2 \lambda = b \left(\cos \beta - \cos \beta_0 \right) \tag{2.5b}$$

 α_0 and β_0 are the angles the incident beam makes with the a and b directions and α and β are the same angles for the diffracted beam, respectively. Any point in the lattice is part of both a and a b rows and has two sets of coaxial cones as given by equations (2.5a) and (2.5b) as shown along the directions OA and OB in Figure 2.8. In general, the two sets of cones will intersect and the intersection is a straight line or rather two straight lines as they intersect going in and coming out. These straight lines at the intersections of the cones simultaneously satisfy equations (2.5a) and (2.5b) and are the directions of the diffracted radiation from the net. Consider Figure 2.6a, and assume that the net is rectangular and lies parallel to the film but perpendicular to the beam. The cones from a will intersect as hyperbolae as shown, but the cones from b will be at right angles to the first set. This will produce a second set of hyperbolae at right angles to the first and create the pattern shown in Figure 2.9. Blackening of the film would occur only at the intersection of two hyperbolae as this is where equations (2.5a) and (2.5b) are simultaneously satisfied and hence where the diffracted X-rays would strike the film. If, on the other hand, the net was oriented parallel to the plane of the paper, the cones coaxial to the *b* direction (OB in Figure 2.8) would have their bases parallel to the film and would intersect the film in a series of concentric circles. The highest order diffraction cone would form the smallest circle and the lower the order, the larger the circle. Diffraction spots would then lie on the intersection of the circles with the hyperbolae from the cones coaxial with the OA or \vec{a} direction.



Figure 2.8 Cones of reflection in three dimensions. The cones are coaxial with the unit cell direction lines OA, OB, and OC. (From *X-ray Crystallography*, M. J. Buerger, John Wiley & Sons, 1942 with permission.)



Figure 2.9 Hypothetical diffraction pattern produced from a two-dimensional lattice by the intersection of cones about the A and B axes in Figure 2.8.

In three dimensions, three sets of cones, coaxial with *a*, *b* and *c*, respectively, need to be considered. A third equation is now required so that

$$m_1 \lambda = a \left(\cos \alpha - \cos \alpha_0 \right) \tag{2.5a}$$

$$m_2 \lambda = b \left(\cos \beta - \cos \beta_0 \right) \tag{2.5b}$$

$$m_3\lambda = c\left(\cos\gamma - \cos\gamma_0\right) \tag{2.5c}$$

The condition for constructive interference or diffraction is that the three equations, known as the Laue equations, be simultaneously satisfied (Nuffield, 1966) The cosines of the angles are the direction cosines of the diffracted and incident beams (Buerger, 1942), in the coordinate system defined by *a*, *b* and *c*, respectively. For simplicity, we assume an orthorhombic lattice and the beam perpendicular to the *ab* nets and parallel to *c*. With the film placed as shown in Figure 2.6, the intersection of the cones with the film would produce two sets of hyperbolae and one set of concentric circles about the center of the film as origin. In general, the three sets of curves will not meet at common points satisfying the three Laue equations (Figure 2.9), and only a small number of spots would appear on the film (Figure 2.10). To obviate this difficulty, the Laue method uses unfiltered radiation so a whole spectrum of wavelengths are diffracted simultaneously by the stationary crystal. For each wavelength, a set of cones develops and the probability of sets satisfying the Laue equations is greatly increased. However, one is still faced with the difficulty that now the wavelength is, in general, unknown.

It can be shown that the Laue equations and Bragg's law are equivalent. This equivalence will not be shown here but the interested reader is referred to Ladd and Palmer (2003). In



Figure 2.10 The lines trace the path of diffracted radiation using monochromatic radiation from a threedimensional lattice, two sets of hyperbola and a set of concentric circles. Note that in general, the three curves do not coincide.

fact if $m_1 = h$, $m_2 = k$ and $m_3 = l$ where hkl are the Miller indices, and a, b and c are the unit cell dimensions then the Laue equations provide the direction cosines for the incident and diffracted beam for each hkl plane. The equivalence of the Bragg and Laue treatments can then be visualized without the mathematical derivation.

2.2.2 Bravais lattices

In constructing the three-dimensional point lattice in the derivation of the Laue equations, we chose to place the points in such a way that $a \neq b \neq c$ but all the angles in the three directions were 90°. This is an orthorhombic lattice. The question arises how many different lattices are possible. Again we fall back on the allowed symmetry elements and their combinations with the proviso that every point in the lattice have identical surroundings. These restrictions lead to just 14 lattices from the lowest symmetry with only a one-fold symmetry axis, triclinic in which $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$ to the highest symmetry, cubic a = b = c, $\alpha = \beta = \gamma = 90^{\circ}$. The 14 allowed lattices are represented in Figure 2.11 as the points that would be present in a single unit cell of the lattice.

However, we note in Figure 2.11 that not all the points are at the corners of the unit cell. A moments reflection should convince you that the corner points are shared by eight unit cells. Thus, only one-eighth of each point lies within one unit cell and because there are eight such points the unit cell contains a single point. Such unit cells are termed primitive and given the symbol *P*. Three of the unit cells have a point in the center of the cell in



Figure 2.11 Representation of the 14 Bravais lattices of three-dimensional space.

addition to the corners and these are designated as body centered, symbol *I*. There are two face-centered cells, cubic and orthorhombic. Face centering, as the name implies, places points in the center of all six faces of the unit cell. Such points are shared by two unit cells contributing three points for a total of four per unit cell. The designation of such cells is *F*. Finally, we may have side centering or base centering where a point resides in a single set of faces of the unit cell. In the monoclinic system the set of points is restricted to the face that contains the 2-fold axis or the 90° angles. For example, if the *b*-axis is perpendicular to the *ac* face, the non-right angle is β and the point is in the *ab* face. Then the unit cell is designated as *C*-centered. Alternatively, the *c*-axis may be perpendicular to the *ab* plane, the point is in the *ac* face and the unit cell is *B*-centered. The choice is arbitrary, but the first

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alternative is preferred. In the orthorhombic system the centering can be in any face, *A*-, *B*-, or *C*-centered.

A simple method of designating the positions of points in the unit cell is to use fractions of unit cell dimensions *a*, *b*, *c*. Thus, the origin point is 000 meaning that the point is at 0*a*, 0*b*, 0*c*. A point in a particular face center is $\frac{1}{2}\frac{1}{2}0$ or $\frac{1}{2}0\frac{1}{2}$ meaning $\frac{1}{2}a$, $\frac{1}{2}b$, 0*c* and $\frac{1}{2}a$, 0*b*, $\frac{1}{2}c$, respectively. We could also designate points at other corners than the origin as 100, 010, and so forth, but because there must be a repetition of the points in every unit cell it is understood that 000 means points at each corner with one whole point within the cell.

2.2.3 Miller indices

We now need to connect the actual diffraction diagram or X-ray powder pattern to the axial system and unit cell through Bragg's law or the Laue equations. According to Bragg's law a set of planes will diffract, when it is oriented at an angle θ to a monochromatic X-ray beam. Knowing this we obtain the interlayer spacing of the set of planes.

Consider a plane within a unit cell that is oriented to the XYZ axes as shown in Figure 2.12. The unit cell axes *a*, *b*, *c* lie along X, Y, Z, respectively. The orientation of the plane can be given as the intercepts of the plane along the crystallographic axes. Let the intercepts be a/h, b/k, c/l where *hkl* are integers. For example, let the intercepts be $\frac{1}{3}a$, *b*, $\frac{1}{2}c$. Then

$$\frac{a}{h} = \frac{1}{3}a, \quad h = \frac{a}{1/3a} = 3$$
 (2.6)

Similarly, k = 1 and l = 2 and the plane is designated as the 312 plane or for the set of planes (312). Let us now consider a plane that cuts the *a*-axis at *a* and is parallel to the YZ



Figure 2.12 Intersection of a plane with the crystallographic axes.

plane. That is, the plane does not intercept the Y or Z axes except at infinity whose reciprocal is zero. Thus, the plane is designated 100 and the entire set (100).

In centered lattices, points occur halfway between the (100) planes. Planes can be drawn through them parallel to the (100) planes, but they cut the X axis at $\frac{1}{2}a$. These planes and all others in the stack, at intervals of $\frac{1}{2}a$ (including those at $a, \frac{3}{2}a$, etc.) have indices (200). It may seem curious that the (100) planes have now become part of the (200) stack; however, we see that what is important in X-ray diffraction is the spacing between planes. Thus, for the Miller indices (100) we mean that the plane is at a distance *a* from the origin of the axial system and all those at intervals of *a* from it to infinity. For (200) the interval is $\frac{1}{2}a$, and so on.

Crystal axes extend in both positive and negative directions. Thus, it is possible for a plane to cut an axis in the negative directions. In Figure 2.13, we have drawn both a (111) plane and the $(\bar{1}11)$ plane. In general, an *hkl* plane has eight faces as follows: (*hkl*), (*hk*

Consider a plane that cuts the X-axis at 2*a*, the Y-axis at $\frac{1}{2}b$ and the Z-axis at $\frac{1}{3}c$. The Miller indices are by definition $h = \frac{1}{2}$, k = 2, l = 3 or $\frac{1}{2}23$. However, we said that *hkl* should be integers hence we need to double the indices to (146). What this tells us is that the plane whose designation was $(\frac{1}{2}23)$ is not the first plane of the set of parallel planes. The first plane cuts the X-axis at 1, Y at $\frac{1}{4}$, and Z at $\frac{1}{6}$. The interlayer or *d*-spacing is the distance from the origin of the axial system to the first plane, that is, the perpendicular distance from the origin to the first plane. Imagine a plane parallel to (146) but passing through the origin of the axial system as in Figure 2.12. Then the vector *ON* is perpendicular to the two planes and is the *d*-spacing. Bragg's equation provides a list of *d*-spacing (inter-planar spacings) as a function of the angle at which diffraction from that set of planes occurs. *d* is represented as the vector *ON* in Figure 2.12. Therefore, *d* has a direct relationship to *hkl* in



Figure 2.13 Orientation of two planes 111 and 111 relative to the unit cell axial directions X, Y, Z.

System	d _{hkl}
Cubic	$\left[\frac{1}{a^2}(h^2 + k^2 + l^2)\right]^{-1/2}$
Tetragonal	$\left[\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right]^{-1/2}$
Orthorhombic	$\left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right]^{-1/2}$
Hexagonal	$\left[\frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2}\right]^{-1/2}$
	$\left[\frac{1}{a^2} \frac{(h^2 + k^2 + l^2)\sin^2 \alpha + 2(hk + kl + lh)(\cos^2 \alpha - \cos \alpha)}{1 - 2\cos^3 \alpha + 3\cos^2 \alpha}\right]$
Monoclinic	$\left[\frac{(h^2/a^2) + (l^2/c^2) - (2hl\cos\beta/ac)}{\sin^2\beta} + \frac{k^2}{b^2}\right]^{-1/2}$
Triclinic	$\left[\left(\frac{h^2}{a^2} \sin^2 \alpha + \frac{k^2}{b^2} \sin^2 \beta + \frac{l^2}{c^2} \sin^2 \gamma + \frac{2hk}{ab} (\cos \alpha \cos \beta - \cos \gamma) + \frac{2kl}{bc} (\cos \beta \cos \gamma - \cos \alpha) + \frac{2lh}{ca} (\cos \gamma \cos \alpha - \cos \beta) \right) \right]$
	$(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos \alpha \cos \beta \cos \gamma) \bigg]^{-1/2}$

Table 2.2 Values of the inter-planar spacing (d_{hkl}) in the six crystal systems

terms of a, b, c. This relationship for a cubic lattice is given by

$$d = \frac{a}{\left[h^2 + k^2 + l^2\right]^{1/2}} \tag{2.7}$$

There is obviously such a relationship for all lattices or unit cells as shown in Table 2.2 (Ladd and Palmer, 2003; Suryanarayana and Norton, 1998; Nuffield, 1966). From a knowledge of the *d*-spacing it is possible to assign a set of Miller indices to each peak in the powder pattern or to each reflection obtained from a single crystal. Correct assignment of *hkl* values yields the unit cell dimensions but there is an added bonus. There may arise a set of systematic absences in the reflection data, which identifies the space group to which the compound belongs. The space groups will be described in more detail later but sufficient to say that the space groups reveal the arrangement of all the symmetry elements to which the arrangement of the atoms or molecules adhere.

2.3 Scattering theory and treatment of X-ray diffraction data

In solving the crystal structure of a particular compound, we have set ourselves the task of determining the position relative to the unit cell axes of every atom in the unit cell. By definition, the repetition of the unit cell contents by *a*, *b*, *c* and their negatives reproduces the crystal. Nothing in Bragg's or the Laue equations provides for locating the individual atoms. This can be done only from a consideration of the reflection intensities. The connection here is that X-rays are scattered by electrons and atoms are collections of electrons. It is the *phase relationships* of all the electrons from all the atoms in the unit cell (actually the whole crystal but we need only consider one unit cell) that are responsible for the reflection intensities. Therefore, we must consider the electron scattering problem.

2.3.1 Scattering of X-rays from a single electron

Let us first consider the X-rays as an electromagnetic wave that is sinusoidally propagated with time. An oscillating electric and magnetic field are created at right angles to the direction of propagation. Because an electric field exerts a force on a charged particle, the oscillating electric field will set any electron into oscillatory motion about its mean position. An electron set into such oscillating motion is continuously accelerating and decelerating and, in so doing, extracts energy from the incident wave and emits this energy as a new electromagnetic wave. This wave is said to be scattered. The scattered beam has the same wavelength as the incident beam and is referred to as *coherent* with it because there is a definite relationship between the phase of the scattered beam and the incident beam. The X-rays are scattered in all directions but because of the oscillatory motion of the electric field, the intensity is angle dependent. J.J. Thomson derived the following expression for the intensity (Cullity and Stock, 2001; Jenkins and Synder, 1996):

$$I = I_0 \left(\frac{e^4}{r^2 m^2 c^4}\right) \sin^2 \phi \tag{2.8}$$

where ϕ is the angle between *E*, the electromagnetic field vectors and the direction of the incident beam (Figure 2.14), *e* = electron charge, *m* = electron mass, *c* = speed of light, *r* = distance from electron.

Because $\phi = 90^{\circ} - 2\theta$ and $\sin \phi = \sin(90^{\circ} - 2\theta) = \cos 2\theta$

$$I = I_0 \left(\frac{e^4}{r^2 m^2 c^4}\right) \cos^2 2\theta \tag{2.9}$$

We see that the scattered beam is polarized so that the actual intensity is modified as a result of polarization.

$$I = I_0 \frac{(K)}{r^2} \frac{(1 + \cos^2 2\theta)}{2}, \quad K = \frac{(e^4)}{m^2 c^4}$$
(2.10)

At a fixed distance *r* the scattered beam will have its maximum value when $\cos^2 2\theta = 1$, that is, 0° and 180°. Absolute intensities are difficult to measure, but from equation (2.10), we can obtain the relative intensities by simple calculations. During crystal structure solution, the relative intensity scale can be converted into an absolute one.



Figure 2.14 Scattering by an electron. The incident beam is along the X-axis and encounters the electron at *O*. The electron scatters a ray in the direction of *P*, making an angle f with the component of the electric field along the Y-axis (*OP* lies in the XY plane).



Figure 2.15 Elastic collision of photon and electron (Compton effect).

There is a second kind of scattering by an electron that we need to consider. Suppose the electron has no constraints so it is free to respond to the X-ray beam. We now consider the beam as a stream of photons of energy hv_1 . When a photon strikes the electron, some of the kinetic energy of the photon is transferred to the electron displacing it from its position (Figure 2.15). As a result of the energy transfer, the photon has less energy, hv_2 , and the wavelength associated with this photon is larger than that of the incident beam. The change in wavelength is given, to a good approximation in equation (2.11).

$$\Delta \lambda \cong 0.0486 \sin^2 \theta \tag{2.11}$$

Since the wavelength change depends only on the angle θ , which in turn depends on the amount of kinetic energy change, there is no phase relationship between the scattered and incident beam. This radiation is termed "Compton Radiation" (after A.H. Compton, 1923, who discovered this effect) or incoherent radiation. It has the effect of increasing the background in diffraction patterns.

2.3.2 Scattering of X-rays from atoms (Jenkins and Synder, 1996; Nuffield, 1966)

The scattering centers in crystals are the electron clouds associated with the atoms. If the atoms were essentially point scatterers, the scattering power of each atom would be $Z \times I_e$ where I_e is the intensity of scattering from a single electron. However, the diameters of the atomic electron clouds are of the same order of magnitude as the wavelength of X-rays impinging upon them. Hence, scattered wavelets from individual electrons within the electron cloud will have phase differences and these are angle dependent.

Consider the diagram in Figure 2.16. The waves scattered at $2\theta = 0$ have the same phase as the incident radiation. Thus, at this angle

$$I_A = Z \times I_e \tag{2.12}$$

where I_A = intensity of scattered radiation from the atom.

However, consider the waves scattered from electrons *A* and *B* at angle 2θ . The path length difference is (CB - AD) and therefore they are out of phase along a wavefront given by YY'. In general, there is no regular path length relationship among all the electrons. This has the effect of decreasing the intensity as a function of the angle θ . The calculation needs to be made for all the electrons in the atom. We define a quantity f_j as the atomic scattering factor.

$$f_{j} = \frac{amplitude \text{ of the wave scattered by the atom } j}{amplitude \text{ of the wave scattered by an electron}}$$
(2.13)

A typical curve in terms of $\sin \theta / \lambda$ is given in Figure 2.17. The function $\sin \theta / \lambda$ is chosen because $\sin \theta$ is directly related to λ so that the values of f_j are the same for any wavelength used in the experiment. Because the scattering factor is a ratio, it has no units. Neon has 10 electrons. Therefore, by equation (2.12) at $2\theta = 0$ the value of $f_j = 10$. This designation



Figure 2.16 X-ray scattering by an atom.



Figure 2.17 Atomic scattering factor curve for neon.

means that neon has ten times the scattering power of a single electron. However, the scattering power is rapidly reduced as θ increases.

The values of f_j given in the compilations were calculated on the assumption that the atoms are at rest (Ladd and Palmer, 2003). That is, they have no thermal motion. However, at temperatures above 0 K the atoms undergo rapid oscillations about their mean positions in the crystal lattice. This has the effect of smearing out the electron clouds and further reducing the values of f_i . At any temperature above absolute zero, the value of f is given by

$$f_j = f_0 e^{-B(\sin^2\theta/\lambda^2)} \tag{2.14}$$

where f_0 = atomic scattering factor for atoms at rest and

$$B = 8\pi^2 \bar{\mu}^2 \tag{2.15}$$

where $\bar{\mu}^2$ = mean square amplitude of vibration.

Equation (2.14) assumes that the atomic vibrations are isotropic. If they are not, then more complicated expressions using six *B* terms to define an *ellipsoid* must be used. However, equation (2.14) is a good first approximation and we use it in what follows. Each atom will have a *B* factor which depends on how rapidly it vibrates. The larger is *B*, the smaller is f_i .

2.3.3 Scattering from a unit cell: the structure factor (Glusker and Trueblood, 1985)

In the unit cell there are many atoms, each of which are located by their positional parameters x, y, z. These parameters are given in terms of fractions of the unit cell dimensions a, b, c, where x = 0.142 means a distance 0.142a in the +X direction, y = 0.245 means a distance of 0.245b along the +Y axis, and so on. Thus, atom positions are designated as *xyz*. Each



Figure 2.18 Phase relationship in Bragg diffraction.

atom in a unit cell scatters the incident beam separately. Since the atoms may be anywhere within the unit cell, the scattered wave from atom *i* at $x_iy_iz_i$ and atom *j* at $x_jy_jz_j$ will be out of phase. In reality, the scattered wavelets from each atom must be added with their phase differences to obtain the scattered wave intensity at the detector. We need to know the amplitude of the wave, which will depend upon Σf_j values and the phase angle of the scattered wave. We will now consider a one-dimensional case for simplicity.

Let us again consider the case of diffraction from the (100) planes, a topic already discussed in Section 2.2. Assume that the unit cell we are dealing with is centered so that atoms also exist in planes half-way between the d_{100} distance. At the Bragg angle for diffraction from the (100) planes, the wavelets from the planes halfway between are exactly out of phase with those from the (100) planes. This can be shown exactly in the following manner. Referring to Figure 2.18, we see that $EG + GF = 1\lambda$ and $EG = \frac{1}{2}\lambda$. By similar triangles AB/DB = EG/DG and $AB/(\frac{1}{2}d_{100}) = (\frac{1}{2}\lambda)/d_{100}$, solving for AB yields $AB = \frac{1}{4}\lambda$ and $AB + BC = \frac{1}{2}\lambda$. So the wavelets from the (200) planes are precisely out of phase with the (100) planes as shown in Figure 2.18.

Suppose we also have a plane at some general distance x_j from the (000) plane (dashed line in Figure 2.18). Its path length difference is HI + IJ and by similar triangles

$$\frac{HI + IJ}{EG + GF} = \frac{x_j}{d_{100}} = \frac{HI + IJ}{\lambda}$$
(2.16)

But the 100 plane cuts the X-axis at a/h where h = 1 in this case, but in general is the index of the plane producing first-order diffraction in the Bragg sense. Therefore,

$$HI + IJ = \frac{\lambda x_j}{a/h} = \frac{h\lambda x_j}{a}$$
(2.17)

The phase difference ϕ between any two planes is always $2\pi/\lambda$ times the (path difference) so that by equation (2.17)

$$\phi = \frac{2\pi}{\lambda} \left(\frac{h x_j \lambda}{a} \right) = 2\pi \left(\frac{x_j}{a} \right) h \tag{2.18}$$

However, we have chosen to define x in fractions of the unit cell so $x = x_i/a$ and therefore

$$\phi = 2\pi (hx) \tag{2.19}$$

In the case of diffraction in three dimensions

$$\phi = 2\pi (hx + ky + lz) \tag{2.20}$$

The meaning of equation (2.20), is that for the set of planes represented by *hkl*, an atom whose positional parameters in the unit cell are *xyz* will produce a scattered wave whose phase contribution relative to the plane is $2\pi (hx + ky + lz)$.

In order to determine the intensity of a particular X-ray reflection, we must consider all the scattered wavelets from the entire unit cell. Each atom in the unit cell will produce a wavelet of amplitude proportional to the scattering factor f_j of the atom, that is the number of electrons, responsible for the scattering. The scattered wavelets may be considered to be cosine waves and/or sine waves and the net effect of adding them all up is given by the complex amplitude F_{hkl} , where

$$F_{hkl} = \sum_{j=1}^{N} f_j e^{i\phi} = \sum_{j=1}^{N} f_j e^{2\pi (hx + ky + lz)}$$
(2.21)

and

$$F_{hkl} = \sum_{j=1}^{N} f_j [\cos 2\pi (hx + ky + lz) + i \sin 2\pi (hx + ky + lz)]$$
(2.22)

N =total number of atoms in unit cell

 f_i = atomic scattering factor of the *j*th atom.

Let us illustrate how equations (2.21) or (2.22) determine the intensity of diffraction from particular planes. Consider first a primitive unit cell. This cell will have atoms at all of its corners, but the total number of atoms contained within one unit cell volume is one. Therefore, we only need the coordinates for a single atom in equation (2.22). The one at the origin, 000, will do. Note that the positions of the atoms are given in fractions of the unit cell dimensions a, b, c, so 000 means $0 \cdot a, 0 \cdot b, 0 \cdot c$. Substitutions of these values into equation (6.13) yields

$$F_{hkl} = f_j [\cos 2\pi (h0 + k0 + l0)] + i \sin 2\pi (0)$$

= $f_j [\cos 2\pi (0) + i \sin (0)]$ (2.23)
 $F_{hkl} = f_i$

Because f_j decreases with increasing angle, the intensities from different planes would differ by this decrease as well as changes resulting from absorption and Lorentz and polarization factors that are discussed later.

Now, consider a side-centered cell with centering in the *ab* face, that is, *C*-centering. This cell contains two atoms, one located at 000 and the other at $\frac{1}{2}\frac{1}{2}0$. Therefore,

$$F_{100} = f_j + f_j [\cos 2\pi (1x\frac{1}{2}) + i \sin 2\pi (1x\frac{1}{2})]$$

$$F_{100} = f_j + f_j [\cos \pi + i \sin \pi] = f_j - f_j = 0$$

$$F_{200} = f_j + f_j [\cos 2\pi (2x\frac{1}{2}) + i \sin 2\pi (2x\frac{1}{2})]$$

$$F_{200} = f_j + f_j = 2f_j$$

 $F_{110} = f_j + f_j [\cos 2\pi (1x_2^1 + 1x_2^1) + i \sin 2\pi (1x_2^1 + 1x_2^1)]$ $F_{110} = 2f_j$ and so forth.

The reader should note that the *h*, *k* and *l* which appear in equation (2.22) are the Miller indices for the plane whose structure factor is being calculated, while the *xyz*'s are the coordinates for each of the atoms in the unit cell. Thus, if there are 10 atoms in the unit cell, the summation in equations (2.21) or (2.22) will have 10 terms (N = 10). Each atom will have its own scattering factor f_j .

Body centering

There are two points in a body-centered cell 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

$$F_{hkl} = f_j \left[\cos 2\pi (0) + i \sin 2\pi (0) + \cos 2\pi \left(\frac{1}{2}h + \frac{1}{2}k + \frac{1}{2}l \right) \right. \\ \left. + i \sin 2\pi \left(\frac{1}{2}h + \frac{1}{2}k + \frac{1}{2}l \right) \right] \\ F_{hkl} = f_j \left[1 + \cos 2\pi \left(\frac{1}{2}h + \frac{1}{2}k + \frac{1}{2}l \right) + i \sin 2\pi \left(\frac{1}{2}h + \frac{1}{2}k + \frac{1}{2}l \right) \right]$$
(2.24)

Suppose h + k + l = 2n, then the cosine term will always be a multiple of $\cos 2\pi$, but the sine term will be zero. Thus, $F_{hkl} = f_j[1 + 1] = 2f_j$.

However, if h + k + l = 2n + 1, $\cos \pi (hx + ky + lz) = -1$ and $(i \sin 2\pi \times ((h + k + l)/2) = 0)$.

Therefore, all reflections for which h + k + l = odd, will be absent.

A more convenient way to determine the systematic absence is to use exponential notation.

C-centering, 000,
$$\frac{1}{2}\frac{1}{2}0$$

$$F_{hkl} = f_j \left[e^{2\pi i (0h+0k+0l)} + e^{2\pi i \left(\frac{1}{2}h + \frac{1}{2}k + 0l\right)} \right]$$

$$F_{hkl} = f_j \left[e^{2\pi i (0)} + e^{2\pi i \left(\frac{1}{2}h + \frac{1}{2}k\right)} \right]$$

$$F_{hkl} = f_j + f_j e^{2\pi i} \left(\frac{h+k}{2}\right)$$
(2.25)

It is evident that when h + k = 2n, that is, is even, $F_{hkl} = 2f_j$ but when h + k = 2n + 1, $F_{hkl} = 0$. This systematic absence is easily observed from the indexed set of X-ray reflections.

Face-centering

The lattice points are now 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$.

$$F_{hkl} = f_j \left(1 + e^{2\pi i} \left(\frac{h+k}{2} \right) + e^{2\pi i} \left(\frac{h+l}{2} \right) + e^{2\pi i} \left(\frac{k+l}{2} \right) \right)$$
(2.26)

If any of the pairs of Miller indices are odd, the exponential term is -1 and if even +1. Thus, for F_{hkl} to be zero, two of the indices must be even and one odd. This condition is avoided if all the indices are either even or odd but not mixed. We will find that there are many other cases where systematic absences occur and these help us to solve crystal structures. But for now, we will consider the working equation for X-ray intensities.

2.4 The intensity formula (Nuffield, 1966)

We have seen that scattering of X-rays arises from interactions of the electrons in the solid with the electromagnetic field. The overall interaction is quite complicated but for our purposes we need only consider the end result as it effects crystal structure determination. Contained within the intensity formula is the structure factor term which is sensitive to the positions of the atoms in the crystal and it is this term, which we must extract from the intensity formula. By intensity we mean the total blackening for each spot on a film or the area under a peak for a reflection measured by counter methods. This is known as the integrated intensity. The proper formula is then

$$I_{hkl} = \left(\frac{N^2 e^4 \lambda^3 V}{2m^2 c^4}\right) |F_{hkl}|^2 \left(\frac{TLp}{A}\right)$$
(2.27)

I = integrated intensity for the *hkl* set of planes

N = number of unit cells per unit volume

- V = volume of the crystal
- e = electron charge
- c = speed of light
- m = mass of electron
- T = temperature factor
- Lp = Lorentz and polarization factors
- A = absorption factor
- $F_{hkl} =$ structure factor.

Note that since mass appears in the denominator to the second power, the particles in the nucleus are too heavy to make any appreciable contribution to I in comparison with the electrons.

In practice, absolute intensities are difficult to obtain. Instead a set of intensities relative to a standard are collected. When a counter diffractometer is used, two or three reflections are designated as standards and scanned periodically throughout the data collection process. With CCD area detectors (see Chapter 3) about 30 frames are rerun at the end of data collection to see if the intensities decreased. All the data are then placed on the same relative scale by a least-squares procedure. All of the terms in the first set of parentheses in equation (2.27) are then treated as a single constant, and the equation can be rearranged to

$$kT |F|^2 = \frac{IA}{Lp} \tag{2.28}$$

The path traveled by the X-ray beam within the crystal is a function of the angle θ . The longer the path, the greater the absorption and the more the intensity of the diffracted beam is reduced. Thus, the intensity of the reflections relative to each other is adversely affected. As we see, part of this error is compensated by the temperature factor but if absorption

is large, a correction for this effect must be made. This correction is now done routinely because the major programs contain methods to correct for absorption.

X-rays are polarized when scattered by electrons in that, the component of the electric vector of the reflected beam perpendicular to the reflecting plane, E_y is less than the parallel component (Ladd and Palmer, 2003; Nuffield, 1966). The Lorentz factor is geometric in origin and can be visualized as follows. Assume that the lattice points in reciprocal space (see next section) have a finite size and that the reciprocal sphere is actually a shell of finite thickness. Then a given plane will diffract as long as the point in the reciprocal lattice representing this plane touches any part of the sphere of reflection. The time taken for a point to traverse the shell of the sphere of reflection depends upon the path followed and is angle-dependent as can been seen in Figure 2.19.

The Lorentz factor then depends upon how long it takes for the total volume to traverse the thin shell of the sphere. The traversal gives rise to a peak as shown in Figure 2.20.

The thickness of the curve depends upon the value of θ and has the form



Figure 2.19 The sphere of reflection visualized as a thin shell of finite thickness and the different paths followed by two points in the reciprocal lattice rotated through the sphere.



Figure 2.20 Diffraction by a crystal rotated through the Bragg angle. From Cullity & Stock, 2001.

Both the Lorentz and polarization factor can be calculated exactly and the absorption factor, though less accurately, still sufficiently well to produce a highly accurate set of F values. How these F values will be used to determine the structure is described in a later section. We will now delve a little further into diffraction phenomena. Before doing so we need to interject a most important understanding of the phase problem in crystallography.

Reference to equations (2.27) and (2.28), shows that the structure factor appears in the intensity equation to the second power. The values of *F* can be positive or negative but only positive values arise from the data. Furthermore, in the general case there is a phase angle, ϕ , lost in taking the square root of an absolute number. This is illustrated in equation (2.21) where F_{hkl} is shown to be a complex quantity. This being the crux of the phase problem (Glusker and Trueblood, 1985; Pecharsky and Zavalij, 2003), which mitigated against a direct solution of the crystal structure and indirect methods such as Patterson functions were required to locate a number of atoms within the unit cell. Fourier analysis methods were then applied to complete the structure. With the advent of Direct Methods, solutions arise directly from the data. These aspects of structure solution will be covered in Chapter 7.

2.5 The reciprocal lattice (Buerger, 1942; Ladd and Palmer, 2003)

It is instructive for our purposes to write Bragg's law in the form of equation (2.1)

$$\sin\theta = \frac{n\lambda}{2d}$$

When reasonably monochromatic radiation is used for the diffraction experiments, equation (2.1) can be written as

$$\sin\theta = \frac{k}{d} \tag{2.30}$$

where $k = \text{constant} = \frac{1}{2}n\lambda$. We see from equation (2.30) that the sine of the diffraction angle is directly related to the *reciprocal* of the interlayer spacing. The larger is *d* (small *hkl* values) the smaller is $\sin \theta$. Thus, as the Miller indices of a plane become larger, the plane moves in closer to the origin and its *d*-spacing becomes smaller. At the same time, the peak in the diffraction pattern due to the plane appears farther and farther from the origin since θ is *increasing*.

For example, consider the (100) planes. The first one cuts the X-axis at \vec{a} . Remember that the *d*-spacing is the perpendicular from the origin to the plane and in non-orthogonal axial systems may not be equal to *a*. In general, the *d*-spacing for a particular plane (*hkl*) is labeled d_{hkl} . Thus, for the (100) plane we designate the inter-planar spacing as d_{100} . This means that in the crystal, there exists a stack of planes which are parallel to the YZ plane and cut the X-axis at *a*, *2a*, *3a*, and so on. However, there may also be planes half-way between the (100) planes (and they may have the same or different compositions). These planes will have half the inter-planar spacing of d_{100} . They are called the (200) planes and $d_{200} = (d_{100}/2)$. But the (200) planes include the first stack as well. The distinction between the two sets of planes is that the diffraction angles for d_{100} and d_{200} are different. If the value of $d_{100} = 5.0$ Å
and CuK α radiation is used, then sin $\theta = 1.542$ Å/10 Å = 0.1542, $\theta = 8.87^{\circ}$. At this angle, the path length difference traveled by the X-ray wavelets from any two adjacent (100) planes, 5.0 Å apart, is one wavelength. However, the planes halfway in between will also diffract, but wavelets from these planes will be exactly out of phase with those from (100). If the atomic content of the (100) and (200) planes is identical, no diffraction peak would be observed at 8.87°. In general, this is not the case and a weak diffraction peak would appear on the film, resulting from the differences in scattering intensity generated from the two sets of planes.

For the (200) planes, the d_{200} value is 2.5 Å and $\theta = 17.96^{\circ}$. Now wavelets from all the planes are in phase since the path length differences are twice those for the (100) case. An intense reflection will appear in the pattern for the (200) planes, but removed farther from the origin than for (100). The reciprocal lattice concept allows us to make this association of position in the pattern with *d*-spacing in a straightforward manner.

$$d_{hkl}^* = \frac{1}{d_{hkl}} \quad \text{and} \quad \mathbf{d}_{hkl}^* = \left| \frac{1}{d_{hkl}} \right|$$
(2.31)

where d^* is a vector in reciprocal space whose magnitude \mathbf{d}^* is $1/d_{hkl}$ and whose direction is the same as that of d_{hkl} .

Consider an orthorhombic lattice where *a*, *b*, *c* are the unit cell vectors in real space and they are mutually orthogonal to each other. In this case

$$d_{hkl}^* = \frac{1}{d_{hkl}}$$
(2.32)

but \vec{d}_{100} is directed along *a* and because of the orthogonality of the axes $d_{100} = a^*$. Thus,

$$a^* = \frac{1}{a} = d^*_{100} \tag{2.33}$$

Similar equations can be written for d_{010}^* and d_{001}^* . The reciprocal cell will be orthorhombic also, but the smallest real space unit cell dimension becomes the largest reciprocal dimension and vice versa. To create the reciprocal lattice, we place a point at 000 and translate it by the vector

$$T_l = l_1 a^* + l_2 b^* + l_3 c^* \tag{2.34}$$

where again l_1, l_2, l_3 can have values of $0, \pm 1, \pm 2, \ldots, \pm n$.

We now consider a monoclinic (or hexagonal) unit cell. In the parallelogram lattice of Figure 2.21, \vec{d}_{100} is directed perpendicular to the (100) planes and therefore to the *b*-axis and has magnitude $a \cos(90^\circ - \gamma) = a \cos(90 - \gamma)$

$$d_{100}^* = \frac{1}{a\cos(90-\gamma)} = \frac{1}{a\sin\gamma} = \frac{1}{d_{100}} = a^*$$
(2.35)

Example: Let a = 10 Å and $\gamma = 110^{\circ}$. The \perp between the (100) planes is $a \cos(\gamma - 90^{\circ})$ or 9.397 Å = d_{100} . Therefore, according to equation (2.35)

$$d_{100}^* = \frac{1}{d_{100}} = \frac{1}{9.397} = 0.1064 = a^*$$



Figure 2.21 Relationship between the direct (real) lattice shown in heavy outline and the reciprocal lattice for a monoclinic unit cell in which γ is the non-right angle.

Similarly,

$$d_{010}^* = \frac{1}{b\sin\gamma} = \frac{1}{d_{010}} = b^*$$
(2.36)

Note that a^* is directed perpendicular to the *bc* plane of real space and b^* is perpendicular to the *ac* plane. This is always true. A reciprocal lattice vector is always perpendicular to a plane in the real lattice and vice versa. Also note that $\gamma^* = 180^\circ - \gamma$, since $\gamma^* = \gamma - 2(\gamma - 90^\circ)$.

The reciprocal lattice net is again constructed by translating a point at the origin by a vector $T_l = l_1 a^* + l_2 b^*$ and the result is shown in Figure 2.21.

Since the real *c*-axis is directed perpendicular to the *ab* net in the monoclinic system, d_{001} lies along the *c*-axis as does c^* . Thus, the complete reciprocal lattice will have nets exactly like the one shown in Figure 2.21 stacked on top of each other at distances along real *c* of c^* , where

$$c^* = \frac{1}{d_{001}} = \frac{1}{c} \tag{2.37}$$

The indices of the points in the first net will be the same as in the zeroth (l = 0) net, except now l = 1. In the second net l = 2, and so forth. In the general case of a triclinic unit cell, the nets in reciprocal space will be offset from each other and the reciprocal angles do not



Figure 2.22 Sphere of reflection of unit radius.

have a simple relationship to the real ones. Remember the reciprocal lattice net extends in the negative directions also.

We are now in a position to show the utility of constructing reciprocal lattices. Let us draw a circle of radius one, a tangent to the circle and a diameter perpendicular to the tangent as shown in Figure 2.22. A line drawn from *A* to any point *P* on the circumference of the circle makes an angle θ with the diameter. $\leq APO$, made by completing the triangle with side *OP*, is a right angle because every angle inscribed in a semi-circle is a right angle. Thus, $\sin \theta = OP/2$ and if we let $OP = \lambda/d$, then

$$\sin\theta = \frac{\lambda}{2d} = \frac{\lambda d^*}{2} \tag{2.38}$$

Furthermore, the line *SP*, drawn from the center of the crystal to the point *P* makes an angle 2θ as a property of circles. This construction has some important properties in relation to X-ray diffraction photographs. Let *AO* be the direction of a monochromatic X-ray beam incident to a crystal centered at *S*. As the crystal is rotated, one of its planes will become oriented in a position to diffract. This plane will be at angle θ to the incident beam and therefore, will have the same slope as the line *AP*. The diffracted beam would take the direction *SP*. The same conditions hold true for a sphere because the circle of Figure 2.22 can be rotated 360° about the diameter *AO*, centered at the point *S*, generating a sphere without violating any of the angular relationships.

Equation (2.38) has the same form as equation (2.30). If now we construct a reciprocal lattice, such as that of Figure 2.21, but multiply d_{100}^* , d_{010}^* and d_{001}^* by λ , then the vector from the origin to any point in the lattice will be λd_{hkl}^* . This reciprocal lattice is now placed with its origin at 0 and the direction of a real axis parallel to the rotation axis of the crystal at *S* as shown in Figure 2.23. Because a real axis is always perpendicular to a reciprocal plane, the a^*b^* planes are oriented perpendicular to the direction of *c*. It should be understood that the nets extend along the $\pm X$ directions, the $\pm Y$ directions and additional nets are



Figure 2.23 Relationship of reciprocal lattice to sphere of reflection. Only a portion of the layers are shown.

located above and below the two shown. As the crystal rotates the nets also rotate about the line marked the "*c*-axis direction." Whenever a point in the reciprocal lattice just touches the surface of the sphere of reflection, the conditions for diffraction are met. The direction of the diffracted beam is *SP* and the vector *OP* is $\lambda \vec{d}_{hkl}^*$. It is easy to see that the net with l = 0 will cut the sphere of reflection in the great circle at the center of the sphere. A cylinder of film coaxial with the rotation axis will record diffraction from the central circle as a straight row of spots passing through the center of the film. Each of these spots represents diffraction from a plane with indices (*hk*0). The first net above the zeroth one has indices (*hk*1) and intercepts the sphere in a smaller circle. Lines drawn from the center of the sphere to this circle generate a cone, which on extension to the film cuts it in a circle. All spots on this row have indices (*hk*1). Note that *h* and *k* can be positive or negative. Each diffraction spot on the film is related to a point in the reciprocal lattice and its distance from the center of the film is related to a d* for that point. The exact relationship can be calculated and a chart constructed to index the photograph.

Indexing a rotation photograph has certain disadvantages. The *layer lines* are generally densely packed with spots and a small error in measurement can result in a wrong indexing. Furthermore, it is possible for two or more spots to have the same λd^* value and so coincide on the film. Overlap can be avoided by rotating through a small angle, say 10°, but then many such films are required. These difficulties are largely avoided by modern digital diffractometers. In a diffractometer using a charge-coupled area detector (CCD) (see Chapter 3) the crystal is rotated through a small angle; say every 0.3° and the reflections recorded digitally. In a four circle diffractometer, each set of planes is brought to the position to diffract and record individually.

It should be clear now that equation (2.34) can be rewritten as

$$d^* = ha^* + kb^* + lc^* \tag{2.39}$$



Figure 2.24 An illustration of a two-dimensional reciprocal lattice (top) and its one-dimensional projection on the 1/d axis (bottom). The reciprocal lattice point (32) is shown as a filled black circle both in the lattice and in its projection together with the corresponding reciprocal vector d^*32 . Reprinted from Pecharsky, V. K. & Zavalij, P. Y. *Fundamentals of Powder Diffraction and Structural Characterization of Materials*. Copyright 2003, with kind permission of Springer Science and Business Media.

where a^*, b^*, c^* are the reciprocal lattice vectors. A full treatment of the reciprocal lattice concepts using vector analysis is very elegant for which the reader may consult references (Buerger, 1942; Ladd and Palmer, 2003). Equation (2.39) brings out the three-dimensional nature of indexing every reflection recorded from a single crystal. However, this is not the case for powders. An XRPD is one dimensional so that all the reflections in threedimensional spaces are projected into this single dimension. What is derived from the pattern is the length vector or the distance from the origin of the reflection. What is lost is the dimensionality in space of the length vector. This is illustrated from a diagram (Figure 2.24) borrowed from the very excellent book by Pecharsky and Zavalij (Pecharsky and Zavalij, 2003). It illustrates again a portion of reciprocal space in two dimensions. When a distance to a particular reflection of magnitude d^* is rotated through the reciprocal lattice plane it may contact more than one point in the lattice. Then all the points contacted would fall to the same or overlapping positions in the powder pattern. This condition makes it difficult to unambiguously index the powder pattern. Often a false unit cell is obtained. The correct unit cell is the smallest parallelepiped in reciprocal space that completely indexes all the observed data and in real space displays the full three-dimensional symmetry of the structure. In order to grasp the meaning of this last statement we need to consider *f* symmetry and space groups.

2.6 Crystal symmetry and space groups (Buerger, 1971; Hammond, 2004)

We have already mentioned that the external shapes of crystals can give rise to symmetry elements whose combination yields a point group. The external crystal shape or habit



Figure 2.25 Operation of a mirror plane and a translation perpendicular to it, creates a new mirror m_3 .

mirrors how the crystals grow and the external faces are parallel to important sets of planes within the crystal. However the internal symmetry, that is the symmetry of the unit cell, contains new symmetry elements that arise from the combination of the lattice translations with the symmetry elements of the point group. As an example let us consider a mirror plane and a translation vector perpendicular to the mirror as illustrated in Figure 2.25. The mirror is originally at m_1 , and reflects one of the arrows into its mirror image. A perpendicular translation of T_l brings the mirror to m_2 bringing with it the two arrows. This translation creates a new mirror m_3 half the distance between them. Translations always create new symmetry elements.

2.6.1 Glide planes

The arrow in Figure 2.25 could be translated parallel to a mirror first and then reflected and the operation repeated indefinitely. A symmetry element which moves objects in this fashion is called a *glide plane*. In Figure 2.26, the glide lies in the XZ plane and the translation is $\frac{1}{2}a$. There are five glide motions possible. The one illustrated in Figure 2.26 is termed an *a* glide because the translation is $\frac{1}{2}a$. Similarly, a glide plane is designated *b* or *c* if the translations are $\frac{1}{2}b$ or $\frac{1}{2}c$, respectively. In addition, a glide motion along a cell diagonal $(T_l = \frac{1}{2}a + \frac{1}{2}b \text{ or } \frac{1}{2}a + \frac{1}{2}c \text{ or } \frac{1}{2}b + \frac{1}{2}c)$ is called an *n* or diagonal glide. Finally, in face- and body-centered lattices, it is possible to have a diagonal glide, *d*, with translations $\frac{1}{4}a + \frac{1}{4}c$, $\frac{1}{4}a + \frac{1}{4}b$, and so forth, and for body-centered cells, $\frac{1}{4}a + \frac{1}{4}b + \frac{1}{4}c$. These glides are called diamond glides. The action of an *n* glide is shown in Figure 2.27. The several types of glide planes are summarized in Table 2.3.

What we have just shown is that a symmetry element operated on by a parallel translation moves the symbol or atom to create a new symmetry element in a way that leaves no points unmoved. Such symmetry elements are allowed in three-dimensional space and give rise to space groups. Parallel translations coupled with rotation axes give rise to screw axes.

2.6.2 Screw axes

The reader should satisfy himself or herself that if a 2-fold axis is moved by a perpendicular translation, a new 2-fold axis is created halfway between the two. Similarly, a combination



Figure 2.26 Illustration of the operation of an *a*-glide plane. The glide plane is in the XZ plane.



Figure 2.27 Action of a diagonal glide with translation $(\vec{a} + \vec{b})/2$. The glide plane is in the XY plane.

of a rotation axis with a translation *parallel* to the axis gives a *screw axis*. The translation must be a subintegral fraction of the unit translation in that direction. For example, a 2-fold screw (lying along *c*) means a rotation of 180° followed by a translation of $\frac{1}{2}c$. This is shown in Figure 2.28. The equivalent points for such a 2-fold screw axis are *xyz*, \bar{x} , \bar{y} , $z + \frac{1}{2}$. The second operation is another 180° rotation followed by a translation of $\frac{1}{2}c$ to bring the arrow one unit cell away from the original arrow.

An *n*-fold screw axis is one whose operations consist of an *n*-fold rotation followed by a translation of m/n of the repeat distance along this axis. Here, *m* is an integer smaller

Symbol	Significance of symbol	Translation component		
a		$\frac{a}{2}$		
b	Axial glides	$\frac{b}{2}$		
С		<u>c</u> 2		
n	Diagonal glide	$\frac{a}{2} + \frac{b}{2}, \frac{a}{2} + \frac{c}{2}, \frac{b}{2} + \frac{c}{2}$		
d	"Diamond" glide	$\frac{a}{4} + \frac{b}{4}, \frac{a}{4} + \frac{c}{4}, \frac{b}{4} + \frac{c}{4}, \text{ or}$		
		$\frac{a}{4} + \frac{b}{4} + \frac{c}{4}$		
т	"Mirror"	Zero		

 Table 2.3
 Symbols used for glide planes



Figure 2.28 Operation of a 2-fold screw.

than *n* and written as the subscript (Table 2.4) of the *n*-fold axis. For example, a 3₁ axis (n = 3, m = 1) requires a counter-clockwise rotation of 120° followed by a translation of $\frac{1}{3}$ (Figure 2.29). The rotation operations are repeated until the object being operated upon returns to its original position but one unit repeat away. Thus, a second operation of the 3₁ axis takes the object around to 240° from the starting point and $\frac{2}{3}$ along the repeat. A final rotation–translation completes the 3₁ operations. Similarly, a 3₂ axis requires a clockwise rotation of 120° but a translation of $\frac{2}{3}$ (Figure 2.29). The second operation translates the object to $\frac{1}{3}$ in one unit cell away, and a third operation takes the object two unit repeats away from the origin. However, the action of the 3₂ screw axis cannot be considered complete at

Symmetry	Symbol	Designation if parallel to plane of projection	Designation if perpendicular to plane of projection
Center	ī	π	π
2-fold axis	2	\longleftrightarrow	α
3-fold axis	3		χ
4-fold axis	4		ϕ
6-fold axis	6		φ
2-fold screw axis	21	<i></i>	β
3-fold screw axis	3 ₁		δ
3-fold screw axis	3 ₂		ε
4-fold screw axis	41		γ
4-fold screw axis	42		η
4-fold screw axis	43		L
6-fold screw axis	61		К
6-fold screw axis	62		λ
6-fold screw axis	6 ₃		μ
6-fold screw axis	64		ν
6-fold screw axis	65	_	0
Mirror	т		
a-glide plane	а	→	
<i>b</i> -glide plane	b	4 ┐	
c-glide plane	С		5
<i>n</i> -glide plane	n		··
<i>d</i> -glide plane	d	3 8 8	

 Table 2.4
 Symbols for symmetry elements

this stage because the two unit repeats differ from each other. The way out of this dilemma is to recognize that axes and lattices are infinite. Thus, if a completely similar set of operations to the ones just described were begun one unit repeat from the first, the combination would fill in all the missing slots in the first cell. Another way of looking at the situation is to recognize that the operations of 3_2 could be thought of as a rotation of 120° in a clockwise direction followed by a translation of $\frac{1}{3}$! The reader may find it more convenient to think of the 3_2 axis in this way. Thus, we see that 3_1 and 3_2 are related as right- and left-handed screws. They are said to be *enantiomorphs*.

There are 11 screw axes in all of which four pairs are enantiomorphs. The reader at this point should work through the operations of 4_2 and 6_3 so as to be convinced that the pictorial representation in Figure 2.30 for the 4-fold screw axes is understood.

Screw axes have handedness. Because we always choose a right-handed axial system, we always designate screw axes as right-handed. If we rotate the X-axis into the Y-axis, the screw will advance in the positive Z- or c-axis direction. The symbols that are used to describe symmetry elements in space groups are listed in Table 2.4.



Figure 2.29 Illustrations of 3-, 3_1 -, and 3_2 -fold axes. Each unit cell must have three points so the $\frac{4}{3}$ operation places a point at $\frac{1}{3}c$ in the opposite direction of the 3_1 axis.



Figure 2.30 Complete placing of points for symmetry allowed 4-fold axes.

2.6.3 Monoclinic space groups

In deriving space groups we need to make use of all the geometrical factors we have described in previous sections. The unit cell must be one of the two monoclinic Bravais lattices, Pand C. There are two choices of axial systems; either the axis perpendicular to the plane containing the non-right angle is the *c*-axis or the *b*-axis. That axis could be a 2-fold or a 2_1 -axis. In addition, we may have mirror or glide planes.

The first symmetry group to consider is $C_s-\overline{2}$. Cs in point group theory or $\overline{2}$ in Shoenfliess notation is a mirror plane (s is for spiegle or mirror in German. In crystallographic notation,

 $\overline{2}$ (two bar) means a rotation of the origin point by 180° followed by an inversion. Thus if the coordinates of the origin point is *xyz*, the symmetry operation takes the point to *xyz* or *xy–z*. This operation places a mirror in the XY plane at Z = 0. The capital letters stand for the axes in the X and Y directions and the lower case letters locate points within the unit cell. For example, x = 0.112 indicates that the point is a distance 0.112a along the X-axis where *a* is the magnitude of the *a*-axis in the unit cell. We could indicate it as 0.112a which provides both the magnitude and direction. A point may then be designated as $\frac{1}{4}\frac{1}{2}\frac{1}{4}$ which means $\frac{1}{4}a$ along X, $\frac{1}{2}b$ along Y and $\frac{1}{4}c$ along Z. Point group C_s – $\overline{2}$ is compatible with both. Let the mirror plane be (001) where *c* is the perpendicular axis. The mirror plane is then in the XY plane and another is one unit along Z due to the *c* translation. This automatically places a mirror plane at $\frac{1}{2}c$ as a result of the action of a perpendicular translation (*c*) on the mirror plane at 0. This space group is identified by the symbol $P\mathbf{m}$ (P = primitive, $\mathbf{m} =$ mirror). Since the mirror plane is the only symmetry element in this space group, there are two points within the unit cell, *xyz* and *xyz*. The space group diagram is shown in Figure 2.31.

Replacing the mirror by a glide allows a choice of *a*, *b*, or *n* glide motions. All of these have the same symmetry characteristics and are lumped together as a single space group *Pb*. That *Pn* is equivalent to *Pb* can be deduced from the fact that any two non-coplanar vectors perpendicular to the *c*-axis, that is, in the XY plane, can be chosen as the *a*- and *b*-axes. Thus, if the original *ab* diagonal is chosen as a new *b*-axis, the *n* glide becomes the new *b* glide. The space group diagram is shown in Figure 2.32 and the equivalent points are *xyz*; *x*, $y + \frac{1}{2}$, \overline{z} . The reader should be sure that he or she understands how the equivalent points were obtained from Figure 2.32.

Next we consider the centered lattice, either *A* or *B*. Because both are equivalent and depend merely upon choice of axes, convention dictates a *B*-centered lattice, that is, the point is in the *ac* plane or at $\frac{1}{2}0\frac{1}{2}$. This lattice has two translations, $T_l = l_1a + l_2b + l_3c$ and $T'_l = \frac{1}{2}a + \frac{1}{2}c$. The first translation places mirror planes at c = 0 and $\frac{1}{2}$ parallel to the XY plane similar to the placement of mirror planes in *Pm*. However, the second translation has a perpendicular component of $\frac{1}{2}c$ and this puts a mirror at $\frac{1}{4}c$ and $\frac{3}{4}c$. But the translation of $\frac{1}{2}a$ is parallel to the mirror and thus converts it into an *a* glide. The space group is *Bm* and its diagram is shown in Figure 2.33. Reference to Tables 2.3 and 2.4 should help make clear



Figure 2.31 Space group *Pm* with the *c*-axis perpendicular to the mirror plane showing the *ab* plane (a) and the *bc* plane (b).



Figure 2.32 Diagram of space group *Pb* with two points at *x*, *y*, *z*; *x*, *y* + $\frac{1}{2}$, *z*.



Figure 2.33 Monoclinic space group diagrams containing mirror and glide planes. The *c*-axis is perpendicular to the plane.

the various designations of the mirror and glide planes. The equivalent points are x, y, z; x, y, \overline{z} ; $x + \frac{1}{2}, y, \frac{1}{2} - z$; $x + \frac{1}{2}, y, \frac{1}{2} + z$. Note that the *a* glide adds $\frac{1}{2}$ to *x* but the glide is at $\frac{1}{4}c$ and this changes *z* to $\frac{1}{2} - z$.

If we now replace the mirror plane in *Bm* by *a b* glide, the *a* glide at the $\frac{1}{4}c$ becomes an *n* glide, because the parallel component is now $\frac{1}{2}a + \frac{1}{2}b$. The space group consists of

alternating *b* and *n* glides and is labeled *Bb*. In the International Tables, a second designation, *Cc*, appears for this space group. This is not a new space group, but one in which the *b*-axis is now perpendicular to the XZ plane and the centering is in the *ab* face instead of the *ac* face. Note that the centering points must be in the face that has the perpendicular axis to the other plane. As an exercise, draw these space group diagrams for *Cm* and *Cc*, where the \perp axis is the *b*-axis.

We now turn our attention to the monoclinic point groups containing 2-fold axes. The simplest is C_2 -2 combined with a primitive monoclinic lattice to yield the space group P2. The 2-fold axis must, by definition, be perpendicular to the oblique plane. Another space group $P2_1$ arises by replacing the 2-fold by a 2_1 axis. Finally, B2 results from the combination of a *B*-centered lattice with a 2-fold axis. Since the centering is in the *ac* face, the translation is $\frac{1}{2}a + \frac{1}{2}c$. Translation of the 2-fold axis by $\frac{1}{2}a$ places another 2-fold axis at half this distance and the translation of $\frac{1}{2}c$ converts it into a 2_1 axis. Thus, B2 and $B2_1$ are identical and only one need be listed. Space group diagrams for the three groups just described are given in Figure 2.34.

The reader might be wondering how a translation perpendicular to a 2-fold axis produces another 2-fold axis at half the translation distance. To satisfy yourself on this point, one



Figure 2.34 Space groups with 2-fold axes with no mirror or glide planes. C2: xyz; $\bar{x}y\bar{z}$; $\frac{1}{2} + x\frac{1}{2} + yz$; $\frac{1}{2} - x\frac{1}{2} + y$, \bar{z} . B2: xyz; $\bar{x}\bar{y}z\frac{1}{2} - x\bar{y}\frac{1}{2} + z$; $\frac{1}{2} + xy\frac{1}{2} + z$.

need only draw the diagram with equivalent points inserted to see that this is so. This is why the space group diagrams for P2 and $P2_1$ have axes not only at the ends of each translation but their midpoints also (Figure 2.34).

Finally, we turn our attention to point group 2/m. Combination of 2/m with a primitive lattice gives space group P2/m (Figure 2.35). Note that 2/m contains a center of symmetry indicated by an open circle in Figure 2.35. Systematic replacement of the 2-fold axis by 2_1 and **m** by a glide plane leads to three additional space groups $P2_1/m$, P2/b, and $P2_1/b$. In these space groups, the origin is placed at the center of the symmetry which in the latter two groups is offset by $\frac{1}{4}b$ from the 2 or 2_1 axes because of the glide motion. This is illustrated in Figure 2.36, where two arrows have been placed about a 2-fold axis and then subjected to a *b*-glide motion (Figure 2.36a). The center of symmetry is thereby placed at 0, $\frac{1}{4}b$, 0. Shifting the origin by $\frac{1}{4}b$ produces the diagram in Figure 2.36b and the full diagram for space group P2/b in Figure 2.35. Similarly, in space group $P2_1/m$, the combination of a 2_1 axis with a mirror plane at 0 and $\frac{1}{2}$ creates a center of symmetry at $z = \frac{1}{4}$. We choose the center as origin by shifting it to Z = 0 and this moves the mirror planes to $\frac{1}{4}$ and $\frac{3}{4}$. This combination also creates a 2_1 as shown in Figure 2.35, space group $P2_1/m$. In the case of $P2_1/b$, the 2_1 is shifted to $\frac{1}{4}b$ as for the 2-fold axis in 2/b.

The origin is then chosen at $\frac{1}{4}b$ and this causes a change in the 2-fold axis to the new position, $\frac{1}{4}b$. The points are now $x, y, z, \overline{x}, \overline{y}, \overline{z}, x, \frac{1}{2} + y, \overline{z}; \overline{x}, \frac{1}{2} - y, z$ in P2/b and for $P2_1/b$, xyz, $\bar{x}\bar{y}\bar{z}$; x, $\frac{1}{2} + y$, $\frac{1}{2} - z$; \bar{x} , $\frac{1}{2} - y$, $\frac{1}{2} + z$. For B2/m, I have included an actual page from the earlier 1969 issue of the International Tables for Crystallography, Vol. 1 (Henry and Lonsday, 1969). The more recent edition is even more elaborate. We note at the top, the Schoenflies symbol, C_{2h}^3 and the space group No. 12. The controlling symmetry is 2/m and by now, the student should realize that a 2-fold axis \perp to a mirror always produces a center of symmetry. B-centering means we have the added translation of $\frac{1}{2}a + \frac{1}{2}c$ and that perpendicular to the mirror plane is the \vec{c} axis direction. The diagrams represent projections onto the *ab* plane. The origin is in the upper left-hand corner and the *a*-axis comes down and the b-axis across (always). There are eight equivalent points. The 2-fold axis produces 2, the mirror doubles this number and the B-centering produces four more. This is indicated by (000; $\frac{1}{2}0\frac{1}{2}$). The 4 points grouped around the center of symmetry at the origin are those designated *j* (Wyckoff positions, named after one of the pioneers of geometrical crystallography) and the additional four are obtained by adding $\frac{1}{2}0\frac{1}{2}$ to the original four. Thus, $x + \frac{1}{2}$, y, $\frac{1}{2} + z$; $x + \frac{1}{2}$, y, $\frac{1}{2} - z$; and so forth. Let us now consider the diagram in Figure 2.37. The points *xyz* and $\bar{x}\bar{y}\bar{z}$ are grouped about the center of symmetry at 000. We note at the far right, that the mirror plane is at 0 and $\frac{1}{2}$. This mirror produces x, y, \overline{z} from x, y, z and $\overline{x}, \overline{y}, z$ from $\bar{x}, \bar{y}, \bar{z}$. The - + symbols tell where these four points are placed. The same arrangement holds for the *B*-centering at $\frac{1}{2}0\frac{1}{2}$. So, we see four more points $\frac{1}{2} - \bigoplus_{\frac{1}{2}}^{\frac{1}{2}}$, and so forth. This puts a 21 axis at $\frac{1}{4}a$ and all related positions. For example, the four points x, y, z, x, y, \overline{z} and $\frac{1}{2} - x$, \bar{y} , $\frac{1}{2} + z$ and $\frac{1}{2} - x$, \bar{y} , $\frac{1}{2} - z$ are related by the 2₁. Similarly, there is an *a* glide at $\frac{1}{4}c$ parallel to the *ab* plane, as indicated by the arrow in the lower right-hand corner of the second diagram. This can be seen by considering the points $x, y, z, x + \frac{1}{2}, y, \frac{1}{2} - z; x, y, \overline{z}$, and $x + \frac{1}{2}$, $y, \frac{1}{2} + z$.

Consider now the "Conditions limiting possible reflections." This means systematic absences. Under "General," it states that in order for reflections to appear, there are three



⁺α|ε

Figure 2.35 Monoclinic space groups containing combinations of 2-fold axes, mirror and glide planes. Reprinted from Buerger, M. J. (1971) Introduction to Crystal Ceometry, with permission of McGraw-Hill Education.



Figure 2.36 Combination of a 2-fold axis and a *b* glide places points depicted by arrows (a) and creates a center of symmetry. Moving the origin to the center yields (b).

categories. For *hkl* reflections only those for h + l even will appear. When the sum of these indices is odd, they will not be observed. This condition arises from the *B*-centering condition. The other absences arise from the *a* glide \perp to *c hk*0 present only when h = 2n and the 00*l* reflections with l = 2n arises from the 2_1 axis. The perceptive student will recognize that all the absences arise from symmetry elements that have non-integral translations; *B*, $\frac{1}{2}a + \frac{1}{2}c$, *a* glide, $\frac{1}{2}a$ and 2_1 , $\frac{1}{2}c$.

Returning to the column of "number of positions" we see that position *i* places a point on the mirror plane at 0. As a result, z = 0 and $x, y, z \to x, y, 0, \bar{x}, \bar{y}, \bar{z} \to \bar{x}, \bar{y}, 0$ and only two additional points are obtained from $\frac{1}{2}0\frac{1}{2}$. For position *h* and *g*, the points are on 2-fold axes. The point *h* is on the 2-fold at $\frac{1}{2}b$ and point *g* places the point on the axis at 0,0.

Systematic absences occur with all non-primitive unit cells and wherever glide planes and screw axes occur. A compilation of all the possible systematic absences is given in Table 2.5. Examination of these systematic absences then fixes the type of unit cell and in many, but not all, the space groups.

The space group that occurs most frequently is $P2_1/c$ or $P2_1/b$. They are the same, except for the choice of axes. $P2_1/b$ has the 2-fold axis along *c* and the *b* glide whereas in $P2_1/c$, the *b*-axis is the 2_1 and the non-90° angle is β . We consider only one more monoclinic case, C2/c (Figure 2.38). The diagram is a rectangle because the axes shown are always *a* and *b*. The *c*-axis is then inclined to this plane by angle β . In this direction, the full-sided arrow is the symbol for a 2-fold axis and the arrow with half-head is 2_1 . The *C*-centering provides the vector $T_l = \frac{1}{2}a + \frac{1}{2}b$. The 000 point is chosen at the center of symmetry so this provides x, y, z and $\bar{x}, \bar{y}, \bar{z}$. The *c* glide is \bot to the *b*-axis at *x* zero. Thus, it will change the coordinates of *y* to \bar{y} and vice versa and add $\frac{1}{2}$ to *z*. These changes yield $x\bar{y}z + \frac{1}{2}$ and $\bar{x}, y, z - \frac{1}{2}$. The final 4 points are obtained by adding $\frac{1}{2}\frac{1}{2}0$ to the first four. Note that the

		2/ <i>m</i>	Nc	0.12	B 112/m			2/ <i>m</i>	Monoclinic	
			$a^{-\bigoplus +}_{12+\sqrt{2}}$)+	12-0 -0+/2 -0	$\frac{- \oplus + b}{b}$ $\frac{1}{2} + \oplus + b$ $1 \oplus - \oplus $		9 1 9 1 9 1 9 1 9 <u>1</u>		
	1st	setting		Orig	in at cer	ntre (2/ <i>r</i>	n); unique	e axis <i>c</i>		
Nui W an	mbe /yck d po	r of positio off notatic int symme	ons, n, etry	Coordi	nates of (0,0	equival ,0;	ent positi ¹ 2) +	ons	Conditic possible	ns limiting reflections
8	j	1		<i>x,y,z</i> ;	<i>x,y,</i> Z ;	<i>x</i> , <i>y</i> , <i>z</i> ;	$\overline{X}, \overline{Y}, \overline{Z}.$		General: hkl: h + l = hk0: (h = 00l: (l = 2	= 2n 2n) n)
4	i	т		<i>x.v.</i> 0:	$\overline{x},\overline{v},0$.				Special: a	is above, plus
4	h	2		0, <u>1</u> , <i>z</i> ;	0, <u>1</u> , <u>7</u> .				no extra c	conditions
4	g	2		0,0 <i>,z</i> ;	0,0, <i>ī</i> .					
4	f	ī		$\frac{1}{4}, \frac{1}{2}, \frac{1}{4};$	$\frac{1}{4}, \frac{1}{2}, \frac{3}{4}$.]	
4	е	ī		$\frac{1}{4}, 0, \frac{1}{4};$	$\frac{1}{4}$,0, $\frac{3}{4}$.				b hkl: h = 2n; (l = 2n)	
2	d	2/ <i>m</i>		$0,\frac{1}{2},\frac{1}{2}.$]	
2	с	2/ <i>m</i>		0, <u>1</u> ,0.						
2	b	2/ <i>m</i>		$0,0,^{1}_{2}.$					> no extra c	conditions
2	а	2/ <i>m</i>		0,0,0.					J	
				5	Symmetr	y of spe	ecial proje	ections		
(00	1) p	2; <i>a'</i> = <i>a</i> /	2, <i>b'</i> = <i>b</i>		(100)	omm; t	o' = b, c' =	= <i>c</i> /2	(010) <i>cmm</i> ;	c'=c, a'=a

Figure 2.37 Space group *B2/m*. Reprinted from Buerger, M. J. (1971) *Introduction to Crystal Geometry*, with permission of McGraw-Hill Education.

c glide is represented as a dotted line \perp to \vec{b} at 0 and $\frac{1}{2}$. The 4 points about *i* at 000, arise from *i* and the *c* glide. However, that combination places the 2-fold axis at $\frac{1}{4}c$. The *C*-centering just moves these 4 points to $\frac{1}{2}a + \frac{1}{2}b$ and this introduces an *n* glide, represented by the dot-dash lines at $\frac{1}{4}b$ and $\frac{3}{4}b$. The remainder of the diagram should now be self-explanatory. This space group shows how new symmetry elements arise from combinations of symmetry elements and centering. There is no $C2_1/c$ because C2/c contains a 2_1 axis.

2.6.4 Orthorhombic space groups

To derive orthorhombic space groups, we need to consider point groups D_2 -222, $C_{2\nu}$ -2mm, and D_{2h} - $\frac{2}{m}\frac{2}{m}\frac{2}{m}$ combined with *P*, *I*, *F*, *C*. These combinations give rise to 58 space groups of

Symmetry element	Affected reflection		Condition for systematic absence of reflection	
2-fold screw (2_1)	а	h00	h = 2n + 1 = odd	
4-fold screw (4_2) along	Ь	0k0	k = 2n + 1	
6-fold screw (6 ₃)	С	00/	l = 2n + 1	
3-fold screw $(3_1, 3_2)$	<i>c</i> *	00/	l = 3n + 1, 3n + 2	
6-fold screw (6 ₂ , 6 ₄)			that is, not evenly divisible by 3	
4-fold screw $(4_1, 4_3)$ along	а	h00	h = 4n + 1, 2, or 3	
	Ь	0k0	k = 4n + 1, 2, or 3	
	С	00/	l = 4n + 1, 2, or 3	
6-fold screw (61, 63) along	с*	00/	l = 6n + 1, 2, 3, 4, or 5	
Glide plane perpendicular to	а			
translation $b/2$ (b glide)		0 <i>kl</i>	k = 2n + 1	
c/2 (c glide)			l = 2n + 1	
b/2 + c/2 (<i>n</i> glide)			k+l = 2n+1	
b/4 + c/4 (<i>d</i> glide)			k + l = 4n + 1, 2, or 3	
Glide plane perpendicular to	Ь			
translation a/2 (a glide)		h0l	h = 2n + 1	
c/2 (c glide)			l = 2n + 1	
a/2 + c/2 (<i>n</i> glide)			h+l = 2n+1	
a/4 + c/4 (<i>d</i> glide)			h + l = 4n + 1, 2, or 3	
Glide plane perpendicular to	С			
translation a/2 (a glide)		hk0	h = 2n + 1	
c/2 (c glide)			k = 2n + 1	
a/2 + c/2 (<i>n</i> glide)			h+k=2n+1	
a/4 + c/4 (<i>d</i> glide)			h + k = 4n + 1, 2, or 3	
A-centered lattice (A)		hkl	k+l = 2n+1	
B-centered lattice (B)			h+l = 2n+1	
C-centered lattice (C)			h+k=2n+1	
Face-centered lattice (F)			h+k=2n+1	
			h+l=2n+1	
			k+l = 2n+1	
Body-centered lattice (1)			h+k+l=2n+1	

 Table 2.5
 Systematic absences arising from centered cells and translational symmetry

* Note that in the crystal classes in which 3- or 6-fold screw occur as cell axes, these are conventionally assigned to be c, so only the 00/ reflections need be considered.

which only a few will be derived. The simplest is *P* combined with 222. The three 2-fold axes are mutually perpendicular and are represented as shown in Figure 2.39, where the arrows indicate 2-fold axes parallel to *a* and to *b* and the \bullet symbol means a 2-fold axis parallel to *c*. The axes are listed in the order *A*, *B*, *C* lying along the *a*, *b*, *c* directions, respectively. Thus, 222₁ means that the *c*-axis is a 2-fold screw axis while the *a*- and *b*-axes are 2-fold. Whenever one or more of the axes are 2₁, we have a corresponding movement of $\frac{1}{4}$ or $\frac{1}{4} + \frac{1}{4}$ of another axis. To see how this comes about consider 222₁. The *c*-axis is 2₁ and gives the points *x*, *y*, *z* $\xrightarrow{2_1}$ \overline{x} , \overline{y} , *z* + $\frac{1}{2}$; there is also a 2-fold axis along the *a*-axis. This takes the point



(001) <i>cmm</i> ; <i>a</i> ′ = <i>a</i> , <i>b</i> ′ = <i>b</i>	(100) $pgm; b' = b/2, c' = c$	(010) $p2; c' = c/2, a' = a/2$
--	-------------------------------	--------------------------------



x, y, z to x, \bar{y}, \bar{z} and the point $\bar{x}, \bar{y}, \frac{1}{2} + z$ is taken to $\bar{x}, y, \frac{1}{2} - z$. This situation is illustrated in Figure 2.40. There are four equivalent points, two from 2₁ and two from the 2-fold axis along *a*. This combination creates a 2-fold axis along *b* but at $\frac{1}{4}c$ which does not create new points. Space groups related to *P*222₁ are *P*2₁2₁2 and *P*2₁2₁2₁. Remember that when half integral translations such as 2₁ are introduced there is a shift in another symmetry element. This is illustrated for *P*2₁2₁2 in Figure 2.41. Note that the 2₁ along *a* introduces a translation of $\frac{1}{2}a$ and that along *b* of $\frac{1}{2}b$. These translations have the effect of moving *c* to $\frac{1}{4}\frac{1}{4}0$ as shown in Figure 2.42.

We now consider point group $C_{2\nu}$ -2mm. Interaction with lattice P creates space group Pmm2 (remember the 2-fold axis is parallel to c). We now replace 2 by a 2_1 axis and systematically replace the mirrors by glide planes. The sequence in nomenclature is to list



Figure 2.39 Representation of three mutually perpendicular 2-fold axes.



Figure 2.40 A diagrammatic illustration of how the symmetry axes interact to produce the equivalent points.

mirrors or glides in order of those \perp to *a*, *b*, *c*, in that order. *Pmm2* means the unit cell is primitive with a mirror \perp to *a*, a second $\mathbf{m} \perp$ to *b* and a 2-fold axis parallel to \vec{c} (axes are given in the parallel direction). Replacing 2 by 2₁ creates *Pmc2*₁, that is, the 2₁ transforms the mirror \perp to *b* into a *c* glide (Figure 2.43).

By systematically replacing the mirrors by glides and 2 by 2_1 we obtain *Pcc2*, *Pma2*, *Pnc2*, *Pba2*, *Pnn2*, *Pca2*₁, *Pmn2*₁, *Pna2*₁. All of these space groups have only 4 equivalent points and are non-centrosymmetric. As we add *C*-centering or *A*-centering we create 4 more points. There are seven *C*- and *A*-centered space groups, three body-centered and two face-centered space groups. The latter two have 16 equivalent points arising from the face centering condition, points at $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$ acting on the four non-centered points.

We now must consider the point group D_{2h} with the lattice translations. This requires $\frac{2}{m}\frac{2}{m}\frac{2}{m}\frac{2}{m}$ symmetry. The simplest of these space groups is *Pmmm* to be understood as $P\frac{2}{m}\frac{2}{m}\frac{2}{m}$ with 8 equivalent points. $\frac{2}{m}$ yields 4 points and a second mirror doubles that number.



Figure 2.41 Spatial illustration of the points created by 2_1 perpendicular to 2, which also generates a 2-fold axis parallel to *b*, but shifted by $\frac{1}{4}c$.



Figure 2.42 The disposition of the 2-fold axes in $P2_12_12_1$.

The remaining symmetry elements do not create additional points. Once again we replace the 2-fold axes systematically by 2_1 and the mirrors by glides. This produces 16 primitive, 5 *C*-centered, four body-centered, and two face-centered space groups. We will only consider *Pnma* (Figure 2.44). Note that the full symbol is $P\frac{2_1}{n}\frac{2_1}{m}\frac{2_1}{a}$. Further, we recall that $\frac{2}{m} = i$ but we recognize that $\frac{2_1}{m}$ will offset the center from the mirror. Given the fact that there are three 2_1 in this space group tells us that the three axes will not intersect and given two glides



Figure 2.43 Representation of space group *Pmc*2₁.

indicates that the mirrors and glide will be offset from *i* and will not coincide with 2₁ axes. The result is the distribution of symmetry elements in Figure 2.44. The two points about the center are always *x*, *y*, *z*, \bar{x} , \bar{y} , \bar{z} . There is an *n* glide \perp to *a* (dot-dashed lines in Figure 2.43), therefore,

$$\begin{array}{cccc} x,y,z & \longleftrightarrow & \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z\\ \updownarrow i & & \updownarrow i\\ \bar{x},\bar{y},\bar{z} & \longleftrightarrow & \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z \end{array}$$

Next, we deal with the mirror \perp to *b*. It is at $\frac{1}{4}b$. It will act on all four points to create the necessary 8 equivalent points.

$$x, y, z \longleftrightarrow^{m} x, \frac{1}{2} - y, z$$

$$\uparrow i \qquad \uparrow i$$

$$\bar{x}\bar{y}\bar{z} \xleftarrow{m} \bar{x}, \frac{1}{2} + y, \bar{3}$$

$$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z \xleftarrow{m} \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$$

$$\uparrow i \qquad \uparrow i$$

$$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z \xleftarrow{m} \frac{1}{2} + x, y, \frac{1}{2} - z$$

These points create the *a* glide \perp to *c*, that is, \perp to the 2₁ at $\frac{1}{4}a$ as shown by the bent arrow at the upper right-hand corner. The systematic absences arise as follows. The *n* glide with glide components of $\frac{1}{2}b + \frac{1}{2}c$ gives rise to 0kl = 2n + 1 are absent. *hk0*: h = 2n from the *a* glide, *h* must be even for a reflection to appear. The 2₁ axes give rise to *hk0*, 0*k*0,



Figure 2.44 Space group *Pnma* as presented in the International Tables of Crystallography, Vol. 1, 195.

and 00*l* requirements, odd absent, even values are present. A complete listing of systematic absences are given in Table 2.5.

2.6.5 How knowledge of the space group aids in crystal structure solution

At this juncture, the student may be wondering why we went through so much trouble to master space group theory. It turns out that every crystal (we need not consider incommensurate structures and quasi-crystals) belongs to one of the 230 space groups. To solve the structure, we will need to consider the contribution of every atom in the unit cell to each reflection. That is, we need to know the magnitude of F_{hkl} for every reflection by adding up the wavelets from every atom in the unit cell for every I_{hkl} recorded. Suppose we measured

2000 reflections and there are 144 atoms in the unit cell. We then would have 144 terms to add for each of 2000 reflections or 288 000 additions. However, suppose our space group is *Pmna*? The number of equivalent points is eight. This means that we need to find *x*, *y*, *z* for one of the eight atoms, say cobalt. The positional parameters for the seven other cobalt atoms are immediately given by the equivalent points. Furthermore, each cobalt makes the same contribution to the intensity, so we need to calculate *F*_{hkl} for one cobalt and multiply by 8 to get the contribution to the unit cell for this atom. Thus, we need 144/8 = 18 terms, that is, one term for each atom in the calculation for *F*_{hkl} and then multiply by 8. Furthermore, we need only collect data from $\frac{1}{8}$ of the unit cell and calculate the electron density for this portion of the cell. The transport of this electron density by the symmetry elements of the space group reproduces the electron density of the entire unit cell. The reduction in the computational labor is enormous and allows most of it to be done on a desktop computer. Of course, the situation is not quite that simple. Some atoms may be on special positions, which reduce the number of equivalent points, but the general idea is the same.

2.6.6 Space group determination

Figures 2.38 and 2.44 show that many space groups exhibit systematic absences. In order for systematic absences to occur, the space group must have translations that are non-integral. For example, every glide plane and screw axis has a non-integral translation. Non-primitive unit cells also have non-integral translations. We have already seen that certain absences arise from centered lattices. Once the unit cell type, axial system and systematic absences are determined, the choice of space group is evident. However, for some systems, two or three space groups have the same systematic absences. Always choose the centrosymmetric one first and refine the structure. If the reliability indices are high or some temperature factors are unreasonable, or strange bond distances are calculated, then refine in the lower symmetry space group. But remember that in the lower symmetry you have more degrees of freedom, so you must be sure that the improvement is in the structure and temperature factors and not just in the reliability indices.

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Chapter 3 Practical Aspects

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3.1 Generation of X-rays: general concepts and terminology

X-rays are produced by the collision of high-velocity electrons with a stationary or rotating metallic target. The most useful X-rays for the home laboratory have energies between 4 and 21 keV, which relates to wavelengths of 3.1–0.59 Å (1 Å = 10^{-10} m). X-rays with energy below 4 keV are readily absorbed by air, while X-rays above 21 keV will return condensed powder patterns that can be difficult to interpret.

In practice, the metallic target is made of chromium (Cr), cobalt (Co), copper (Cu) or molybdenum (Mo). These metals produce X-rays in the 4–21 keV range while providing stable heat conduction and corrosion resistance. The production of X-rays generates large quantities of heat, which must be dissipated rapidly in order to prevent the metallic targets from melting; therefore, the metals must be durable and conductive to both heat and electricity.

The continuous and characteristic spectrum of X-ray radiation is produced when highvelocity electrons strike the metallic target. The continuous spectrum or Bremsstrahlung radiation is produced when the path of the electron that enters the target is altered by interactions with the metal atoms (McCall, 1982). The bending or braking action causes the electrons to lose momentum and release X-ray radiation. The Bremsstrahlung radiation displays a continuous spectrum due to the fact that not every electron will decelerate in a similar manner. The electrons that are completely stopped by the impact will release all of their energy at once, and thus produce the maximum energetic and lowest wavelength X-ray. The energy is thus described by the equation:

$$eV = hv_{max} = \frac{hc}{\lambda_{min}}$$

 $\lambda_{min} = \frac{hc}{eV} = \frac{12.4 \times 10^3}{V}$

where λ is in Å (10⁻¹⁰ m) and V is the applied voltage. If one plots the intensity of the Bremsstrahlung radiation against increasing wavelength, one would etch a curve that begins at λ_{\min} and rapidly increases to a maximum of a few tenths of an Angstrom above λ_{\min} and then slowly decreases as one proceeds to longer wavelengths.

The characteristic spectrum, on the other hand, is composed of sharp intensity maxima at critical wavelengths and is superimposed on the continuous spectrum. These narrow peaks are characteristic of the metal used in the target material and are associated with the K, L, and M shells of the electronic structure of the element that constitutes the metal. The K, L, and M shells, which corresponds to the principle quantum numbers n = 1, 2,and 3 respectively, represent the three lowest energy orbitals surrounding the central nucleus of the target element, with the K shell representing the lowest orbital. If one of the electrons that collide with the target has sufficient energy to eject the electron from the K shell, an electron from a higher energy shell will immediately fall to the K shell to fill the void, emitting a photon of high energy in the process. The energy of the photon is fixed and is known as the characteristic wavelength for the K radiation.

The energy released by the cascade of an electron from the higher energy orbital to the lower *K* shell is specific for the element of the target metal. The transition from the *L* shell to the *K* shell is known as the $K\alpha$ radiation while the transition from the *M* shell to the *K* shell is known as the $K\beta$ radiation. Furthermore, the $K\alpha$ transition is the most probable event given the proximity of the *K* and *L* shells over the $K\beta$ transition, which in turn gives rise to a much more intense $K\alpha$ line in the characteristic spectrum of the element.

The electronic transitions from the *L* shell to the *K* shell are described by quantum mechanics and only two transitions from the *L* shell to the *K* shell are allowed. These transitions split the $K\alpha$ radiation into the $K\alpha_1$ and the $K\alpha_2$. The same rules apply to the $K\beta$ transition, only in this case the energy difference is zero and the two radiations convolute to one. In practice, the $K\alpha$ radiation has a peak width of less than 0.001 Å and it is possible to separate the two radiations with a good experimental setup. The $K\beta$ radiation is also present and can be eliminated with various techniques (see Section 3.3). The energy of the X-ray produced must not be confused with the intensity of the X-ray. The common units for X-ray intensity are *flux* (number of photons produced per second), *brightness* (*flux* per squared milliradians), and *brilliance* (*brightness* per squared millimetre).

The intensity of the X-rays produced by the methods described is directly related to the target element (*Z*), voltage (*V*) and the number of electrons striking the target element (*i*). For example, the intensity of the characteristic X-ray spectrum for molybdenum is about 90 times that of its continuous spectrum. For the characteristic X-ray spectrum of molybdenum it should be noted that the $K\alpha$ radiation is about 5 times more intense than the higher energy $K\beta$ radiation and that the $K\alpha_1$ is about two times more intense than the $K\alpha_2$ (McCall, 1982).

3.1.1 The sealed X-ray tube sources

The sealed tube is the most commonly used source for the production of X-rays at the home laboratory. The tube consists of a coiled tungsten wire cathode and a water-cooled base metal anode that are sealed in a glass or ceramic insulator. On the sides of the tube are placed beryllium windows that allow the X-rays generated inside the tube to pass through. The tube is evacuated to high vacuum and sealed. Electrons are freed from the cathode when an electrical current is applied to the tungsten wire and are accelerated toward the base metal anode, which produces X-rays at the surface of the metal. The X-rays radiate toward the walls of the sealed tube and eventually escape through the beryllium windows (see Figure 3.1).

The cathode is positioned above a rectangular anode in such a way as to allow the long axis of the anode to be parallel to the long axis of the cathode wire. This affords two different



Figure 3.1 Cut-away view of a ceramic copper tube and the cartoon representation. Electrons are generated at the filament (A) by application of an electrical current and are accelerated toward (B) by a high electrical potential. The electrons de-accelerate when they strike the metallic anode (B) and generate X-rays and heat. The heat is dissipated by circulating water through the base of the tube, while the X-rays escape the tube through the beryllium window (C).

types of X-ray focal shapes. A line focus (actually it is rectangular) is observed when viewed from an angle perpendicular to the long axis of the rectangle, while a point focus is observed when viewed perpendicular to the short axis. The point focus will afford a narrow, intense X-ray beam while the line focus will produce a wider less intense X-ray beam. Excess heat generated by the production of X-rays is dissipated by a circulating chilled water system.

3.1.2 The rotating anode X-ray sources

The rotating anode X-ray source is much more complicated, but still operates by the same principles. The limitation of the sealed tube system is how rapidly one can cool the metallic target in order to prevent meltdown. This is, of course, dependent on the choice of the target material, but an upper limit for the standard laboratory setup is around 2000 W. One method to increase the heat dispersion is to allow the target to rotate rapidly while it is being subjected to electron bombardment. The rotating anode must still be water cooled, but now the upper limit for heat dispersal is around 20 000 W. The high heat load levels allows for about a 10-fold increase in the intensity return of the X-ray radiation.

The problem with rotating the anode is that the target must rotate freely in a vacuum chamber with the motor and water source for the rotation mechanism located outside the vacuum chamber. This complicated mechanism involves ferro-magnetic fluidic seals that will allow the shaft of the anode to rotate freely while allowing for a good high-vacuum seal to be maintained. Once a good seal is obtained the vacuum chamber containing the rotating

anode and tungsten filament must be evacuated and a high vacuum must be maintained by a turbo molecular pumping system.

The seals, bearings and other mechanical devices found with the rotating anode assembly are expensive to repair and maintain. The seals themselves must be replaced once every one to two years, while the belts, pulleys, o-rings, vacuum oil and filaments all must be replaced on a routine basis.

Given the complexity of the rotating anode system one must weigh the benefits of a 10-fold increase in X-ray flux with the disadvantages of high maintenance costs and labourintensive anode and filament replacement. The choice of X-ray source will thus depend on the types of experiments and materials that are to be studied and the quality of the data that is necessary for successful completion of the investigator's projects.

3.1.3 Other X-ray sources

In recent years, the micro-focus and pulsed tube has been developed to deliver high flux X-ray beams at much lower electrical potentials. For the micro-focus tube the electron beam that is emitted from the cathode is focused by an electrostatic cup to a very small focal spot on the metallic target. By concentrating the electrons at a particular region, one can achieve very high X-ray flux with an electrical potential of only a few hundred volts. The disadvantage of the micro-focus tubes is that the X-ray beam produced is only about 1% the size of the normal X-ray tube ($\sim 0.1 \times 1$ mm for the line focus and 50 µm for the point). The micro-focus tubes often have built-in X-ray optics that increase the flux and focuses the X-ray beam. The micro-focus tubes are expensive to build and maintain but can deliver a brilliant X-ray beam that is comparable with the rotating anode sources.

3.2 Typical laboratory experimental setups

The word typical is far from an ideal description of the various X-ray diffraction instruments that are available to the modern investigator. In this sense, we will focus on the most common instruments that any researcher will encounter in their investigations. Any and all of the instruments described can be modified and adapted to fulfill the investigators needs. It is the versatility of these instruments that renders their usefulness in the modern analytical laboratory (see Chapter 1).

3.2.1 X-ray cameras

Powder diffraction was recognized as one of the most important analytical tools in the late 1930s and several powder diffraction patterns were collected and tabulated. These were used as fingerprints, and in some simple cases, the complete structure of the material was realized. The initial developments of powder X-ray diffraction were based on the camera methods. The first powder diffraction camera was devised by Debye and Scherrer (1916) and independently by Hull (1917). Figure 3.2 shows a schematic of a Debye–Scherrer camera. It essentially consists of a chamber where the film is mounted. The X-ray enters through



Figure 3.2 Debye–Scherrer–Hull camera. X-rays enter the camera through the collimator and strike the specimen (normally placed in a capillary tube) at the center of the camera. X-rays are diffracted in all directions and expose the film that is positioned at the edge of the camera. Undiffracted X-rays are stopped by an exit tube that is located behind the specimen.

a conical collimator, irradiates the specimen, and the Debye rings generated (part of the rings) are recorded onto the film residing on the inner surface of the chamber. There is also a conical beam stop, which reduces the secondary scattering from the camera itself. The specimen is usually in the form of a rod or filled in a capillary, and is rotated constantly for maximum possible randomization.

The amount of specimen used in this method is usually very small. This leads to, in extreme cases, insufficient particles to give a statistical distribution (see particle statistics). This problem is overcome by the Gandolfi camera, which can be considered as a modified Debye–Scherrer method, where the specimen is mounted at 45° to the normal specimen rotation axis (Figure 3.3). During data collection, the specimen rotates about this 45° inclined axis and also the entire specimen mount rotates about the normal specimen axis. In terms of a four-circle single crystal diffractometer this can be considered as chi-axis at 45° and simultaneous rotation of omega and phi circles (preferably at different speeds). Depending on the resolution required the camera diameters range from 50 to 200 mm.

Although extensively used, one of the major disadvantages of the Debye–Scherrer and Gandolfi geometry is the low resolution. This could be attributed to the diverging beam once it exits the collimator. This can be overcome by using a Guinier camera, which employs focusing optics, namely, a monochromator (Figure 3.4).

Another arrangement where the X-rays from the source diverges on to the powdered specimen and refocuses at the film (or a detector) is termed para-focusing condition. The cameras using this geometry yield powder patterns of increased resolution without increased exposure time compared to the aforementioned cameras of similar radius. These cameras were first independently devised by Seemann and Bohlin, and were often called Seemann–Bohlin cameras. In practice, several slits are used to limit the X-rays that fall only on the specimen, and also to limit the diverging beam after diffraction.



Figure 3.3 Schematic representation of the attachment necessary to convert a Debye camera into a Gandolfi camera. The sample is mounted at a 45° angle to the normal.



Figure 3.4 Schematic representation of Guiner camera. Convergent X-rays strike the specimen and diffract. The diffracted X-rays are themselves convergent and scatter in all directions and are detected.

Another means to obtain powder diffraction patterns is pinhole methods. Here X-rays from a monochromated pinhole source and a flat film is used (Figure 3.5) for data collection. The experimental setup for the pinhole method is very similar to the Laue camera for single crystals, except for the white radiation used in the latter. Since whole diffraction rings can be collected, it is convenient to detect variations along any particular ring. Thus preferred orientation, distortions in the lattice could be easily studied by this method. In addition, by increasing the specimen to detector distance, low angle diffraction can be collected with great ease making it suitable for specimens with large interplanar spacings as usually seen in clay minerals, fibrous proteins, and so on. The specimen is usually in the form of a thin



Figure 3.5 Schematic representation of a typical pinhole camera. X-rays enter the camera through the collimator and strike the specimen in the capillary. The diffracted X-rays scatter in all directions and will expose the detector that is positioned behind the specimen.

sheet. This method can be used in both transmission as well as back-scattering, similar to corresponding Laue techniques.

The errors arising from the camera methods are common and the factors most affected are fixed camera radius and film shrinkage. Additional problems such as specimen displacement and/or transparency errors are shared by all powder diffraction methods. When sufficient care is taken, the resolution and accuracy of the data obtained from the Guinier camera are comparable to the modern laboratory X-ray diffractometers. Compared to the latter, data processing in camera methods are more labor intensive and are prone to errors. Camera methods are used only in a very small number of present day X-ray diffraction facilities.

3.2.2 Diffractometers

Modern powder diffractometers essentially use the geometries of the various cameras described above, but instead of films, some form of electronic detection is used (see Section 3.4 for details on X-ray detectors). The essential components of a diffractometer, hence, are: (i) a source of radiation which is common to cameras and diffractometers, (ii) a detector, other than film, and associated counting electronics, and (iii) a goniometer which has, at least, two angular movable circles, which could move synchronous to each other at a predetermined ratio of speeds.

The most common form of diffractometer seen is the parafocusing Bragg–Brentano instrument. The geometry of the Bragg–Brentano diffractometers can be compared to the Seemann–Bohlin cameras, but the specimen is usually flat in the former.

A combination of two or more angular movements of the goniometer arms attached to various components, namely, X-ray tube, specimen stage, and the detector result in the Bragg condition yielding the powder diffraction pattern (Figure 3.6). The common combinations



Figure 3.6 Schematic representation and image of a typical Bragg–Brentano para-focusing powder diffractometer. X-rays that diverge from the source and strike the sample are diffracted and "focused" on to a movable detector. The sample can be spun about an axis perpendicular to the plane of the specimen holder to minimized preferred orientation.

are (i) θ - θ where both X-ray tube (attached to the outer circle) and the detector (attached to the inner circle) synchronously move to a θ degree while the specimen stage is stationary, and (ii) θ -2 θ , where the X-ray tube is stationary, specimen stage and the detector (attached to the inner and outer circles respectively) synchronously move in the angular ratio 1:2. In both the conditions, spinning the specimen along the axis perpendicular to the plane

of the specimen itself improves the particle statistics of the powder pattern. In addition, to improving on the quality of the data several forms of optical components such as slits, monochromator, Göbel mirror, filters are frequently used. Usually, Bragg–Brentano method is well suited for specimens with low X-ray penetration.

When transmission mode is desired, either a primary beam monochromator or a Göbel mirror are used to maximize the flux at the narrower specimen (usually specimens filled in capillaries of 0.1–1 mm in diameter). By this method, preferred orientation is reduced to a great extent. Also, this method is favored for compounds containing lighter elements to avoid the effects of broadening seen in Bragg–Brentano geometry.

3.2.3 Micro-diffraction

With the advancements in two-dimensional detectors and synchrotron X-ray sources, use of methods similar to pinhole cameras, are also used extensively in powder diffraction. These methods are very convenient where the amount of specimen available is very limited (few micrograms).

The specimen stage on the micro-diffractometer can readily be selected to suit the investigators needs. These stages include such devices as a three-quarter χ cradle and programmable XYZ platforms (Figure 3.7, see Chapter 1). High throughput analysis and irregularly shaped specimens are a few of the experiments that are available with the micro-diffractometer.



Figure 3.7 The micro-diffractometer with a high throughput XYZ stage. Image courtesy of Bruker AXS.

3.3 X-ray optics: monochromators and Göbel mirrors

Most of the powder X-ray diffraction studies involve monochromatic X-rays. A common method for producing a monochromatic X-ray is through filtering, the objective is to have only the $K\alpha$ component of the radiation. For this, a thin metal foil, functioning as a filter, is used to absorb the unwanted $K\beta$ radiation. Absorption of X-rays follows the equation:

$$\frac{I}{I_0} = e^{-\mu_l \lambda}$$

where, μ_l is the linear absorption coefficient, *X* is the pathlength of the X-rays in the absorber and I_0 is the initial intensity. Thus it follows that the filter used with a particular value of μ , depends on the characteristics of the anode material used for producing X-rays. A suitable filter is one whose *K* absorption edge falls between the $K\beta$ and $K\alpha$ wavelengths of the X-ray target, for example, nickel foil is used to filter copper $K\beta$ radiation. The thickness of the foil necessary can be calculated from the above equation. Although using a filter will reduce the $K\beta$ radiation to a minimum, the filtered radiation is not strictly monochromatic.

For producing strictly monochromatic radiation, usually, a high-quality single crystal is used. The crystal is placed either, adjacent to the source, and before the specimen, in which case it is called as a primary monochromator, or located just before the detector, in which case it is identified as diffracted beam monochromator. The primary monochromator removes $K\beta$ as well as the $K\alpha_2$, giving perfect monochromatic $K\alpha_1$ radiation. The secondary monochromator, on the other hand, removes only $K\beta$ radiation, leading to a powder pattern with both $K\alpha_1$ and $K\alpha_2$ components. The advantage of the latter design is that it eliminates the fluorescent radiation and Compton (incoherent) radiation resulting in a very low background. Fluorescent radiation arises from excitation of specimen electrons by X-ray beam. For example, specimens containing Fe, Co, and Ni fluoresce strongly when the radiation is Cu $K\alpha$.

Primary monochromators are used for determination of precise unit cell dimensions as complications arising from the $K\alpha_2$ components are missing. They are also the only monochromators that can be used with linear or area detectors. The disadvantages include a high intensity loss, and lengthy protocols for precise alignment.

X-rays, unlike optical light, cannot be reflected or deflected easily by mirrors; however, specially deposited multilayers of low-Z and high-Z materials can be used to reflect and monochromatize the X-rays based on Bragg's condition. Typically, combinations of W–B₄C, W–Si, Ni–C, and a combination of such layers are employed to create what are called Göbel mirrors. With these mirrors, the diverging X-ray beam from conventional sources could be made into a parallel or focused beam. The major advantage of Göbel mirrors is the near removal of specimen displacement error ($\sim \pm 200 \,\mu$ m), increased intensity and removal of fluorescent radiation (when used on the diffracted beam side). These mirrors are extensively used in the studies of thin films, and in stress/strain analysis.

3.4 Detection of X-rays: general concepts and terminology

All diffraction experiments depend on the collection and measurement of the scattered X-ray radiation. Without good X-ray detection, the powder diffraction experiment would

be severely limited in both time and quantity of sample material. The process of detecting X-rays is simply a matter of counting each X-ray photon that is scattered by the specimen and converting these events into electronic signals. In principle, the detection of X-rays can be restricted to a single point in space (referred to as point detection), a one-dimensional line (referred to as line detection) or a two-dimensional area of space (referred to as area detection). X-ray detectors can be flat or curved; they can be mobile or fixed depending on the size and utility of the detector itself. The choice of the detector is primarily focused on the type of diffraction experiment, the required results, the speed of data collection and the budget of the investigator (Hanley and Denton, 2005).

The four general types of detectors are proportional, Geiger, scintillation and the semiconductor. Each detector type functions in a similar manner. An X-ray photon enters the detector, interacts with an atom (or atoms) in the detector, the atom in turn is excited or ionized and is "counted" when it returns to its ground state. Often the count is multiplied by a series of electron events to produce a stronger signal. In other cases, the excited atom produces a photon of energy (light) that is measured by another detector (such as a CCD camera), which in turn is proportional to the original X-ray event. Whichever the case may be, there are three characteristics of the detector that should be measured: the inadvertent loss of signal, the detective quantum efficiency (DQE) and finally the energy resolution.

In an ideal situation every X-ray photon that strikes the detector is counted, processed and the information stored for later analysis. In practice, the counting of X-ray photons is far from ideal. For instance, the counting of an individual X-ray photon is not an instantaneous event. The electronics of the detector takes a finite time to process the electrical signal and send that information to a data collection station. For example, take two photons that strike the detector, where the first photon is *t* seconds ahead of the second, if the detector is busy processing the signal from the first photon it will not count the second photon. In this situation, we say that the second X-ray photon is lost. If the number of X-ray photons that strike the detector is high (several thousand per second) then the detector can become saturated and the signal that is produced is significantly underestimated. The minimum time between counting one X-ray photon and the next is called the dead time and is dependent on the detector. In general, the dead time does not exceed a few microseconds. In practice, one must choose a detector that displays a linear behavior between the X-ray photons counted and the X-ray intensity observed and displays a good dynamic range that is the ability to accurately measure very weak X-ray events and very strong X-ray events.

The quantum efficiency of the detector (detector quantum efficiency or DQE) is related to how many X-ray photons that strike the detector during the recording cycle (not during the dead time) that are actually counted (Illers *et al.*, 2005). The efficiency of the detector depends on the detector itself (detector efficiency) and the "windows" of the detector that allow X-rays to pass through but keep air and dirt out. No matter what material you choose, it is certain that the detector window will absorb a fraction of the X-ray photons that strike the detector. These windows are therefore constructed of low X-ray absorbing materials such as beryllium metal or organic polymers.

Most detectors have efficiencies greater that 80% (eight out of ten X-ray photons are counted); however, their efficiencies are correlated to the energy (wavelength) of the X-ray photon itself. The investigator must examine this efficiency with respect to the wavelength of radiation that will be used. Table 3.1 lists a few detector types and their efficiency for
Table 3.1 Comparison of selected X-ray photon detectors for the home laboratory (copper source). Detectors are graded on a scale of A to C where an A = excellent characteristics and C = acceptable characteristics

Detector	Detective quantum efficiency ^a	Dynamic range ^b	Linearity ^c	Energy resolution ^d	Area ^e	Spatial ^f	Speed ^g
Point detectors (0D)							
Gas proportional	А	_	С	В	_	_	А
Scintillation	А	_	А	С	_	_	А
Silicon drift (Si/Li)	В	-	А	А	_	-	А
Linear detectors (1D)							
Gas proportional	А	С	С	В	С	А	В
Hybrid micro-gap	А	А	А	В	С	А	А
Curved knife-edge	А	С	В	В	А	А	А
Micro-strip silicon	В	В	В	В	С	В	А
Image plate	С	А	А	С	А	А	С
Photographic film	С	С	С	С	А	В	С
Area detectors (2D)							
Multi-wire proportional	А	С	В	В	С	С	А
Hybrid micro-cap	А	В	А	В	С	В	А
CCD/phosphor	В	В	В	С	С	С	В
Image plate	С	А	А	С	А	В	С
Photographic film	С	С	С	С	А	В	-

^a QE or DQE is a measure of the detector efficiency with regard to detecting X-ray photons, where the higher the DQE the more sensitive the detector. The detective quantum efficiency \sim X-ray photons counted by the detector/actual number of X-ray photons by the diffraction event.

^b The dynamic range or DR of a detector is the range in X-ray intensities that a detector can record without overloading. DR \sim max intensity recorded/minimum intensity recorded.

^c The intensity of the X-rays detected should be linear to the number of the X-ray photons striking the detector from the lowest intensity to the highest.

^d Energy resolution is the ability of the detector to distinguish between X-ray photons of different energies (not intensities). ^e The area of the detector is the measure of one- and two-dimensional face of the detector in which X-ray photons can be detected and is limited to the physical characteristics of any given device.

^f The spatial resolution is the measure of how closely in real space two X-ray measurements can be differentiated on the detector face.

^g The speed of the detector is the time between the moment an X-ray photon is detected to the time when the detector is ready to detect the next X-ray photon.

X-ray radiation near 8 keV (X-rays generated by a copper metal X-ray tube) (Eatough *et al.*, 1999; Brugeemann and Gerndt, 2004).

The efficiency of the detector is also directly tied to the energy of the X-ray photon that is absorbed. In an ideal case, an X-ray photon of energy *E* will produce a voltage of *V* in the detector. In practice, the X-ray photons will produce a range of voltages from V_{\min} to V_{\max} which peaks at *V*. The shape of the peak described by the voltages when plotted against the counts/s of the X-ray photons describes the energy resolution of the detector, where the sharper the peak the better the energy resolution. This is critical to resolving the $K\alpha$ from the $K\beta$ peak (recall that the $K\beta$ has higher energy than the $K\alpha$). A detector with a sufficiently high-energy resolution will only measure one of the two closely spaced radiation lines. Unfortunately, no detector has been developed that has high enough energy resolution to separate the $K\alpha_1$ line from the $K\alpha_2$ line.

3.4.1 Gas detectors for X-ray powder diffraction

The proportional counter is so named because the signal produced by such a device is proportional to the energy of X-ray photon that strikes the detector. The proportional counter is a metal container with an X-ray transparent window fixed to its side or the end. A wire is then fixed in the container in such a fashion as to insulate it, and the container is then filled to about 1 atm pressure with a noble gas (Ar, Kr, or Xe) and a small amount of a quenching gas such as methane or carbon dioxide (Saui, 2001). An electrical potential is then generated between the wire and the container in such a manner to make the wire the anode and the container the cathode. When an X-ray photon enters the container through the X-ray transparent window, it will interact with a noble gas atom, which in turn results in the ejection of an electron from the gas atom (photoelectric and Compton recoil). The ionized gas atoms will then move toward the cathode while the ejected electrons will move (via the gas atoms) toward the anode. The movement of the charged particles will result in an electrical current that can be measured by the appropriate circuitry.

If the electronic potential is below 200 V, then the measured current is directly related to the number of X-ray photons striking the detector (about 10^{-12} amps per photon). This device is known as an ionization chamber and has relatively low sensitivity to X-rays, but simple, low-voltage electronics. The ionization chamber was the first non-film X-ray detector but is now mainly employed for radiation survey meters.

If the electronic potential on the wire is raised to above 1000 V then a new phenomenon is seen that transforms the detector to a proportional counter. When the electrical field is high enough, the acceleration of the electrons toward the anode increases dramatically. The collision of the electron with other gas atoms in the chamber causes the ionization of those atoms. Their electrons in turn are accelerated toward the anode causing yet more collisions. The result is a cascade effect until some 10⁴ electrons are produced by a single X-ray photon. The electrical current generated by this number of electrons is readily detected. The electrical current is momentarily stored in a capacitor until a rate meter can measure and record its value. The result is a pulse of electrical current of a few millivolts. The size of the pulse is directly proportional to the energy of the X-ray photon. By discriminating between the sizes of the pulse one can distinguish X-ray photons of different wavelengths. This discrimination is accomplished by selection of the appropriate voltage for the radiation employed. The shorter the wavelength of the X-ray employed, the higher the current at the detector. Even though we see a cascade of electrons, the ionization is still localized to the region where the initial absorption of the X-ray photon occurred.

A Geiger–Muller counter is created when the electronic potential on the wire is raised above 1500 V. In this situation, the number of atoms that are ionized by a single X-ray photon in the container reaches saturation point. The electrical event is no longer localized to the region where the X-ray quantum was absorbed, but is now seen along the entire length of the wire. The signal produced by such an event is many times larger than that seen in the lower voltage cases. In this case, the signal is of the order of 1–8 V and can be measured with a simple voltmeter; however, the electrical pulse is now the same size no matter what the energy of the X-ray photon is and so discrimination between X-rays of different wavelength is now impossible. Geiger–Muller counters are presently employed in radiation survey meters where one meter can detect photons of widely varied energies.

3.4.2 Scintillation detectors

The simplest X-ray detector is the X-ray fluorescent screen. This screen is made by coating a piece of cardboard with a thin layer of zinc sulfide containing trace amounts of nickel. When enough X-ray photons strike the screen it will emit a pale yellow light. The efficiency of the screen is very low and is only useful for very intense X-ray beams; however, the amount of light produced is directly proportional to the number of X-ray photons that strike the screen. The principles are sound and apply to other materials that fluoresce in the presence of X-rays.

One such material that is far more efficient in X-ray detection is sodium iodide (NaI) crystals doped with small amounts of thallium. These scintillation crystals will emit a photon in the violet light region of the visible spectrum, when irradiated by X-ray radiation (see Figure 3.8). When an X-ray photon strikes the NaI crystal, some of the electrons in the crystal are raised to the conduction band. These electrons transfer their energy to the thallium cation exciting the cation to a higher energy state. When the high-energy cation returns to the ground state a photon of light (scintillation) is produced and passes into a photomultiplier tube, which employs the energy of the light to produce an electron. The electron is multiplied by a series of metal plates (dynodes) until a gain of 10⁶ electrons is



Figure 3.8 Scintillation detector with graphite monochromatic attachment and Soller slits. Image courtesy of Bruker AXS.

produced, which in turn will produce 1–10 V of electrical current. The entire process is very rapid (on the order of a microsecond) and the detector can count rates as high as 10⁵ events or more.

The scintillation detector is extremely efficient and the pulse size is directly proportional to the energy of the X-ray. On the other hand, the size of the pulse is less well defined for the scintillation counter as compared to the gas counters and it is more difficult to discriminate between X-ray photon energies.

3.4.3 Semi-conductor X-ray detectors

Silicon and germanium semiconductors will produce electrical signals when they are struck by X-ray radiation. Silicon is an intrinsic semiconductor that has high electrical resistivity. The electrical signals are produced when X-ray photons excite electrons from lower nonconducting valence bands to the higher conduction bands in the material. These electrons will create a pulse, which is detected by accumulating charge in an electrical field. Each X-ray photon will produce around a thousand free electrons and the corresponding number of free holes in the silicon or germanium material.

The silicon must be intrinsic (i), which implies that there are no impurities that render it an *n*-type (electron-rich) or *p*-type (electron-poor) device. To accomplish this degree of purity is extremely difficult and expensive (Bettaa *et al.*, 1997). To aid in the manufacture of the device, it is necessary to introduce small amounts of lithium to a *p*-type (boron doped) material. The material is heated and an electrical field is applied to diffuse the lithium cations into and throughout the solid. With equal amounts of lithium and boron spread evenly, the material is rendered intrinsic and suitable for X-ray detection. Such a solid is given the name Si(Li) or *silly*. [Germanium detectors are named Ge(Li) or *jelly*.] The detector is then constructed by application of very thin layers of *p* and *n* silicon on opposite sides. The entire device constitutes a *P*-*I*-*N* diode (Figure 3.9).

The Si(Li) detector operates in the same manner as the ionization chamber, except that the solid-state detector produces electrical pulses. Also the solid-state device has a detectable background, caused in part by the thermal excitation of the electrons in the intrinsic silicon. To lower the background it is necessary to cool the detector to temperatures of 80–100 K, which is accomplished with either liquid nitrogen or Peltier cooling.



Figure 3.9 Cartoon of a *P-1-N* diode. An intrinsic layer of silicon separates a *p*-type boron-rich silicon wafer from a *n*-type arsenic-rich silicon layer. X-ray will generate electrons in the intrinsic silicon which will be drawn toward the *p*-type layer while the "holes" will be drawn toward the *n*-type layers. The movement of the charges will in turn generate an electronic signal.

One major advantage of the Si(Li) detector is its high-energy resolution. Good energy resolution means high selectivity in wavelength discrimination. For powder diffraction this allows one to detect only the $K\alpha$ radiation of the scattered X-rays with no optical components necessary and hence overcomes the resulting loss of intensity.

3.4.4 Film and image plates for X-ray detection

So far we have considered real-time detectors, that is, detectors that will produce electrical signals at the time of the X-ray photon detection. Since the first days of X-ray diffraction, there have been detectors that produce visual signals in the presence of X-ray radiation. For example, we have already mentioned the zinc sulfide fluorescent screen, which will glow when X-rays strike the material. Photographic film is another medium that will change its visual characteristics when exposed to X-rays.

X-ray film is made from the same materials used for normal visual light photography except that the material is thicker and has larger internal grain sizes. To produce the film, a silver halide is dispersed in a gelatine material and coated to a thin plastic film. Although X-rays will directly interact with X-ray films, a phosphor is generally employed to generate an image which is recorded on the film. When X-rays or light photons from the phosphor strike the silver halide in the film, a chemical reaction occurs that will darken the exposed area. The darkness of the area is directly proportional to the intensity of the X-ray. The relationship between the film darkening and the X-ray intensity is not linear and calibration curves are necessary for accurate intensity measurements. After exposure to X-rays, the film must be developed in a chemical bath to complete the reaction and to fix the film to prevent further darkening. The film in turn is normally scanned with a densitometer to convert the darkening into a digital intensity reading.

The Polaroid Land camera is a modification of the X-ray film. In this case, the Polaroid camera has a fluorescent screen, which serves to convert the X-ray radiation into visible light. The visible light can be captured by conventional photographic procedures. The film is processed in the camera, in a fashion similar to a normal Polaroid camera, and a final product is ready in about 90 s. As with the X-ray film, the Polaroid film must be scanned by an external device to produce digitized intensities. For this reason, Polaroid and X-ray films are now employed for qualitative analysis or specialized diffraction research.

The image plate is a viable replacement for X-ray films and was developed initially for medical research. It was known that a BaFBr material, that was doped with Eu^{2+} ,would interact with X-ray photons in such a way as to produce a detectable change. In this case, the Eu^{2+} cations in the material are ionized by the X-ray photons to Eu^{3+} . The electrons freed by this ionization are transferred to the *F*-centres (defects in the lattices of the BaFBr material) to form a high-energy state in the BaFBr material. This state is meta-stable and will release the electron when it is illuminated by visible light (~632 nm). The electron will then recombine with the Eu^{3+} converting the cation back into the Eu^{2+} and producing visible light (~398 nm) as a by-product. Large sheets of the material can be produced in any size or shape. The image plate is then exposed to the X-rays. A laser scans the phosphor while a photomultiplier tube is employed to read any visible light that is produced by the scan. Finally, exposing the plate to a high dose of visible light bleaches the plate and the process is ready to begin again. Image plates are much faster than ordinary X-ray film detectors

and their output is linear to the intensity of the X-ray photon (to more than 10⁶ counts per second).

3.4.5 Zero-dimensional or point detectors

The zero-dimensional detection system is essentially a point-by-point X-ray photon detector. In its most fundamental mode, this system moves to a particular position in space and measures a single point and then moves on to the next point and repeats the measurement. The point dimensions are very small compared to total dimension of the data collection (less than 0.04° in most cases). These systems include the scintillation counter, the gas proportional counter and the solid state Si(Li) counters. Often slits are employed to limit the area of space that the detector sees. For the zero dimension detectors, the resolution limit is directly dependent on the size of receiving slit (RS) employed. Of course, if one collects data sets point-by-point then the entire process will take a considerable amount of time. On the other hand for very low angle data, the ability to collect only one point at a time has definite advantages.

3.4.6 One-dimensional detectors

The one-dimensional detectors are able to collect data at more than one point in space simultaneously. These detector systems can range from short 4° data collections to a very wide 120° range. They are basically divided into three classes: the gas proportional counters, the solid-state counters, and the image strip/film cameras.

The gas proportional counters can be subdivided into wire and knife-edge detectors. The wire detector consists of a single wire that is drawn tight in a sealed container. A long X-ray transparent window is then positioned in front of the wire. When the X-rays come into contact with the detector they pass through the window and ionize gas atoms in the tube which will cause a pulse in the wire. The timing of the resistance detected in the pulse determines the position of the incoming X-ray photon, while the intensity of the pulse determines the photons flux. Unfortunately, the wire must remain linear and since the detector must follow the arc of the diffraction sphere, the total length of the detector itself must be kept to less than 8° of the arc. The detector must therefore move along the arc to collect a full set of data. Another disadvantage of the wire detector is the sensitivity of the wire itself. If the wire is exposed to the direct beam while in the operational mode the detector will overheat and be ruined. This limits the detector to 5° and greater in 2θ . A hybrid wire detector has been developed to counter some of the disadvantages of the traditional wire detectors (Durst et al., 2003). This detector employs both the single wire as the anode and a printed copper inlaid circuit board as the cathode. The detector has a much higher dynamic range than the normal single wire detector and can handle the higher intensity associated with lower 2θ angles and the direct X-ray beam. In addition, the hybrid detectors can measure up to 12° in 2θ and thus can cover more space in less amount of time.

A gas detector that does not utilize a wire, but instead employs a series of razor sharp metallic probes can be shaped to fit the arc of the diffraction sphere and thus can be made to cover a much wider 2θ range. This detector consists of a curved chamber where thousands



Figure 3.10 A silicon strip detector with Sollar slit assembly. Image courtesy of Bruker AXS.

of individual knife-edged anodes and segmented cathodes are orientated to face an X-ray transparent window (Evain *et al.*, 1993). The chamber is filled with an argonne–ethane gas. When an X-ray photon enters the chamber a charge collects on the knife-edge anode and a signal is generated.

The solid-state one-dimensional detectors are named silicon strip or simply strip detectors. They consist of an array *p-i-n* reverse biased diodes made from a single silicon substrate (Kotz *et al.*, 1985). Each diode is a few microns thick and deep and is separated by approximately 100 μ m along the 300 μ m deep substrate. As with the *P-I-N* detector, the absorption of an X-ray photon will result in the production of electron–hole pairs in the diode. An electrical field can then be applied to sweep the diodes and generate an electrical signal that is dependent upon the position that the X-ray interacts with the silicon strip. The strip detectors have high backgrounds (Morton *et al.*, 2002) because they are not generally cooled to low temperatures. Compared to the wire detectors, the silicon strip detectors have better efficiency and higher counting rates (see Figure 3.10).

An image strip or strip of X-ray film can be cut from a larger plate and fixed to the surface of a curved camera. The image strip works on the same principle as the larger image plates, while the film is exposed and developed in the normal fashion. The readout device for the image strip is normally attached to the curved plate and moves across the plate to read and erase the data. This setup is found in the newer Guinier cameras that have been developed in recent years (Ståehl, 2000).

3.4.7 Two-dimensional X-ray detectors

The first X-ray detection instruments were the X-ray film cameras employed by von Laue (Friedrich *et al.*, 1912). These films were in fact two-dimensional area detectors and were



Figure 3.11 An image of a multi-wire promotional counter (MWPC). Image courtesy of Bruker AXS.

used frequently during the early years of structural exploration. X-ray film is still a viable detector and is employed for special experiments (Blanton, 2003); however, the expense, handling, and non-linearity of the film limits its use.

The multi-wire proportional counter or MWPC were originally developed for highenergy particle detection but were later adapted for X-ray detection (Figure 3.11). The detector is essentially a wire/gas proportional counter consisting of two arrays of wires that are normal to each other and a third array of wires parallel to the first. The resolution of the detector is limited to the space between the wires, which in turn is determined by the electronics. The carrier gases normally used are xenon and methane. These gases will degrade with time and must be replenished (Lewis, 1994; Bergese *et al.*, 2001). The MWPC has a limited dynamic range, which in turn limits its use with high-intensity diffraction experiments. A hybrid of the MWPC is the micro-gap detector or MGWC (Hall *et al.*, 1995; Khazins *et al.*, 2004), which is similar to the MWPC with the exception that the bottom layer of wires has now been replaced by a printed circuit board with inlaid copper strips. This allows the separation between the wire and the circuit board to be much smaller than the gap between the wire layers in the MWPC and thus improves the resolution and the dynamic range of the detector.

The two-dimensional CCD/phosphor detector (Philips *et al.*, 2002) was initially developed for single-crystal X-ray diffraction, but can be employed for powder diffraction experiments. Unfortunately, the resolution of the CCD/phosphor is limited to the thickness of the phosphor itself. A very thin phosphor (<100 μ m) is necessary for resolution for powder diffraction; however, the efficiency of the phosphor decreases as the thickness of the phosphor decreases. In addition, the CCD detectors suffer from a relatively high background



Figure 3.12 Curved image plate. Image courtesy of Rigaku USA.

noise. At this time, the use of CCD/phosphor detectors at the home laboratory is limited; however, future developments in CCD cooling and phosphor manufacturing could greatly facilitate their uses.

Image plates have been utilized with great success for X-ray powder diffraction. The image plate's major limitation, their efficiency and slow readout speed, are compensated by their ability to be formed into a variety of shapes and sizes. In fact, the image plate can be curved in an arc of fixed radius that can be wrapped around the specimen in such a fashion to collect 150° in 2θ or more data in one exposure (see Figure 3.12). Unfortunately, the curved image plates have fixed specimen to detector distances, which limits their use for a variety of experimental setups.

Collecting data in two dimensions has several advantages over the conventional zero and one-dimensional methodologies. The integrated data returns better intensities and the statistics are better for specimens that show texture or have larger grain sizes (He *et al.*, 2002). Two-dimensional detectors can collect data over a wide range of 2θ angles without moving the detector. With a 2D detector, the measured diffraction is not limited to the data in the plane of the diffractometer; rather a large portion of diffraction pattern or Debye ring can be measured simultaneously. Thus, not only the phase identification is possible but also percent crystallinity, particle size, texture, and stress can be measured.

The disadvantage of the 2D detectors is their lower spatial resolution and expense. The 2D detectors are more complicated to build and maintain than the zero and 1D detectors. They are generally limited to how closely you can pack the X-ray detection mechanisms in space and thus the limit of the resolution of the detector. In conclusion, the 2D detectors will return far more information than conventional zero and 1D detectors but with the price of much lower spatial resolution.

3.4.8 X-ray detector comparisons

Comparing detectors is akin to comparing two favorite foods, the choices are all good. With this said there are some detectors that work well in one situation and not in another. Table 3.1 lists a few detector comparisons based on the detector's efficiency, dynamic range, linearity, energy and spatial resolution, area, and speed of use. The table is based on a grading system from C to A. The type of materials you are examining and the manner in which you would like to examine it will ultimately decide the choice of the detector. For example, if data below $1.0^{\circ} 2\theta$ is often required or the investigator's samples contain elements that will fluoresce in a given radiation then a one-dimensional scintillation counter with a diffracted beam monochromator or a SiLi detector with fixed slits is warranted. On the other hand, if the user desires rapid data collection on multiple specimens, then a two-dimensional silicon strip or linear PSD detector would be better suited to their needs. It is useful to have more than one detector available. Detectors on modern diffractometers can be quickly exchanged, which affords the user a wider choice in data collection modes and methods.

3.5 Specimen mounting methods: general concepts and terminology

There is a difference between what we call a sample and a specimen. The sample is the material to be analyzed and is representative of the bulk while the specimen is that representative portion of the sample (or aliquot) that is prepared and then employed in the analysis (Hagopian-Babikian *et al.*, 1998). The specimen must be representative of the whole sample or else the data collected and evaluated is only of limited value. It is therefore critical that the investigator employs standard analytical sampling techniques to prepare a specimen that is representative of the bulk material. The specimen discussed in this section will be a small-grained crystalline powder obtained from a homogeneous sample.

A powder, by its definition, is a solid containing small particles that will flow when agitated. A particle may be a single crystallite, a clump of crystallites, a shard of glass or an amorphous solid. The powder itself may be dry or wetted, but must retain its solid state. Crystalline powders are of particular interest, due to the nature of their diffraction phenomenon (called Bragg scattering) and will be considered in greater detail.

The single crystal is well noted for its unique size and shape. The external structure of the crystal hints at the internal structure of the atoms that it contains. The crystal itself has directionality due to the orderly packing of the atoms that constitute its composition. As a consequence, the orientation of the crystal is critical when it is examined with diffraction techniques.

Bragg's law (see Chapter 2) defines the angle of the diffraction, with respect to the primary beam, when an X-ray diffracts from a single crystal. In three-dimensional space, the Bragg angle will trace the base of a cone, where the apex of the cone is anchored at the crystal. The diffracted X-ray will fall somewhere along the circle defined by the base of the cone, where the exact position is dependent on the orientation of the crystal. If one spins the crystal in all possible directions (without translating the crystal in space) then the diffracted X-rays that are produced fall on every position in the circle and a diffraction "ring" (Debye ring) is produced that can be recorded by standard techniques.

An alternative to tumbling the specimen is to replace the single crystal with many smaller crystallites that are orientated in random directions. The key to this technique is the total randomization of the crystallites orientation relative to each other to generate a randomly orientated specimen, a goal that may be somewhat difficult to achieve in real-world conditions. Some specimens do not achieve total randomization and demonstrate a certain degree of preferred orientation, where one (or more) direction of the crystallites is preferred when the powder is packed and prepared for investigation. This can be the case when the crystallites themselves have needle or plate-like morphology.

Finally, ultrasonic vibrations can randomize the orientation of the crystallites. The vibrations tend to "fluidize" the powder and induce a flow of the grains in a manner similar to convection of heat. The action of the vibrations coupled with the design of the specimen holder and the force of gravity will conduct more grains into the X-ray beam and thus act to randomize the specimen. This method, under development for NASA, when coupled with transmission geometry promises to deliver randomized specimens for hard to grind or difficult situations (Sarrazin *et al.*, 2004a,b).

The particle (crystallite) statistics describe how many crystallites in the specimen will diffract and whether the diffracted intensities are sufficient to meet the accuracy required by the investigator (De Wolff, 1958). The goal of the experimenter is to maximize the particle statistics (randomness of the specimen) by any means possible, including tumbling and or grinding the specimen to particles less than 10 μ m.

3.5.1 Specimen preparation

One method to increase particle (crystallite) statistics is to reduce the particle size of the specimen. As stated previously, the ideal particle size is about $10 \,\mu$ m. In practice, such small particle sizes are difficult to achieve by experimental methods. To achieve such sizes, the specimen needs to be ground and sieved.

Grinding specimens is a delicate procedure. The methods required will vary depending on the hardness, sensitivity, and amount of the material at hand. The materials hardness is representative of the internal forces that bind the crystal together. Molecular solids such as organic and organo-metallic compounds will have relatively weak interactions such as hydrogen bonds, dipoles or van der Waals interactions and will require gentle grinding to avoid destruction of the material and/or phase or polymorph conversion. Whenever possible grinding organic compounds should be avoided. Inorganic materials, extended solids and minerals will have much stronger covalent and ionic forces and will require much more energetic methods in their grinding processes. In normal practice, an agate mortar and pestle are employed to crush softer materials to desired particle sizes. A ceramic mortar and pestle should be avoided due to the possibility of contamination. A gentle push and turn procedure will generally crush most soft materials to a fine powder in a matter of minutes. In some cases, an inert solvent is introduced to soften the grinding process. Once ground, the material is allowed to dry before packing into a specimen holder or sieving. The experimenter should keep a careful watch over the process and in extreme cases, an X-ray diffraction pattern should be recorded before and after grinding in order to monitor the procedure.

To retrieve the ground powder, a gentle tapping motion of the mortar on a hard surface should loosen the material and let it flow naturally. A clean stainless-steel spatula can be employed to remove the final traces of the powder; however, care should be taken so that no contamination from the spatula is introduced to the specimen.

Grinding microgram quantities of soft material represents a unique challenge to the laboratory worker. One method that has proven to be useful is to place a small amount of the material in the center of a glass slide. A second glass slide is placed on top of the specimen and the two slides are compressed together. A gentle twisting motion of the slides will complete the grinding process. The slides are then separated and the specimen is gently scraped from both glass slides with a clean sharp razor blade. If necessary, a very small drop of inert solvent or mineral oil is introduced to cushion the grinding.

An agate mortar and pestle can also be employed to grind harder materials; however, the pressures required are much greater than for softer materials. In practice, one must be careful that the material will not be propelled out of the mortar when aggressive grinding methods are employed. For hard materials, a mechanical grinder can be a useful device. It should be remembered that mechanical grinding would introduce considerable stress to the crystallites, and it is possible that the specimen could be ground to a point that its powder diffraction pattern will lose all sharp features that can be mistaken for an amorphous solid.

3.5.2 Spray drying the specimen

A ground specimen can be further treated by a method known as spray drying. This method consists of suspending the particles in water and then spraying the suspension into a heated chamber. As the liquid flash dries in the chamber, the particles will tend to form sphericalshaped agglomerates (Smith and Barrett, 1979). The agglomerates are then collected and used as is. In a typical spray drying apparatus, an airbrush is positioned over a vertical chamber that is heated to 150°C. A solution of 20–40% (weight percent) of ground particles $(\sim 10-30 \,\mu\text{m sized})$ in water and $\sim 0.5\%$ polyvinyl alcohol is introduced and sprayed into the chamber at a low air pressure (10–15 PSI or 68–275 kPa) (Hiller, 1999). The agglomerates quickly dry in the chamber and fall downward, to be collected in a tray. The disadvantage to this technique is that a relatively large quantity of material is necessary since about 20% (or more) can be lost to overspray. Water is the best fluid for suspension of the specimen; however, this limits the method to materials that will not dissolve in water. Other solvents should be avoided due to unsafe conditions such as hazardous vapors, fires and explosions that may result at elevated temperatures. Finally, it should be noted that due care must be exercised when handling very small particles that are suspended in air. A small spark may ignite the material and cause an explosion.

3.5.3 Mounting the powder specimen in the X-ray diffractometer

The two modes of X-ray powder diffraction data collection have been previously described as the reflection and the transmission modes. Each mode will require its own unique methodologies for specimen mounting. The most common method for the reflection mode is known as the flat plate method, while the transmission mode methods are more diverse and a variety of methods are common. Whichever method is employed, the basic principles are the same; the specimen should be mounted in such a manner as to present the most powder specimen to the X-ray beam while minimizing the exposure area of the specimen mount.

The flat plate method is characterized by forming the powder specimen into a flat disk or rectangular shape of variable depths. This is most easily accomplished by the top-loading specimen plate, which is manufactured from a stainless steel, quartz glass or plastic with a depression or dish cut into the center. The powder is pressed into the depression, flattened and smoothed by application of a clean glass slide. The final move is to press the glass slide down until the slide contacts the surface of the plate and then to pull it slowly off to one side while pressing downward. The procedure is known as the "press and pull" method (see Figure 3.13) and is most commonly employed with powders that are not prone to preorientation. The press and pull method produces a mounted specimen with an extremely flat and smooth surface that is at the same height as the specimen plate. The top-loading method is a simple robust procedure for preparing specimens for data collection but renders the surface of the powder perturbed by the pressure of the glass slide. The back-loading method was introduced to address this problem.

The back-loading method was originally developed to provide mounted specimens whose surfaces were unperturbed or less perturbed than normal top-loaded specimens. The back-loaded specimen holder is simply a conventional specimen plate whose specimen cavity has been drilled out forming a large ring-like plate. To fill the holder, one fixes a glass slide either plain or frosted to the topside of the plate. The plate is flipped over and filled from the bottom. When filled, the bottom hole is plugged or capped and the plate is then flipped over again. The top glass slide is removed and the specimen plate is then positioned in the instrument and data collected. The advantage of the frosted glass slide is that it will "roughen" the surface of the specimen, which lessens the bias toward preferred orientation.

The top-loaded and bottom-loaded specimen method can be used in a variety of situations but does bias your specimen to preferred orientation. This is particularly true for specimens that contain crystallites that are needle or plate shaped. The act of pressing the specimen down into the plane of the specimen holder places the crystallites so that



Figure 3.13 Flat plate specimen holder and demonstration of the press and pull specimen loading method. The specimen is loaded into the well and pressed down with a glass slide. The slide is then carefully pulled to the side.



Figure 3.14 The side loaded specimen holder and demonstration on how to load the specimen. The holder is placed on its side with the open end of the well directed upwards. A glass slide is positioned over the lower end of the well and the specimen is introduced. The holder is then repositioned and the glass slide is carefully removed.

their short axis is aligned perpendicular to the plate. A simple method to overcome this disadvantage would be to pack the specimen down *in* the plane of the specimen holder. This can be accomplished by cutting a groove in a top-loading specimen plate that extends from the center depression outward to the edge of the specimen plate. A glass slide is placed over the groove and the specimen plate is then turned on its side (see Figure 3.14). The specimen is introduced in the cavity formed between the specimen holder and the glass plate and is packed into the holder by gently tapping the apparatus on the tabletop. The procedure is then repeated until enough specimen has been collected. The entire apparatus is then turned back and laid flat and the glass slide is carefully removed. The specimen plate is then moved to the diffractometer and data are collected in the normal fashion.

The simplest apparatus for flat plate specimen mounting that will limit the effects of preferred orientation is a round or rectangular quartz glass plate that has been frosted by gentle bead blasting. The specimen is simply sprinkled on the plate, preferably by positioning a sieve directly above the quartz plate and gently tapping the sieve to produce a fine powder. This produces a very thin layer of specimen on the surface of the quartz. The roughness of the surface discourages preferred orientation and promotes a more random alignment of the powder crystallites. The major disadvantage of this method is that the method produces diffracted intensities that are much lower than those produced by standard top mounting methods and will also include background scattering from the amorphous quartz glass will overwhelm the results and render interpretation difficult, it is therefore useful to replace the quartz with a material that would return no background scatter.

The zero-background specimen holder or ZBH was developed to be used with milligram quantities of specimen (see Figure 3.15). The holders are constructed of very large single crystals of silicon or quartz that are cut in such a manner as to expose a chosen crystalline face (Li and Albe, 1993). The face that is chosen corresponds to a Bragg direction that has low or unobserved intensity for that crystal. The background for the ZBH consists only of the diffuse or non-Bragg X-ray scattering from the crystal, which is an order of magnitude lower than the Bragg X-ray scattering.



Figure 3.15 The zero background holder (ZBH). A single crystal of silicon cut parallel to the (510) plane is placed in the well of a flat plate specimen holder so as the top of the crystal is level with the top of the holder. A thin layer of specimen is then placed on the center of the crystal.

3.5.4 Hermetic holders for specimens

Air-sensitive compounds can be measured by placing the specimen in normal specimen holder and covering it with a thin Mylar[®] foil that is attached to the plate with glue to form an airtight chamber. The disadvantage of this holder is the placement of the foil so near the plane of the specimen. In such a position, the foil scatters X-rays and adds to the background of the powder pattern. A special air-sensitive specimen holder can be made from stainless steel and a thin polymer foil that will minimize the background scatter. The specimen holder is constructed with a normal cavity and two metallic wings that are positioned on either side of the cavity to produce a structure with two closed arches. The specimen cavity is open on either side of the plate for the exposure of the specimen and the exit of the diffracted X-rays. Two holes on either side of the holder, lead to openings near the specimen cavity. These holes can be used to flush the specimen chamber with an inert gas. The specimen is moved to a dry box where the cavity is loaded. A layer of glue is placed on the lip of the arches and the top of the holder and a thin film of polymer foil is then attached to the glue in such a way as to form an airtight seal (see Figure 3.16). The specimen chamber is completely sealed and moved to the diffractometer. If necessary, then a stream of inert gas can be used to continuously flush the specimen chamber.

3.5.5 Capillaries and thin foils

Powders to be examined by the transmission mode on X-ray instruments must be positioned in the X-ray beam in such a manner as to expose the maximum amount of specimen. The specimen must be contained and supported by the holder and positioned in such a manner as to keep the holder out of the X-ray beam. The principle methods to accomplish this goal are to employ thin-walled glass and plastic capillaries, form a cylinder of specimen around a central supporting fiber, and enclose the specimen in an inert nylon loop and to attach the specimen on a thin supported foil.

A typical fiber mount can be manufactured from a wide variety of materials, but glass is the most common. A thin fiber can be pulled by gently heating a standard Kimax[®] melting tube in a flame burner. The tube is then cut into short sections and fixed to a metal pin. Hair



Figure 3.16 A Hermetic holder. The specimen is placed in the sample well and a thin film of Mylar[®] is glued to the arches to form an air tight seal. A purge gas is then introduced through the tubes to fill the resulting chamber with inert gas.



Figure 3.17 Cartoon of commercially produced thin-walled glass capillary. The tube is sealed at one end and sample is introduced at the funnel-shaped end.

spray is then applied to the tube and the tube assembly is then rolled gently in the powder. The metal end of the assembly is then mounted to the diffractometer and the specimen centered in the X-ray beam.

A modification of this method is accomplished with nylon loops. The loop is a simple fiber of nylon approximately 20 μ m in diameter and is folded in two and the ends secured to a metal pin. The loops can be made or purchased in a variety of sizes from 100 to 700 μ m in diameter so that the size of the loop can matched to the diameter of the X-ray beam. To mount the powder, the loop is first wetted with mineral oil and the excess oil removed (Bhuvanesh and Reibenspies, 2003). The loop is then inserted into the powder and manipulated to form the powder into a sphere that is approximately the same size as the loop. Depending on the powder it may be necessary to introduce more mineral oil to the specimen before a proper shape can be made, however, it is best to avoid an excess of oil. Once the sphere is made, the loop should surround the specimen and position it in the X-ray beam.

Thin-walled glass capillaries have been the preferred method for mounting powder specimens for transmission mode data collection. The capillaries are generally made from Lindemann glass, quartz or boron-rich glass and stretched to form thin-walled (10 μ m thick) long tubes of various dimensions (Figure 3.17). Commercially available capillaries are sealed at one end and have a larger funnel-shaped glass tube at the other end. The most common tube dimensions for powder diffraction work are 1.0–0.1 mm. To transfer the specimen to the capillary tube, it is critical that the sizes of the powder particles are much smaller than the diameter of the capillary tube employed. Specimen grinding and sieving will produce particle sizes in the desired dimensions. Since only milligrams of specimen are needed it is not necessary to prepare large quantities of specimen.

To load the capillary, a small amount of specimen is introduced into the funnel end and gently tapped into the narrow base. To pack the specimen, the capillary is transferred to long stem funnel with the closed end of the capillary directed downward. The funnel is held perpendicular to the hard surface of a lab bench with the stem end of the funnel touching the bench; the capillary is then dropped in such a way as to allow the tube to fall the length of the stem of the funnel. The capillary strikes the lab bench surface, which in turn packs the specimen in the tube and the process is then repeated several times beginning with the introduction of more specimen and proceeding with packing the specimen.

Another capillary packing method involves employing the same capillaries and specimen introduction. In this case, the specimen is introduced into the funnel end of the tube and the tube is then placed in the narrow end of a pipette with the wide end of the pipette directed downward. A triangular file is then pulled across the surface of the pipette, which in turn introduces a vibration, which shakes the powder causing it to fall toward the closed end of the capillary tube.

Capillaries can also be constructed from other materials besides glass such as plastic. Kapton® and heat shrink PET tubing have also been proven useful for powder diffraction (VonDreele, 2006). The advantage of plastic tubing is its relatively low cost, low X-ray absorption, and ease of use (Reibenspies and Bhuvanesh, 2006). Unfortunately, plastic capillaries cannot be heated above their melting points and therefore cannot be used for high-temperature work; however, the plastic capillaries can be used at extremely low temperatures.

A thin Mylar[®] foil or Mylar[®] tape can also be employed for transmission work. The foil is first cut and fixed to an appropriate mount and the specimen fixed to the foil with adhesives. A simple wire eyelet will work for attaching to the thin foil and hair spray is an excellent and inexpensive adhesive for both attaching the foil to the eyelet and to adhere the powder to the foil. Once constructed, the powder is then sprinkled on the foil to form a thin layer of specimen (Table 3.2).

3.6 Data collection: general concepts

The mode and manner of the data collection is the next step in the overall successful powder pattern. Acquiring data is as important to the eventual quality of the powder diffraction experiment as is the preparation of the specimen. Several instrument parameters including the wavelength, power and monochromatization of the radiation, scanning range and mode of data collection and the data collection time must all be considered and optimized for any given experiment. It is vital to know both the limitations of your instrument and quality of your specimen.

In general, the powder experiment is conducted to optimize the resolution and quality of the data set. By resolution, we are suggesting the ability of the investigator to distinguish between two adjacent diffraction peaks. The parameter often discussed is the full-width at half-maximum or FWHM. Literally this is the width of a given diffraction peak in degrees 2θ , at a position that is one-half of the maximum intensity on the low angle side of the peak

Light absorbers	Тор	Side	ZBH ^a	Foils	Capillary ^b	Loops/fibers
Geometry						
Bragg–Brentano Parallel/focusing	Poor	Poor	Best	Acceptable	Poor	Poor
Reflection Transmission	Poor	Poor	Acceptable	Acceptable	Poor	Poor
Line source Point source	_ _	_	_	Good Good	Best Good	Poor Best
Heavy absorbers	Тор	Side	ZBH ^a	Foils	Capillary	Loops/fibers
Geometry						
Bragg–Brentano Parallel/focusing	Good	Good	Best	Good	Poor	Poor
Reflection Transmission	Good	Good	Best	Good	Poor	Poor
Line source Point source	-	-	-	Good Good	Good Good	Poor Good
Specimen characteristics Minimal preferred orientation Specimen quantity	Bad grams	Poor grams	Good milligrams	Acceptable milligrams	Best ^c milligrams	Best ^c micrograms

Table 3.2 Comparison of specimen holders and optimal data collection conditions for the home laboratory: bad, poor, acceptable, good, best

^a Zero background holder.

^b Glass.

^c With mechanical tumbling.

to a position that is one-half of the maximum intensity on the high angle side of the peak. The resolution will be dependent on the optics of the instrument, the detector, and the specimen itself. A good FWHM for a home lab instrument is $0.1^{\circ} 2\theta$, while a synchrotron source can produce FWHM to 0.005° . The resolution will be one of the many characteristics that will be optimized for the instrumentation.

The wavelength and power of the radiation is one of the first choices that the investigator will make before data collection. For a home laboratory instrument, the choice is made and then set for many experiments, due to the difficulty in changing sealed and rotating anode sources. The most typical choice at the home laboratory is to employ a copper X-ray tube (1.54 Å), which will return good resolution without significant loss of scattered radiation by air. Chromium, cobalt and iron are also used for radiation sources especially when the accuracy of the lattice parameters is of importance.

A synchrotron source will produce a brilliant X-ray beam that can be tuned to wavelengths between 0.5 and 2.0 Å. The synchrotron beam produces X-ray patterns with very good resolution and is therefore useful to tune the X-ray wavelength to 0.7 Å and below for even routine powder data collection. This affords good resolution, compact patterns and low X-ray absorption of the specimen.

When considering the wavelength of radiation the specimen plays an important role. X-ray absorption and fluorescence are key concerns for the investigator. For example, when copper X-ray radiation is employed, specimens containing cobalt will absorb X-rays to a larger degree than specimens containing copper or zinc. Likewise, specimens that contain iron, cobalt, and/or nickel will fluoresce in copper X-ray radiation and add significantly to the background.

3.6.1 Apertures

One parameter that is easily optimized for Bragg–Brentano powder diffraction collection is the incident beam aperture or divergent slit (DS) and the diffracted beam aperture or RS (see Figure 3.18). The DS should be selected to match the diffraction geometry and specimen size. A general rule of thumb is that the DS should be selected so that the incident beam does not exceed the length of the specimen. Table 3.3 illustrates a hypothetical instrument where R = 255 mm and r = 57.3 mm. In this example, a 5.0° DS represents a completely open beam. As seen in the table, a smaller slit illuminates less of the specimen, which is



Figure 3.18 Schematic of a typical Bragg–Brentano X-ray diffractometer. DS = divergence slit, RS = receiving slit, SS = anti-scatter slit, R = radius of the diffraction, d = distance from the X-ray source to the DS, L = length radiated by the divergent X-rays and θ = Bragg angle.

DS width in mm	DS in deg	DS in radians	Beam length at $5.0^{\circ} \theta$ in mm	Beam length at $45^{\circ} \theta$ in mm
0.1	0.10	0.0017	5	0.62
0.2	0.20	0.0034	10	1.22
1.0	1.00	0.017	51	6.12
1.5	1.50	0.025	75	9.4
2.0	2.00	0.034	102	12.5
5.0	5.00	0.087	261	31

Table 3.3 Slit widths and X-ray beam lengths for Bragg–Brentano diffraction

DS deg ~ 57.3/r * DS when r ~ 57.3 then DS width in degrees = DS width in millimeters. Length ~ DS * π * $R/\sin(\theta)$ * 180. worthwhile at lower angles while the wide-open slit illuminates the entire specimen at high angle, however spills over at lower angles.

The intensity of the diffracted X-rays and their resolution are dependent on the DS selection. Higher intensities are gained by employing larger slits, but at the expense of peak resolution. On the other hand, very narrow slits will dramatically increase the resolution, but will reduce the intensity of the diffracted X-rays. At the end, a DS of 1.0 mm or $\sim 1^{\circ}$ is a good compromise for routine data collection. If the investigator wishes to explore low angle they may want to use the smallest DS available and collect data for longer times. Likewise in normal diffraction studies there is only a small gain in the diffracted X-ray intensities for 1.5 and 2.0° DS.

The RS is located after the specimen holder and before the detector. The RS is as important to the quality of the powder pattern as the DS. The RS is inversely related to the resolution of the data in that the smaller the slit the higher the data resolution. The RS has a much greater influence on the resolution than does the DS; in that decreasing the RS will affect the resolution in the order of 3 times the value compared to the same decrease in the DS. Unlike the DS, the RS is not affected by the angle of the measurement, but will affect the measured intensities. In practice, one wants to select an RS that will give good resolution and not compromise the diffracted intensities. An RS of 0.2 mm (0.2°) is good for routine specimens.

A third silt is often employed to reduce the background noise before it can be detected. The anti-scattering slit (SS) is placed between the detector and the RS slit. The SS should be wide enough to transmit the diffracted beam without interference but narrow enough to block the parasitic or background radiation. Normally an SS of 1 mm or 1° is used, but a smaller SS can be employed to reduce the background.

So far we have dealt with out-of-plane divergence with the DS, SS, and RS, but an in-plane or axial divergence is also a source for errors. The axial divergence is found in the plane parallel to the goniometer axis and adds to the asymmetry of the Bragg peaks. To reduce this error, a set of long planks that are parallel to the incident and diffracted beams are placed before the DS and after the RS. These planks known as Soller slits act in a manner similar to Venetian blinds and limit the divergence of the X-ray beam in the plane of the goniometer.

It should be apparent that optimum slit size is a function of the instrument angle. It would be thus beneficial to vary the slit size, especially the DS, while collecting the data. The attachment to accomplish this is called a variable slit and can be located at the DS and the RS positions. With variable slits, the irradiated area of the specimen can be kept constant while collecting the data. This improves the particle orientation averaging and results in higher quality data. Unfortunately the data, once collected, must be numerically processed to provide accurate intensities that reflect a constant incident beam divergence (see the Bragg-Brentano method). If accurate peak intensities are needed, the variable slit method is to be avoided.

3.6.2 Scan modes for the θ -2 θ scan

Once the proper slits have been chosen, the mode of data collection should be considered. The scan mode describes the way the specimen and the X-ray detector move during the data collection. Two possible modes are the step scan and the continuous scan. The step scan involves a series of step, stop, count, and then repeat. The detection occurs during the stage of the scan when the detector is not moving, thus the angle during the measurement is also constant. The resulting data consist of a series of steps or channels where each step has an associated intensity that was measured when the step was motionless.

The user can define the size of the step and the counting time taken to collect the data. The step size is constant throughout the experiment and will normally take on values of 0.005 to 0.06° in 2θ . The step size will define the resolution so normally sizes greater that 0.1° in 2 θ should be avoided. Of course, the smaller the step size the more steps per data collection and the slower the overall experiment. An acceptable working step size is 0.02° , which accommodates good resolution and time considerations. The counting time on the other hand can be fixed or is variable depending on the experiment and the data collection software. The longer the counting time, the higher the signal and the better the signal-tonoise ratio. On the other hand, long counting times will increase the data collection time from minutes to days. The constant count time is normally selected because it will produce intensities that do not need to be normalized by additional data processing. Variable count rates on the other hand are useful for gathering information on weakly diffracting peaks. The continuous data collection mode involves a constantly moving detector and specimen stage. The detector begins counting and the movement of the detector and specimen stage is held at a constant speed until a preset value of $\Delta 2\theta$ interval is reached. At this point, the number of counts is saved along with the median value of the scanned range. The detector counter is reset to zero the detector and specimen stage is moved to the next position and the process repeats. The most important parameters for the continuous scan method are the sampling interval ($\Delta 2\theta$) and the angular velocity.

The powder patterns produced by both methods are identical except that for the continuous scan, the 2θ positions is the median of the $\Delta 2\theta$ interval, while the intensity for any given step in the step scan is associated with the angle of that step. The step scan method is preferred for Rietveld analysis, while the continuous mode is employed for linear detectors.

3.6.3 Scan range

The final decision to be made before the data collection can begin is to decide the scan range of the experiment. Normally, data are collected between 5 and 80° 2θ . At lower angles, the high intensity of the direct beam can damage the detector while above 70° contains little or no useful information for molecular solids. In practice, the lower limit is selected to be a few degrees before the first peak. If the first peak position is unknown, a rapid data collection between 2 and 10° is usually employed to locate the peak. The upper limit is based on many factors but the most common are the limits of the instrument, the purpose of the powder diffraction experiment and finally on the specimen itself. For very precise work with small solid state materials it is usual to collect data to 100 or 120° 2θ , while for organic compounds that do not scatter X-rays one may stop at 50° 2θ .

3.7 Pitfalls and errors

The most common pitfall for the powder investigator is mainly involved in specimen handling and placement. The most common pitfalls are the displacement, transmission, and random specimen error. The displacement error is associated a misaligned diffractometer $(2\theta \text{ zero})$ and/or with placing the specimen at the wrong position in the diffractometer, while the transmission error is associated with measurement of low absorption materials. The random specimen error is the failure to produce a truly randomly orientated specimen.

By carefully aligning the instrumentation and then checking the alignment on a regular basis, one can avoid the 2θ zero displacement error. Alignment of the instrumentation, with a standard such as the alumina plate SRM 1976 (NIST, 2007), normally takes only a few minutes and can be preformed between data collections. A record of the alignment should be kept and consulted when errors occur in the normal collection of data. Modern diffractometers are well designed to avoid displacement error, however even the best diffractometer cannot compensate for poorly packed and/or un-level specimens. When preparing the specimen due care should be taken to avoid displacement error.

Transmission errors are even more difficult to compensate for. This error occurs when the X-ray beam penetrates the specimen to a depth of a few tens of microns. The specimen will diffract X-rays from the surface and from a few tens of microns below the surface. The result is similar to a displacement error where the actual average plane of diffraction is well below the calibrated position at the surface of the specimen. To avoid this error, the investigator must use only a very thin film of material. A zero background holder can be employed and with the powder depth of only a micron or less. Normal top load, side load or bottom loading specimen holders should be avoided with organic and low X-ray absorbing specimens, if one wishes to determine accurate peak positions, however, intensity information should be obtained by the top-, side-, or bottom-loaded specimens.

A major pitfall associated with powder diffraction is failure to achieve a truly random sample. As discussed this is often due to poor grinding techniques or failure to rotate the specimen in the X-ray beam. Of course, over grinding a specimen may lead to more errors especially with soft organic specimens. The instrumentation itself may not afford one the option to tumble or rotate the specimen, which would limit the options for obtaining a good powder pattern.

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Chapter 4 Profile Analysis

Arnt Kern

4.1 Introduction

Powder diffraction provides information about the atomic structure (dimension and symmetry of unit cell, atom positions and displacements) of crystalline materials via the positions and intensities of the diffraction reflections. Analysis of the width and shape of diffraction-line profiles, furthermore, allows extraction of microstructural information, for example in terms of crystallite size and lattice defects.

An accurate description of the line profile shapes in a powder pattern is critical to the success of any application, but is hampered by reflection overlap, intrinsic to the method. In powder diffraction, a three-dimensional diffraction pattern is collapsed onto one-dimension by spherical averaging, inevitably leading to both systematic and accidental reflection overlap. The degree of overlap, which depends on both structural complexity (unit cell dimensions and symmetry) and line broadening effects (instrument and specimen contributions), increases with Bragg angle. As a consequence, profile parameters may be uniquely determined only for relatively few reflections.

The primary method used today for profile analysis is profile fitting, where a suited model function, specifically referred to as profile shape function, is used to describe observed line profile shapes. Using an appropriately parameterized profile shape function, severe reflection overlaps as well as very complex line profile shapes and their dependence on *hkl* and Bragg angle can be successfully characterized.

The present chapter provides a general overview about the origin and modeling of line profile shapes, with the focus on a convolution-based approach to X-ray and neutron powder data. The principles discussed are equally valid for all currently employed profile fit methods including (i) single line fitting, (ii) whole powder pattern fitting, (iii) whole powder pattern decomposition according to Pawley (1981) and Le Bail *et al.* (1988), (iv) Rietveld refinement (Rietveld, 1967, 1969) and (v) *ab initio* structure determination from step intensity data (Coelho, 2000).

4.2 Origin of line profile shapes

Line profile shapes are the result of the convolution of a series of instrument contributions, including the wavelength distribution (source emission profile) and geometrical effects, and specimen contributions to the diffraction process (Jones, 1938).

Full exploitation of the diffraction information requires an accurate description of all instrument and specimen contributions to the observed line profile shapes. This is particularly true for microstructure analysis, requiring accurate knowledge of the instrument contribution. In this respect, synchrotron and neutron diffractometers have been less well studied than laboratory diffractometers.

For synchrotron and neutron diffractometers, instrument functions are usually determined by convolution-based methods, Monte-Carlo-based ray tracing methods or by measurements of reference materials, exhibiting only low levels of line broadening. In contrast to laboratory diffractometers, a separate treatment of the source emission profile and instrument effects is normally not of interest for instruments utilizing a white light source (synchrotron, neutron reactor sources), as the wavelength distribution in the beam is determined by the instrument characteristics (predominantly monochromator assembly), rather than the source. An exception is energy dispersive diffraction, where the source emission profile strongly influences the line profile shape, and can be characterized from first principles (David and Jorgensen, 1993).

The situation is different for X-ray laboratory diffractometers, where narrow-band monochromators (typically tuned to $K\alpha_1$) are not in widespread use, mainly due to the low primary intensity obtained from sealed tubes or rotating anodes. The wavelength distributions obtained from usually only partly filtered characteristic emission lines do not have simple descriptions and need particular consideration.

In this chapter, the physical origin of the line profile shapes for both divergent and parallel beam diffractometer configurations will be discussed.

4.2.1 Source emission profiles in laboratory diffractometers

In the absence of instrumental effects, the spectral shape represents the highest possible resolution of a laboratory diffractometer. Above 90° 2 θ the source emission profile is the dominant contribution to the line profile. The full-width-at-half-maximum (FWHM) of actual diffraction lines from commercial diffractometers depend on the choice of slits, and are typically in the range 0.04° to 0.10° 2 θ at angles $2\theta \le 40^\circ$. This is considerably larger than the source emission profile width, which is $\le 0.01^\circ$ 2 θ for sealed tubes and rotating anodes. In this angular region, the geometrical aberrations of the instrument tend to swamp the contribution of the source emission profile. With increasing 2 θ angles, the source emission profile starts to dominate over the instrument contributions and at angles of $2\theta > 100^\circ$ the profile shape conforms closely to the source emission profile, as the total breadth of the instrument contributions gets relatively small.

The exact knowledge of the shape of the source emission profile is of central importance to the development of an accurate powder profile description of X-ray laboratory data. With the high-quality data obtainable from modern commercial diffractometers in terms of intensity, FWHM, and peak-to-background ratio, the characteristics of source emission profiles become remarkably evident.

4.2.1.1 Natural source emission profile shapes

The form of an example source emission profile is shown in Figure 4.1 for $CuK\alpha_{1,2}$. For Cu as well as all other transition element anodes used in X-ray diffraction, both the



Figure 4.1 Phenomenological representation of the CuK α emission profile based on four Lorentzians. From Cheary *et al.* (2004) *Journal of Research, National Institute of Standards and Technology*. Figures reproduced owing to the courtesy of the National Institute of Standards and Technology, Technology Administration, U.S. Department of Commerce. Not copyrightable in the United States.

 $K\alpha_1$ and the $K\alpha_2$ lines are asymmetric with extended high angle tails. In addition, the asymmetries and FWHM of the $K\alpha_1$ and $K\alpha_2$ peaks are different. The natural asymmetry of the source emission lines arises from the multiplet structure of the transitions, the $K\alpha_1$ and $K\alpha_2$ peaks are each doublets (Deutsch *et al.*, 1995). A phenomenological representation accurately describing the asymmetric Cu emission profile was first used by Berger (1986), where the $K\alpha_1$ and $K\alpha_2$ lines are each represented as the sum of two Lorentzian profiles as shown in Figure 4.1. A systematic study by Höltzer (Höltzer *et al.*, 1997) has shown that the phenomenological representation is well suited to accurately represent the $K\alpha_1$ and $K\alpha_2$ emission profiles for Cr, Mn, Fe, Co, Ni and Cu down to an R factor of 1%, although in some cases, up to seven Lorentzians had to be used.

Another feature of $K\alpha$ emission lines is the satellite multiplet structure in the highenergy tail as shown in Figures 4.2 and 4.3 for Cu. For Cu, these collectively have an intensity of $\approx 0.6\%$ of the $K\alpha_1$ emission line, rising uniformly with decreasing atomic number up to 1.4% for Cr (Parrat, 1936). In X-ray diffraction studies it is sufficient to represent the $K\alpha$ satellite group as a single broad Lorentzian; thus, the total Cu $K\alpha$ spectrum can be accurately represented by the sum of five Lorentzians (Figure 4.3).

From Figures 4.1 to 4.3 it will be clear that the shape of the source emission profiles in laboratory diffractometers is much more complex than the simple $K\alpha$ doublet/ $K\beta$ singlet model used in traditional profile fitting software. As soon as the source emission profile starts to dominate the line profile shapes, such inappropriate modeling contributes significantly to the total misfit in profile fitting. This is typically the case for measurements of highly crystalline specimens on a modern laboratory powder diffractometer configured for high resolution.



Figure 4.2 CuK α emission profile showing the satellite group of lines and the extent of the tails from the $K\alpha_1$ and $K\alpha_2$ emission lines, covering a range of approximately 90 times the FWHM of $K\alpha_1$. This profile was recorded using the 400 line from a silicon single-crystal wafer. From Cheary *et al.* (2004) *Journal of Research, National Institute of Standards and Technology.* Figures reproduced owing to the courtesy of the National Institute of Standards and Technology, Technology Administration, U.S. Department of Commerce. Not copyrightable in the United States.



Figure 4.3 Single line fit to the 331 line of CeO₂ (Balzar, 2004) at about 76.7° 2θ . Divergent beam data have been taken with a D8 ADVANCE (Bruker AXS). The $K\alpha$ satellites contribute significant intensity to the total profile, taken into account by using a phenomenological representation of the Cu $K\alpha$ emission profile based on five Lorentzians. Figure copyright Bruker AXS.

4.2.1.2 Monochromatization

As the natural shape of a source emission profile is Lorentzian, the tails can extend a considerable distance from the central peak as shown in Figure 4.2. Laboratory diffractometers normally operate with some form of monochromatization such as metal ($K\beta$) filters or



Figure 4.4 CuK α emission profile obtained using the 400 line from a silicon single-crystal wafer. Each pattern was recorded sequentially using the same sample, first with no filter or monochromator in the beamline, later with a NiK β filter, and finally with standard curved graphite diffracted beam monochromator. From Cheary *et al.* (2004) *Journal of Research, National Institute of Standards and Technology*. Figures reproduced owing to the courtesy of the National Institute of Standards and Technology, Administration, U.S. Department of Commerce. Not copyrightable in the United States.

crystal monochromators; as a result the tails are attenuated to varying degrees (Figures 4.4 and 4.5a,b).

4.2.1.2.1 *Kβ* filters

For metal-filtered characteristic radiation there is only a small variation in the attenuation across the source emission profile as seen in Figure 4.4. This variation is owed to the increase in the linear absorption coefficient with increasing wavelength, but does not significantly affect the profile shape. However, absorption edges can lead to a significant step in the low-angle tail intensity (Figure 4.4). For measurement data taken from highly crystalline specimens, such absorption edges may form a major portion of the least-squares residual due to profile mismatch.

4.2.1.2.2 Divergent beam diffractometers - focusing on monochromators

The inclusion of a focusing wide-band monochromator (pyrolytic graphite, usually mounted in the diffracted beam) greatly reduces the range of wavelengths resulting in profile tails that diminish more rapidly than the natural emission profile (Figure 4.4). Such a monochromator can also affect the relative intensity $I_{K\alpha2}/I_{K\alpha1}$ by up to $\pm 10\%$ depending on the alignment and setting of the crystal: There is a common tendency to actually misalign diffracted beam monochromators in a way to obtain maximum intensity for $K\alpha_1$. This, however, results in a suppression of $K\alpha_2$ and therefore in a deviating $I_{K\alpha2}/I_{K\alpha1}$ ratio. For the monochromated spectrum shown in Figure 4.4, the relative intensity of the Cu $K\alpha_1/K\alpha_2$ is approximately 0.46 rather than the expected ~0.514 as in the unfiltered spectrum.



Figure 4.5 Wavelength spectrum emerging from an asymmetrically cut Ge111 ground and bent incident beam monochromator presented linearly (a) and logarithmically (b). The $K\alpha$ satellites are completely removed, but the $K\alpha_2$ is still present at $\approx 0.02\%$ of $K\alpha_1$ even in a well aligned system. From Cheary *et al.* (2004), *Journal of Research, National Institute of Standards and Technology*. Figures reproduced owing to the courtesy of the National Institute of Standards and Technology, Technology Administration, U.S. Department of Commerce. Not copyrightable in the United States.

Johannson-type focusing monochromators (quartz, silicon, but mainly germanium usually mounted along the incident beam) are able to achieve near perfect focusing and to select a very narrow band of wavelengths, when correctly aligned. Figure 4.5a,b shows the CuK α source emission profile from an asymmetrically cut, ground, and bent Ge crystal used as an incident beam monochromator. The wavelength bandpass of this monochromator type is narrow enough to remove 99.98% of the $K\alpha_2$ component and 100% of the $K\alpha$ satellite group, and to almost completely eradicate the Lorentzian tails of the source



Figure 4.6 Reflection of $K\alpha_1$ and $K\alpha_2$ wavelengths from a parabolic multilayer mirror diffracting off a powder specimen. From Cheary *et al.* (2004) *Journal of Research, National Institute of Standards and Technology*. Figures reproduced courtesy of the National Institute of Standards and Technology, Technology Administration, U.S. Department of Commerce. Not copyrightable in the United States.

emission profile. This form of spectrum can be modeled as a closely spaced doublet of two Lorentzians, or even better two Voigts (convolution of a Lorentzian and a Gaussian function) to better accommodate the tails cut-off at the limiting wavelengths for the monochromator crystal.

4.2.1.2.3 Parallel beam diffractometer optics

Parabolic multilayer mirrors in the incident beam of a diffractometer can also distort the wavelength spectrum (Toraya and Hibino, 2000). As different wavelengths reflect off the mirror in slightly different directions as shown in Figure 4.6 for the $K\alpha_1$ and $K\alpha_2$ components, an inhomogeneous spread in wavelength across the specimen in the equatorial plane will be obtained. Depending on the orientation of the mirror, the separation of the $K\alpha_1$ and $K\alpha_2$ peak maxima, $\Delta 2\theta_{K\alpha_2 1} = 2\theta(K\alpha_2) - 2\theta(K\alpha_1)$, in a line profile is then either larger or smaller than the same profile acquired from a diffractometer without the mirror. For a mirror setup in the orientation shown in Figure 4.6, the separation $\Delta 2\theta_{K\alpha 21}$ is smaller than the value expected from the known $K\alpha_1$ and $K\alpha_2$ wavelengths by an amount corresponding to the difference $\Delta \psi$ in the directions of the two incident beams on to the specimen. As a result, significant aberrations may occur at high 2θ angles as shown in Figure 4.7. The magnitude of $\Delta \psi$ will be dependent on the bandwidth of the mirror, and increases with decreasing bandwidth. Therefore, mirrors with small bandwidths (usually intended for thin film analysis), will normally show stronger aberrations. Generally, parabolic multilayer mirrors should be checked individually for $\Delta \psi$; if significant (e.g., as seen in Figure 4.7), it will be necessary to adapt the source emission profile accordingly.

The inclusion of a channel cut monochromator, typically in the incident beam of a parallel beam diffractometer, gives highly monochromatic patterns with high resolution and low background, but the intensity is invariably less than in divergent beam configurations with focusing monochromators. The aberration profile introduced by a channel cut monochromator is determined by the Darwin profile of the crystal and any divergence of the beam. It is generally very narrow and can be determined by measuring the rocking curve of the crystal. In practice, however, the aberration profile will be additionally broadened by the mosaic structure of the crystal, any stresses in the crystal and any waviness or curvature of the crystal surface. As a consequence, the aberration profile can be dependent on the size of the beam incident on the crystal.



Figure 4.7 Single line fit to the (041)/(322) line of LaB₆ (NIST SRM 660a) at about 99.6° 2 θ . Parallel beam data have been taken with a D8 ADVANCE (Bruker AXS) equipped with a single Göbel mirror in the primary beam and Parrish–Hart analyser slits in the diffracted beam. The $K\alpha_2$ peak maximum (arrow) is significantly shifted towards the $K\alpha_1$ reflection resulting in a significant misfit, if the source emission profile is not modified accordingly as shown here. Figure copyright Bruker AXS.

4.2.1.2.4 Determination of source emission profiles

For diffractometers exclusively equipped with metal K β filters, published source emission profile models with wavelength distributions based on tabulated unfiltered spectra [e.g., by Höltzer (Höltzer *et al.*, 1997)] can be used as is for accurate profile fitting. The same is no longer the case in the presence of monochromators (even low-resolution graphite monochromators) and mirrors, due to their previously discussed influence on the natural source emission profile.

Although first principle calculations of the wavelength transmission function through ideal monochromators and mirrors are possible [see e.g. Masson (Masson *et al.*, 2003)], it is currently more practical to determine experimentally a "learned" spectrum for the various monochromators and mirrors used in the majority of monochromated laboratory powder diffractometers. This can be done by modifying the phenomenological "sum of Lorentzians" representation in energy space or λ space to fit the spectrum entering the detector. In broad terms, monochromators reduce the width of the wavelength distribution and tend to truncate the tails of the spectra. A number of approaches can be used to accommodate these changes

- Represent the components of the wavelength distribution as Voigt or pseudo-Voigt functions rather than Lorentzians, to limit the extension of the profile tails, and modify the relative intensities of the component.
- Represent the effect of the monochromator as a wavelength filter with a transmission function $T(\lambda)$ represented by a simple function, such as a split pseudo-Voigt or split Pearson VII function with up to four refineable parameters, which operates on the tabulated Lorentzian emission profile data. The split functions are used to incorporate asymmetry in the $T(\lambda)$.

• For mirror setups, additionally introduce wavelength-dependent zero errors to accommodate wavelength spreads.

The parameters of each representation can be obtained by analyzing and fitting the high angle profiles from either a reference line profile standard, such as LaB₆ SRM 660a, or a single-crystal disc, such as a 111 wafer of silicon. The advantage of using measured source emission profiles is the inclusion of any aberrations introduced by misalignment into the model; any realignments, however, require re-determination.

4.2.2 Instrument contributions

In a discussion of instrument contributions it is necessary to distinguish between (i) geometrical instrument aberrations and (ii) individual measurement errors mainly due to instrument misalignment and specimen positioning errors (e.g. displacement and tilt). In contrast to the latter, which can be eliminated by appropriate instrument alignment and specimen mounting, geometrical instrument aberrations are inevitable, which are inherent to the given instrument geometry and its configuration (instrument dimensions, choice of optical components) and are discussed below. For a given instrumental setup, their magnitude depends mainly on the chosen slit apertures.

4.2.2.1 Most common diffractometer configurations

4.2.2.1.1 Divergent beam diffractometers

The most widely used divergent beam laboratory diffractometers are equipped with either a Ni filter or a bent graphite monochromator in the diffracted beam, or a Johannson-type germanium monochromator in the incident beam (Figure 4.8). All these configurations have an array of geometrical aberrations in common. The major differences are the respective wavelength distributions given by the monochromatization technique (Section 4.2.1.2) and the detector type used.

For a diffractometer equipped with a point detector, the major principal geometrical instrument aberrations contributing to a line profile, alongside the wavelength distribution are:

- the finite width of the X-ray source
- receiving optics (finite width of the receiving slit)
- horizontal divergence (flat specimen error)
- axial divergence
- defocusing.

For position-sensitive detector (PSD) systems, the receiving slit aberration is irrelevant and the flat specimen aberration is replaced by an aberration function that embraces three effects that are folded together

- defocusing due to asymmetric diffraction
- discharge resolution of the detector
- parallax error.



Figure 4.8 Two common configurations of divergent beam diffractometers showing the principal optical components, with a diffracted beam monochromator (top) and, with an incident beam monochromator (bottom). Figure copyright Bruker AXS.

4.2.2.1.2 Parallel beam diffractometers

For parallel beam diffractometers, typically equipped with an analyser slit or crystal (Figure 4.9), there are two geometrical instrument aberrations

- receiving optics (angular acceptance function of the analyser slit or crystal)
- axial divergence

PSDs used in parallel beam diffractometers are mainly either linear, step scanned detectors as described above, or large curved stationary detectors with acceptance angles of up to $150^{\circ} 2\theta$. In case of a PSD there are additional aberrations dependent on its type; these are

- discharge resolution for both detector types
- parallax error for linear detectors

In laboratory diffractometers, the parallel beam is produced by a parabolic graded multilayer mirror [the so-called "Göbel mirror" (Schuster and Göbel, 1995)] with the line X-ray source positioned at the focus of the mirror. Although the beam may be parallel in the equatorial plane, it will not be parallel in the axial plane and axial divergence is present in



Figure 4.9 Two configurations of parallel beam diffractometer, using analyser slits in the diffracted beam (top) and, using a flat analyser crystal (bottom). Figure copyright Bruker AXS.



Figure 4.10 Simplified aberration model for a long fine focus tube with a source of projected width W_x . Figure copyright Bruker AXS.

both the incident and diffracted beams. Low angle profiles will therefore be asymmetric although not to the same extent as for divergent beam instruments.

4.2.2.2 Geometrical instrument aberrations

4.2.2.2.1 Finite X-ray source width

The finite X-ray source width aberration is present when sealed tubes or rotating anodes are employed. It introduces a symmetric broadening, which is 2θ independent. For long fine focus tubes (target width ≈ 0.4 mm) the source width aberration profile can be expressed as an impulse function of width $\Delta 2\theta_x$ as shown in Figure 4.10. Although this function may not be strictly valid, the exact shape is not critical due to its small broadening contribution.



Figure 4.11 Intensity scan with 50 μ m wide slit of an image formed through a 10 μ m pinhole in platinum of the 0.4 mm wide long fine focus in a Cu anode X-ray tube set at 40 kV, 40 mA. From Cheary *et al.* (2004), *Journal of Research, National Institute of Standards and Technology*. Figures reproduced owing to the courtesy of the National Institute of Standards and Technology, Technology Administration, U.S. Department of Commerce. Not copyrightable in the United States.



Figure 4.12 Aberration model with "tube tails" containing additional parameters $f = I_{tail}/I_{max}$ and angular widths Z_1 and Z_2 from the central maximum. Figure copyright Bruker AXS.

At a take-off angle of 6° the projected width $W_x \approx 0.04$ mm and the aberration profile width $\Delta 2\theta_x \approx 0.01^\circ$.

In broad focus tubes (target width $\approx 2 \text{ mm}$) the projected width $W_x \approx 0.2 \text{ mm}$ at 6° take-off so that the aberration profile width $\Delta 2\theta_x \approx 0.056^\circ$. At this level, the source width contribution dominates and the aberration profile is better approximated by a Gaussian shape rather than an impulse function.

For accurate line profile analysis it may be necessary to modify the simple impulse model to accommodate for the so-called "tube tails" effect (Bergmann *et al.*, 2000), and an example is shown in Figure 4.11. Where "tube tails" are present, the source width aberration function can be better approximated by the sum of a sharp and a broad impulse function as shown in Figure 4.12. The parameters introduced to describe tube tails are the extents of the
high and low angle tails, Z_1 and Z_2 , and the intensity of the tail f is relative to the intensity at the tube focus. In most instances, the intensity of the tails is $\leq 0.1\%$ of the peak intensity and may be only significant when analysing intense lines. The tails themselves are not necessarily symmetric with respect to the tube focus and can extend over a 2θ range up to $1^\circ 2\theta$ on both sides.

4.2.2.2.2 Receiving optics

In divergent beam diffractometers with point detector, a receiving slit is placed at the focus of the diffracted beam, which should have an infinitely small width to achieve perfect focusing. For PSD systems, the receiving slit aberration is irrelevant. In parallel beam diffractometers, the receiving system is usually based on either analyser slits or analyser crystals as illustrated in Figure 4.9 earlier. The aberration functions of all these receiving systems posses different shapes; their contribution are symmetric and angle independent.

Receiving slits: Receiving slit widths typically range from 0.05 mm up to 0.6 mm. The count rate incident on the detector increases with increasing slit width but at the expense of resolution [see e.g., Jenkins and Snyder (1996)]. With slit sizes larger than 0.15 mm, the receiving slit aberration is often the dominant aberration over the angular range $2\theta = 15-60^{\circ}$. The aberration function for a perfectly aligned receiving slit is an impulse function that is angle independent (Figure 4.13).

Analyser slits: Analyser slits act as an angular filter in the diffracted beam. Their aberration profile is a triangle function (Figure 4.14), in which the base width W_r is given by the angular aperture Δ of the slits. An often encountered problem with analyser slits is the appearance of



Figure 4.13 Receiving slit aberration function. Figure copyright Bruker AXS.



Figure 4.14 Triangle-shaped aberration function for a set of analyser slits with an angular aperture Δ where $\Delta/2$ = spacing between the foils/length of the foils. Figure copyright Bruker AXS.



Figure 4.15 Reflection satellite peaks from analyser slit recorded using the 310 line from NIST standard material LaB₆ SRM 660a using the diffractometer on Station 2.3 at Daresbury synchrotron. From Cheary et al. (2004), *Journal of Research, National Institute of Standards and Technology*. Figures reproduced owing to the courtesy of the National Institute of Standards and Technology, Technology Administration, U.S. Department of Commerce. Not copyrightable in the United States.

weak satellite peaks on both the high angle and low angle profile tails due to specular X-ray reflection from the analyser foils (Figure 4.15). This effect can be incorporated into the aberration profile by adding two Voigt functions of unequal intensity, one on each side of the triangular aberration function, to represent the satellite reflections. The Voigt function parameters can be determined by fitting profiles from a reference material. Alternatively, the aberration profile can be determined by a 2θ scan across the incident beam. With the axial divergence of the incident beam kept small, and negligible equatorial divergence, the incident beam scan will have the same shape as the aberration profile (Cheary *et al.*, 2004).

Analyser crystals: An analyser crystal in the diffracted beam can be used for high-resolution diffraction patterns with low background, but with an intensity invariably less than the analyser slit configuration. The aberration profile introduced by the analyser crystal is generally very narrow and can be determined by measuring the rocking curve of the crystal. Similar to channel cut crystals (Section 4.2.1.2.3), for a perfect analyser crystal the aberration profile will be determined by the Darwin profile of the analyser crystal and any divergence of the beam. In practice, however, the aberration profile is broadened by the mosaic structure of the crystal, stresses in the crystal and deviations in the evenness or curvature of the crystal surface. As a consequence, the aberration profile can be dependent on the size of the beam incident on the crystal. A first approximation of the shape of the aberration profile of an *in situ* analyser can be obtained from a 2θ scan of the analyser/detector using a very fine incident beam as shown in Figure 4.16 (Cheary *et al.*, 2004).



Figure 4.16 2θ scan across a 0.1 mm × 0.1 mm incident beam using a Ge111 analyser crystal on beamline BM16 at the ESRF, Grenoble. From Cheary *et al.* (2004), *Journal of Research, National Institute of Standards and Technology*. Figures reproduced owing to the courtesy of the National Institute of Standards and Technology, Technology Administration, U.S. Department of Commerce. Not copyrightable in the United States.



Figure 4.17 Flat specimen aberration function. Figure copyright Bruker AXS.

4.2.2.2.3 Horizontal divergence

In divergent beam diffractometers, the horizontal divergence of the beam causes the so-called flat specimen error, because the surface of the sample is tangential to the goniometer focusing circle rather than on the focusing circle leading to defocusing. It introduces an asymmetric broadening and line shift towards low 2θ angles. The magnitude of the error depends on the horizontal divergence of the beam, and increases with increasing angle. A representation of the aberration function is shown in Figure 4.17. Horizontal divergence is normally controlled by fixed or variable divergence slits. In the presence of a monochromator, however, the maximum divergence may be determined by the monochromator setup rather than the slits.

Fixed divergence slits maintain constant beam divergence with the important advantage that the diffraction volume is kept constant with the angle and are first choice for applications requiring accurate intensities (particularly structure analysis). The slit aperture should be kept small to minimize the flat specimen error and to keep the footprint of the beam within the sample dimensions at all times.

Variable divergence slits vary the horizontal divergence as a function of 2θ to illuminate a fixed sample length. The aberration profile is generally small at low 2θ and increases with increasing 2θ . Importantly, the diffraction volume and therefore the collected intensities vary with 2θ , leading to problems with applications requiring accurate intensities. Data collection over a large 2θ range is not always possible, as the required beam divergence at large 2θ may be larger than can be accommodated by the diffractometer. For example, to maintain a fixed beam length of 20 mm over the range $2\theta = 0-90^{\circ}$, the required angle of divergence increases from 0° up to $\sim 4^{\circ}$, which is close to the maximum value at which most diffractometers can operate, particularly when a pyrolytic graphite monochromator is installed in the diffracted beam (Bowden and Ryan, 1991).

In PSD systems, the flat specimen aberration is replaced by a more complex aberration function (Section 4.2.2.2.6).

4.2.2.2.4 Axial divergence

The axial divergence aberration is due to divergence of the X-ray beam along the diffractometer axis in the plane of the specimen and is one of the most dominant instrument contributions, specifically at low and high angles 2θ .

Generally diffractometers record X-ray counts over a range of measured angles 2ϕ rather than the true diffraction angle 2θ , as illustrated in Figure 4.18. For a particular ray path, the measured diffraction angle 2ϕ for a true diffraction angle 2θ depends on the axial divergence β and γ in the incident and diffracted rays. The maximum axial divergence in the incident and diffracted beams is determined by the source length L_x , sample length L_s and receiving slit length L_r . Even if axial divergence in the incident beam is small as is typically the case for synchrotron instruments, the diffracted beam will display axial divergence.

Axial divergence introduces asymmetric broadening and line shifts, the aberration function is shown in Figure 4.19. The effect is evident at all 2θ values but passes through a minimum in the region $2\theta \approx 110^{\circ}$ (Cheary and Coelho, 1998a,b). At smaller angles, the asymmetric broadening and shift goes towards smaller angles 2θ , and becomes the



Figure 4.18 An illustration of axial divergence in which the incident ray and diffracted ray are at angles of β and γ relative to the equatorial plane; L_x : source length, L_s : sample length, and L_r : receiving slit length. Although the diffraction angle at the sample is 2θ , the diffracted beam is recorded at an angle 2ϕ . Adapted from Cheary *et al.* (2004), *Journal of Research, National Institute of Standards and Technology*. Figures reproduced owing to the courtesy of the National Institute of Standards and Technology, Administration, U.S. Department of Commerce. Not copyrightable in the United States.



Figure 4.19 Axial divergence aberration function. Figure copyright Bruker AXS.

predominant instrument contribution at $2\theta < 50^{\circ}$ and, at angles higher than $2\theta \approx 110^{\circ}$, asymmetric broadening and shift reverses towards higher angles 2θ . Although the asymmetric broadening is as strong for low and high angle lines, the effect on the latter is less noticeable as it is swamped by the dispersion of the source emission profile. The shift varies considerably from large negative values, near $2\theta = 0^{\circ}$, to large positive values as 2θ approaches 180° .

Axial divergence, and therefore the breadth of the aberration profile, can be significantly reduced by introducing Soller slits in the incident and/or diffracted beams, which typically possess angular apertures between about 2° and 5° . With narrow Soller slits included in the beam path, the dimensions L_x , L_r and L_s tend to be redundant parameters in the calculation of the aberration profile as the Soller slits control the maximum axial divergence of the incident and diffracted beams.

In practice it is not always possible to calculate the exact form of the axial divergence aberration function for a particular specimen/diffractometer configuration. The two main reasons for this are

- In specimens with strong preferred orientation, such as thin films and rolled or extruded metals, the diffraction cones are no longer of uniform intensity along the arcs of the diffraction cones.
- The inclusion of a monochromator in the beam path reduces axial divergence, as the optical path length of the beam is considerably extended. Furthermore, monochromators also act as angular intensity filters and their effect on profile shapes is similar to that of Soller slits in the beam path. The effect of a monochromator can therefore be represented as a Soller slit in a profile fitting model.

4.2.2.2.5 Defocusing

Defocusing in divergent beam diffractometers results in broadened diffraction lines and occurs when the receiving slit is not positioned at the focus of the diffracted beam. The most common causes of defocusing are,

- Mis-alignment of the incident beam angle ω so that it is no longer at the symmetric condition ω = θ.
- Wrong position of the receiving slit where the distance of the slit to the sample is larger or smaller than the nominal radius of the diffractometer.



Figure 4.20 Defocusing aberration function. Figure copyright Bruker AXS.

For both of these conditions, the focus of the diffracted beam will be either in front of or behind the receiving slit and in both cases, the aberration profile is an impulse function as shown in Figure 4.20 with the same width as the defocused beam at the receiving slit.

The angle ω is often mis-set to carry out asymmetric diffraction from planes that are not parallel to the specimen surface, such as in macrostrain or texture analysis. Rocking the specimen to improve intensity statistics also introduces this form of defocusing. In asymmetric diffraction, the breadth of diffraction lines increases as the deviation from the symmetric condition increases. Defocusing is larger and varies more rapidly at low 2θ values. Conversely, at high 2θ values, diffractometers will tolerate large defocusing errors with no detectable increase in the breadth of the line profiles. Also, by reducing the angle of divergence, the effects of defocusing can be reduced but at the expense of diffracted intensity.

4.2.2.2.6 Position-sensitive detector aberrations

PSDs with linear angular windows of up to $\sim 10^{\circ}$ (at ~ 200 mm diffractometer radius) are frequently used today in divergent beam laboratory diffractometers to increase the data collection rate. Mounted tangentially to the detector circle, the only position of the detector that is normally in focus is its center. All beams diffracted from planes angled relative to the specimen surface will enter the detector at off-center positions. Instruments equipped with PSDs therefore operate with asymmetric diffraction.

Linear PSDs can be used in a stationary mode where only a fixed angular region of a pattern is recorded, or in a scanning mode where the detector is scanned in θ -2 θ mode with its center maintained at the focusing condition. As the detector is scanned, the total diffraction pattern is formed by adding and averaging the patterns recorded at each step (Göbel, 1979).

In linear PSD systems, the receiving slit aberration is no longer relevant and the flat specimen aberration is replaced by an aberration function that embraces three effects that are folded together:

- Flat specimen error including defocusing
 - Parallax error
 - Thermal noise.

A full treatment of PSD aberrations is given by Cheary and Coelho (1994) and Cheary (Cheary *et al.*, 2004).

4.2.3 Specimen contributions

Specimen contributions affect the width and shape of diffraction-line profiles and may also shift them from their ideal position. The major principal specimen contributions are,

- specimen transparency
- microstructure broadening

In the literature, specimen transparency is usually categorized as a divergent beam instrument contribution, while the parallel beam geometry is insensitive to it. However, in the opinion of the author, specimen transparency should be rather categorized as a specimen contribution, as it depends on both specimen properties (linear absorption coefficient) as well as specimen preparation (specimen thickness and packing density). Different specimens will therefore contribute differently to the diffraction process, which would result in different instrument functions even for one and the same instrument.

Thus, as instrument functions are frequently determined by measurements of reference materials, specimen transparency needs particular consideration for accurate microstructure analysis, see also Section 4.3.2.2.

4.2.3.1 Specimen transparency

In divergent beam diffractometers, specimen transparency introduces an asymmetric broadening and line shift towards low 2θ angles because the incident X-ray beam penetrates a significant depth into the specimen rather than being diffracted from its surface. The magnitude of this contribution is dependent on the mean linear absorption coefficient of the specimen, its thickness and packing density. A representation of the aberration function is shown in Figure 4.21. The specimen transparency effect is greatest for infinitely thick, low absorption materials and is clearly evident for linear attenuation coefficients $\mu < 50 \text{ cm}^{-1}$. The contribution of specimen transparency is greatest at $2\theta \approx 90^{\circ}$ and at this angle the aberration profile has a FWHM $\approx 0.03^{\circ} 2\theta$ when $\mu \approx 50 \text{ cm}^{-1}$; this drops



Figure 4.21 Specimen transparency aberration function. Figure copyright Bruker AXS.

to ~0.005° 2θ when $\mu \approx 200$ cm⁻¹. Specimen transparency effects are particularly strong with loosely bound powders, where the packing density can be as low as 50%.

4.2.3.2 Microstructure effects

The term microstructure encompasses a series of lattice imperfections leading to deviations from the ideal crystal structure and thus causing microstructure (= physical) broadening. In an effort to limit the length of this chapter, only a simplistic but nevertheless very practical approach to microstructure analysis is discussed in terms of size and strain broadening. For a comprehensive overview of the field of diffraction analysis of the microstructure analysis refer to Mittemeijer and Scardi (2003).

Size broadening is caused by the size and shape of diffracting domains ("crystallites"), together with the distribution of size. Size broadening is often associated to specimen grinding, but may also reflect lattice imperfections such as dislocation arrays (small-angle boundaries), stacking faults, twins, or other extended imperfections. Diffraction-line profiles are symmetrically broadened with an angle dependence proportional to $1/\cos\theta$; anisotropic size effects may result in *hkl*-dependent broadening. Size broadening can be described by a Voigt function, with a predominantly Lorentzian character as shown in Figure 4.22.

Strain broadening is a result of lattice deformation (microstrain) due to dislocations, vacancies, interstitials, substitutionals, and similar defects. Diffraction-line profiles can be broadened symmetrically as well as asymmetrically, with an angle dependence proportional to tan θ ; anisotropic effects may result in *hkl*-dependent broadening. Strain broadening can be described by a Voigt function, with a predominantly Gaussian character as shown in Figure 4.23.



Figure 4.22 Size broadening function (Voigt function with predominant Lorentzian character). Figure copyright Bruker AXS.



Figure 4.23 Strain broadening function (Voigt function with predominant Gaussian character). Figure copyright Bruker AXS.

Accurate microstructure analysis requires an accurate separation of instrument contributions, and is dependent on the quality of the instrument function used. Measured instrument functions recorded from reference materials inevitably include some broadening from microstructure (at least size) and possibly also from specimen transparency, coming from the reference material. As a result, microstructure broadening will be underestimated resulting in over-estimated size/strain estimates, particularly at small levels of microstructure broadening, see Sections 4.3.2.2 and 4.3.3.1.

4.3 Convolution-based profile fitting

The most challenging task in profile fitting is the accurate characterization of the line profile shape and its variation with 2θ and possibly *hkl*, particularly in areas of strong peak overlap. Commonly used profile fitting techniques in powder diffraction can be divided into three broad categories:

- 1 "Analytical profile fitting" is generally characterized by peak shape functions (PSFs) with an explicit and relatively simple mathematical form which can be differentiated analytically with respect to each of the refined parameters within the least-squares refinement procedure. The most common PSFs in analytical profile fitting are the Gaussian, Lorentzian, Voigt, pseudo-Voigt and Pearson VII functions (Howard and Preston, 1989; Snyder, 1993). Although convenient to use, a large number of parameters is required to fit line profile shapes well over the whole 2θ range, frequently leading to correlation problems, loss of uniqueness and instability of the refinement procedure.
- 2 In "learned peak shape fitting" PSFs are generated from the actual shapes of a number of well-resolved peaks in a powder pattern by interpolation (Hepp and Bärlocher, 1988). A learned PSF gives an optimal fit to almost any diffraction profile as it is not based on an analytical expression, but requires non-overlapped peaks well distributed over the whole 2θ range and this is often not possible in practice. Additionally, learned PSFs need re-determination if the instrumental set-up or specimen properties change.
- 3 In convolution-based profile fitting, profiles are modeled by convoluting appropriate functions to form the observed profile shape. In direct convolution approaches, PSFs are fitted directly to observed diffraction-line profiles, in contrast to mere synthesis or deconvolution methods.

Convolution-based profile fitting is well known since the landmark publication of Klug and Alexander (1954). Two of the first studies using direct convolution were reported by Taupin (1973) and Parrish (Parrish *et al.*, 1976). Since then convolution has been used as a fundamental parameter approach to profile fitting notably to time of flight neutron data (David and Jorgensen, 1993) and X-ray data (Cheary and Coelho, 1992; Suortti, 1993; Masson *et al.*, 2003).

This section deals with a general direct convolution approach to X-ray and neutron powder data as implemented in TOPAS (Cheary and Coelho, 1992, 1994, 1998a, 1998b; Bruker AXS, 2007).

4.3.1 Convolution basics

The process of convolution is one in which the product of two functions $f(2\theta)$ and $h(2\theta)$ is integrated over all space,

$$y(2\theta) = f(2\theta) \otimes h(2\theta) = \text{If } (2\theta')h(2\theta - 2\theta')d(2\theta')$$

$$(4.1)$$

where

- $y(2\theta)$ is the convolution product
 - $2\theta'$ is the variable of integration in the same 2θ domain, and
 - $\circ \otimes$ denotes the convolution process.

In simple terms, convolution can be understood as "blending" one function with another, producing a kind of very general "moving average." The convoluted function is obtained by setting down the origin of the first function in every possible position of the second, multiplying the values of both functions in each position, and taking the sum of all operations.

The calculation of multiple convolution integrals requires accurate numerical procedures (Cheary and Coelho, 1992). This can be done by representing calculated profiles as histograms and reducing the convolution integrals to summations. Systematic errors are avoided by making the angular step size very small. In TOPAS, a semi-analytical procedure is used for convolution, where two functions are folded together by first evaluating them at equal 2θ intervals and then forming a continuous function by straight line interpolation between adjacent points. As the calculated functions are then a series of linear sections it is possible to calculate the convolution integral analytically. For functions that possess singularities, the effect of singularity can be overcome either by a convolution process or by a smoothing operation (Cheary and Coelho, 1998a).

4.3.2 Application areas

In the literature, convolution-based profile fitting is often associated with microstructure analysis for separation of specimen contributions from instrument contributions (Howard and Preston, 1989; Snyder, 1993). This, however, is only a special case of convolution-based profile fitting.

Generally, the application areas of convolution-based profile fitting are

Empirical profile fitting: The arbitrary parameterization of measured line profile shapes by convolution of any appropriate functions

The explicit discrimination of instrument and specimen contributions: Instrument function approach. There are two cases, dependent on how the instrument function is determined, using

- a measured instrument functions, or
- b calculated instrument functions.

4.3.2.1 Empirical profile fitting

Convolution-based profile fitting can be used for a fully empirical parameterization of diffraction-line profile shapes $Y(2\theta)$. For a convolution of *n* functions $F_i(2\theta)$, this process can be written as

$$Y(2\theta) = W \otimes F_1(2\theta) \otimes F_2(2\theta) \otimes \dots \otimes F_i(2\theta) \otimes \dots \otimes F_n(2\theta)$$

$$(4.2)$$

where

- $Y(2\theta)$ is the observed line profile shape, and
- *W* is the source emission profile function (e.g. in a phenomenological representation as discussed in Section 4.2.1).

A schematic of which is shown in Figure 4.24. The significance of this approach lies in its ability to construct PSFs with any shape dependence on angle and *hkl* direction, based on an appropriate choice of functions representing the observed line profile shape. In the TOPAS implementation, which also allows the use of user-supplied functions, a mixture of analytical and numerical convolutions is used, and the PSFs are fitted to the observed line profiles, all parameters are refineable.

The notable flexibility of this approach results in a quality of fit, which is normally better than those obtained by other methods, or at least equal to them. This is particularly true for analytical profile fitting, as the same functions can be used in the convolution equation (Figure 4.24).

As always in fitting, the number of refineable PSFs parameters needs to be kept as small as possible to avoid correlation problems; a wise choice of functions $F_i(2\theta)$ will usually require



 $Y(2\theta) = W \otimes F_1(2\theta) \otimes F_2(2\theta) \otimes \cdots \otimes F_i(2\theta) \otimes \cdots \otimes F_n(2\theta)$

Figure 4.24 Schematic representation of the convolution approach as given in (2). The final profile $Y(2\theta)$ is described by the selection of appropriate functions $F_i(2\theta)$ and convoluting them on top of the emission profile W. Note the capabilities of the TOPAS implementation to add functions before convoluting them as shown for the sum of two hat functions as well as to convolute split-type functions. Figure copyright Bruker AXS.

less refineable parameters than other methods, but still provide better fits, see Section 4.3.3. Note, that the refined profile parameters have no physical meaning, just as in any other empirical profile fitting techniques.

Empirical convolution-based profile fitting is therefore an excellent approach for all profile fit applications using any type of instrument and sample, if micro-structure information is not of interest, and if peak overlap is moderate.

4.3.2.2 Discrimination of instrument and specimen contributions

Convolution-based profile fitting implicitly allows the discrimination of instrument and specimen contributions (Jones, 1938),

$$Y(2\theta) = (W \otimes G) \otimes S \tag{4.3}$$

where *G* and *S* are geometric instrument and specimen contributions respectively, which can be modeled separately using appropriate $F_i(2\theta)$ functions according to equation (4.2). In general, for a particular instrumental setup, the entity ($W \otimes G$) represents the instrument function $I(2\theta)$, which can be either measured or calculated.

The discrimination of instrument and specimen contributions is not just a prerequisite for size-strain analysis. Generally, an instrument function constraint is of great advantage for all powder diffraction applications adversely affected by peak overlap; this is particularly true for structure analysis and quantitative phase analysis. An instrument function constraint significantly

- improves the discrimination between profile and background intensity in complex peak overlaps, and
- greatly reduces the number of refineable profile parameters required to describe diffraction-line profile shapes compared to empirical profile fitting approaches.

Unless specimen broadening becomes the dominant contribution, uncertainties due to parameter correlation are reduced, which allows a more successful decomposition of peak overlaps at higher degrees of overlap.

4.3.2.2.1 Measured instrument function approach

Measured instrument functions are normally obtained from powdered reference materials, which ideally do not contribute any specimen broadening to the diffraction process. In this case, the observed line profile shapes will directly represent the instrument function, that is

$$Y(2\theta) = I(2\theta) \tag{4.4}$$

which will be obtained by empirical profile fitting using equation (4.2). For the analysis of actual sample diffraction patterns, all instrument function parameters are kept fixed and are therefore not included in the least-squares refinement process (instrument function constraint). This has a series of important advantages, including

• Any number of functions $F_i(2\theta)$ can be used to define an instrument function, the more the better; the total number of functions and function parameters does not matter.

- Owing to this flexibility any instrument types can be accommodated, the quality of fit
 obtainable surpasses all other currently employed profile fitting techniques.
- For analysis of the actual sample, only a minimal number of refineable profile parameters is required, limited to the description of specimen contributions as needed; if appropriately modeled, refined microstructure parameters have a physical meaning.

For accurate microstructure analysis, a complication arises from the fact that in practice, measured instrument functions inevitably contain specimen contributions coming from the reference material. Even an ideally crystalline reference material will always contribute crystallite-size broadening at minimum. In addition, for divergent beam diffractometers, specimen transparency is another potential source of specimen broadening, whereby the instrument function is linked to specimen preparation (packing density). As a result, the broadening by the actual sample tends to be underestimated. This can get significant at smaller levels of microstructure broadening, leading to overestimated microstructure effects.

4.3.2.2.2 Calculated instrument function approach

The calculated instrument function approach (fundamental parameters approach, FPA) is characterized by functions $F_i(2\theta)$ representing both the aberration functions of the diffractometer as well as the various specimen contributions as illustrated in Figure 4.25. In other words, FPA represents $Y(2\theta)$ in terms of the dimensions of the diffractometer and



Figure 4.25 Schematic representation of the fundamental parameters approach for a divergent beam diffractometer showing the principal optical components and the sample together with their related aberration functions as discussed in Section 2.2.2 including (1) finite X-ray source width, (2) primary axial divergence, (3) horizontal divergence, (4) crystallite size, (5) strain, (6) absorption, (7) secondary axial divergence and, (8) receiving slit width. Figure copyright Bruker AXS.

the physical properties of the specimen. When specimen effects include both transparency S_T and microstructure effects S_M , this can be written as

$$Y(2\theta) = (W \otimes G) \otimes S_T \otimes S_M \tag{4.5}$$

whereby the instrument function in terms of the individual instrument aberration functions $G_i(2\theta)$ is given by

$$I(2\theta) = W \otimes G_1(2\theta) \otimes G_2(2\theta) \otimes \dots \otimes G_i(2\theta) \otimes \dots \otimes G_n(2\theta)$$

$$(4.6)$$

Typical geometrical instrument contributions and their aberration functions have been discussed earlier in Section 4.2.2.

From equations (4.2) and (4.6) it is seen that FPA is a special case of convolution-based profile fitting, where all profile parameters have a physical meaning. From equation (4.5) it is also seen that FPA explicitly distinguishes between specimen transparency and micro-structure, and therefore allows the independent treatment of the effective mean linear absorption coefficient or the thickness of a non-infinitely thick specimen (Kern and Coelho, 1998).

Important advantages are:

- FPA is an universal approach to profile fitting in which parameters fitted are physically identifiable and measurable. The validity of the fitted terms is therefore self-evident.
- Using laboratory instruments, crystallite size broadening up to 2 μm can be detected. The BM16 beamline at the European Synchrotron Radiation Facility (ESRF) synchrotron gives access to crystallite sizes even larger than 3 μm (Masson *et al.*, 2003). This makes FPA ideal for the characterization of standard reference materials.
- FPA automatically corrects peak shifts caused by geometrical instrument contributions and specimen transparency, significantly improving the accuracy of peak positions and derived lattice parameters. As a result, refined zero point and sample height errors no longer serve as the garbage can for misfits. This again makes FPA ideal for the characterization of standard reference materials.
- Using suited standard reference materials (such as NIST SRM 660a, LaB₆, and SRM 640c, Silicon) it is possible to unambiguously identify whether or not a diffractometer is optimally aligned in terms of both 2θ accuracy and resolution for the used set-up.

FPA has already been implemented for most laboratory based X-ray powder diffractometer configurations including conventional divergent beam instruments, parallel beam instruments and diffractometers used for asymmetric diffraction. It can also accommodate various optical elements (multilayers and monochromators) and detector systems (point and PSDs) and has been applied to neutron powder diffraction systems, for example the HRPD at ISIS (David and Jorgensen, 1993), as well as synchrotron-based diffractometers. Masson (Masson *et al.*, 2003) reported a general method applicable to high-resolution instruments with perfect crystals as the resolution-determining elements, and demonstrated its application to the BM16 beamline at the ESRF.

Nevertheless, most applications of FPA are still focused on the conventional divergent beam laboratory diffractometer. Its comparatively simple geometry permits a straightforward push-button implementation and operation of FPA, particularly when operated without optical elements. In instrument setups or geometries employing multilayers or monochromators, FPA has not found widespread use yet: The generation of a measured instrument function is more easily done in practice than a fundamental parameters-based characterization. This is particularly true for laboratory diffractometers equipped with wide-band optics. The source emission profile is modified, even alignment dependent, making a push-button FPA approach difficult.

4.3.3 Examples

4.3.3.1 Size-strain analysis

The instrument function approach discussed above is perfectly suited for accurate and consistent size-strain analysis of all the CeO_2 data made available as part of the size-strain Round Robin conducted by the IUCr (International Union of Crystallography, Commission on Powder Diffraction) CPD (Balzar, 2004; Balzar *et al.*, 2004). The data for the following illustration include:

- Laboratory X-ray data (Bruker AXS D8 ADVANCE)
- Synchrotron X-ray data (NSLS X3B1, ESRF BM16)
- CW neutron data (ILL D1A, NCNR BT1)
- TOF neutron data (ISIS HRPD).

providing a wide range of different line profile shapes. For each instrument two datasets were collected: one well crystallized specimen to determine the instrument functions (in the following referenced as "sharp data"), and one specimen exhibiting strong specimen broadening ("broadened data").

For determination of the measured instrument functions, a maximum of only five refineable parameters was required to fit the sharp data sets including their dependence on angle or d (TOF data). A calculated instrument function (FPA) was applied to the D8 ADVANCE broadened data only, based on the known instrument setting. For size-strain analysis of the broadened data across the whole angular range, two Voigt functions comprising four refinable parameters were convoluted on top of the instrument functions (double-Voigt approach, Balzar and Ledbetter, 1993).

The profile fit results for the measured instrument function approach are shown in Figures 4.26a,b–4.29a,b for the most asymmetric peaks. The sharp data representing the measured instrument functions are shown in Figures 4.26a–4.29a, respectively. The broadened data are shown in Figures 4.26b–4.29b, respectively, together with the instrument functions obtained from the sharp data, scaled to the maximum peak intensity.

The microstructure results are shown in Table 4.1, together with the Round Robin equivalents (Balzar *et al.*, 2004) and the results of a more recent paper (Scardi and Leoni, 2006). The excellent agreement seen quantitatively demonstrates the high performance of convolution-based profile fitting on a wide variety of line profile shapes and diffraction instruments.

However, the good agreement between the calculated and measured instrument function size-strain results is also owed to the high level of broadening in the broadened data. A similar agreement would possibly not have been found if a specimen exhibiting a smaller



Figure 4.26 (a) Laboratory X-ray data, measured instrument function (D8 ADVANCE) and (b) Laboratory X-ray data, broadened data (D8 ADVANCE). Figure copyright Bruker AXS.



Figure 4.27 (a) Synchrotron data, measured instrument function (NSLS X3B1) and (b) Synchrotron data, broadened data (NSLS X3B1). Figure copyright Bruker AXS.



Figure 4.28 (a) CW neutron data, measured instrument function (ILL D1A) and (b) CW neutron data, broadened data (ILL D1A). Figure copyright Bruker AXS.



Figure 4.29 (a) TOF neutron data, measured instrument function (ISIS HRPD) and (b) TOF neutron data, broadened data (ISIS HRPD). Figure copyright Bruker AXS.

L _{Vol} (nm)		Micro-strain								
Measured instrument function approach										
23.43	(0.08)	0.0149	(0.0014)							
23.72	(0.08)	0.0307	(0.0014)							
22.59	(0.05)	0.0143	(0.0010)							
23.29	(0.18)	0.0273	(0.0034)							
23.88	(0.34)	0.0259	(0.0052)							
22.93	(0.06)	0.0193	(0.0021)							
Fundamental parameters approach										
22.59	(0.08)	0.0149	(0.0014)							
22.60	(0.90)	"nearly strain free"								
22.8	(4)	"small but measurable"								
	L _{Vol} (nr 23.43 23.72 22.59 23.29 23.88 22.93 roach 22.59 22.60 22.8	$\begin{array}{c} L_{Vol} \text{ (nm)} \\ \hline \\ 23.43 & (0.08) \\ 23.72 & (0.08) \\ 22.59 & (0.05) \\ 23.29 & (0.18) \\ 23.88 & (0.34) \\ 22.93 & (0.06) \\ \hline \\ \hline \\ coach \\ 22.59 & (0.08) \\ \hline \\ 22.60 & (0.90) \\ 22.8 & (4) \\ \end{array}$	L_{Vol} (nm) Micro-str a approach 23.43 (0.08) 0.0149 23.72 (0.08) 0.0307 22.59 (0.05) 0.0143 23.29 (0.18) 0.0273 23.88 (0.34) 0.0259 22.93 (0.06) 0.0193 coach 22.59 (0.08) 22.59 (0.08) 0.0149 22.60 (0.90) "nearly strain free 22.8 (4) "small but means							

Table 4.1 Microstructure results for the size-strain Round Robin data (Balzar, 2004). Results are also given for the ESRF BM16 and NCNR BT1 data. The Round Robin results are provided in the last row. L_{Vol} represents the volume-weighted column length



Figure 4.30 Laboratory X-ray data, measured instrument function (D8 ADVANCE), region between 136° and 144° 2θ. The fitted line represents the calculated instrument function and demonstrates significant size broadening of the "standard data." Figure copyright Bruker AXS.

level of broadening had been analyzed. This is demonstrated by a FPA-based fit to the sharp data of the D8 ADVANCE in Figure 4.30, calculated instrument function only. Notable but expected is the fact that the pure instrument function as calculated by FPA is not sufficient to describe these "standard data." Because of inevitable size broadening present in the sharp data, an additional Voigt function is required on top of the instrument function to achieve a satisfactory fit, yielding a volume-weighted column length L_{Vol} of 253.75 \pm 2.45 nm,



Figure 4.31 Comparison of an unconstrained single line fit to the Quartz "5 finger peak" with SPVII functions (a) versus a FPA fit of the same data in (b). Figure copyright Bruker AXS.

but no microstrain. This represents the major part of the error in the measured instrument functions, and propagates into the microstructure estimates. Therefore, at smaller levels of specimen broadening, the FPA will normally provide better results compared to approaches using measured instrument functions.

4.3.3.2 Number of profile parameters required

With convolution-based profile fitting, the number of refinable profile parameters required is generally smaller compared to classic analytical profile fitting approaches; this is particularly the case, if an instrument function approach is used. As a consequence, many problems related to over-parameterization such as refinement of redundant parameters and parameter correlations can be effectively reduced.

This is illustrated in Figure 4.31a,b for a single line fit of the "5 fingers" of quartz using three unconstrained Pearson VII functions in Figure 4.31a and FPA in Figure 4.31b. The Pearson VII functions exhibit an almost perfect fit as indicated by the R_{wp} of 2.2%;

Single line fi	tting	Rietveld, Pawley, or LeBail method		
APF (SPVII)	DCA	APF (TCH-Z)	DCA	
2θ _k I fwhm1, fwhm2 m1, m2	2θ _k Ι L, G	U, V, W X, Y, Z A	L, G	
6	4	7	2	

Table 4.2 Minimum number of refineable profile parameters required in classic analytical profile fitting (APF) and direct convolution approaches (DCA) with instrument function constraints

 $2\theta_k$: line position; *I*: line intensity; the split-Pearson VII function (SPVII) is a composite function consisting of two Pearson VII functions and uses two different full-widths at half-maximum *fwhm*1, *fwhm*2 and PearsonVII exponents *m*1, *m*2; the TCH-Z pseudo-Voigt function consists of *U*, *V*, *W*, *X*, *Y*, *Z* parameters describing the angle-dependent line profile shape (Young, 1993); *A*: asymmetry parameter; *L*, *G*: Lorentzian- and Gaussian-type microstructure contributions.

this however is at the expense of largely divergent half-width and shape parameters particularly for the second and third peaks. Introducing an instrument function constraint (FPA, dotted line in Figure 4.31b) and fitting independent crystallite size contributions to each of the peaks results in a slightly worse R_{wp} of 2.8%; however, the half-width and shape divergence problems are removed thus realizing a more stable and physically meaningful refinement.

A comparison of the approximate number of profile parameters required in (i) single line fitting and (ii) whole powder pattern fitting techniques such as the Pawley, Le Bail, or Rietveld method (where profile parameters are constrained by smoothly varying functions with 2θ), is shown in Table 4.2. The use of an instrument function constraint drastically reduces the number of refineable profile parameters required, resulting in

- Improved refinement stability
- Increased refinement speed due to faster convergence, and
- Reduced parameter correlations and therefore more physically meaningful refinement results.

The limit of the instrument function constraint for decomposition of strong peak overlaps is mainly given by both the resolution of the instrument used and specimen broadening. When the latter becomes the dominant contribution to the observed line profile shapes, the instrument function constraint will lose its significance as soon as the line profile shapes are no longer determined by the instrument. Nevertheless, the smaller number of refineable profile parameters required always makes an important difference to classic analytical profile fitting approaches.

4.3.3.3 Anisotropic line broadening

Specimen contributions such as anisotropic size and strain distributions or stacking faults will result in anisotropic line broadening, where the line profile shape additionally varies as a function of both, *d*-spacing and *hkl*, imposing additional challenges on the accurate characterization of line profile shapes.

In the literature, numerous models have been proposed to describe *hkl*-dependent line profile anisotropy. Currently, most popular approaches are second-rank tensors (Le Bail and Jouanneaux, 1997), symmetrized spherical harmonics (Popa, 1998) or multidimensional distribution of lattice metrics (Stephens, 1999). All these approaches can easily be used in the context of convolution-based profile fitting.

In Figure 4.32a,b the qualitative application of symmetrized spherical harmonics is shown for the powder pattern of Norbornane (Fitch and Jobic, 1993), refined between 14 and 100° 2 θ . An isotropic Pawley refinement using a Voigt function with Gaussian and Lorentzian components varying with *d*-spacing (two refineable profile parameters) leads to the fit shown in Figure 4.32a. The misfit due to the anisotropic line shapes is evident, resulting in final profile *R* values of $R_p = 10.6\%$ and $R_{wp} = 16.1\%$. Using symmetrized spherical harmonics to introduce an additional *hkl* dependence of the width of the Gaussian and Lorentzian components (11 refineable profile parameters) results in the fit shown in Figure 4.32b, with $R_p = 4.5\%$ and $R_{wp} = 6.5\%$.

It is interesting to compare these results with those obtained from classic analytical profile fitting using second-rank tensors (Le Bail and Jouanneaux, 1997) on the same dataset, refined in the same angular region 14–100° 2θ . Here, 25 refineable profile parameters were required to obtain $R_p = 6.9\%$ and $R_{wp} = 7.8\%$. The combination of convolution-based profile fitting with symmetrized spherical harmonics leads to a significantly better fit requiring less than a half of refineable profile parameters.

Even more challenging are line profile shapes, where anisotropic specimen contributions such as stacking disorder introduce an additional line profile asymmetry varying with hkl. An example is shown in Figure 4.33 for a Pawley fit to talc in a geological sample (S. Hillier, pers. comm.). To qualitatively describe the extreme anisotropic profile asymmetry of the talc peaks for quantitative phase analysis, an additional exponential function has been convoluted with symmetrized spherical harmonics to introduce an hkl dependence. The result is an almost perfect fit to the clay peaks as shown by the bold curve in Figure 4.33, allowing reasonable quantitative phase analysis of phases with unknown structures.

4.3.3.4 2θ accuracy

In Figure 4.34, an FPA example fit to the (100) reflection of LaB₆ at 21.35° 2θ is shown. Note that the calculated peak maximum position is offset from the actual Bragg 2θ position, this is expected and there are two reasons for it. First, the FPA intrinsically corrects for errors in 2θ due to geometrical instrument and specimen contributions. Second, the Bragg 2θ calculation is based on the actual wavelength of $K\alpha_1$, and not the peak maximum of the emission profile. Therefore, FPA gives Bragg 2θ positions as if the data were collected with a "perfect sample" on a "perfect instrument" with pure $K\alpha_1$ radiation. Especially at low angles, the calculated 2θ positions do not generally coincide with the peak maximum.



Figure 4.32 (a) Pawley fit to Norbonane in the region between 14.5° and $19^{\circ} 2\theta$ assuming isotropic sample broadening and (b) As in Figure 4.32(a), but using spherical harmonics to describe the line anisotropy. Figure copyright Bruker AXS.

In Figure 4.34, the 2θ difference between the observed and calculated line profile positions is ~0.01° 2θ , and is mostly due to both axial and horizontal divergence (2.3° Soller slits, 0.3° horizontal divergence slits). Larger slit apertures and additional sample transparency can easily lead to line profile shifts $\gg 0.01^\circ$, and may adversely affect, for example indexing and lattice parameter determination, if not appropriately taken into account.



Figure 4.33 Pawley fit to talc in a geological sample using spherical harmonics to describe the anisotropic line asymmetry. Figure copyright Bruker AXS.



Figure 4.34 FPA example fit to the (100) reflection of LaB_6 . Note the offset between the calculated peak maximum position and the Bragg 2θ position (line marker). Figure copyright Bruker AXS.

This is demonstrated in Table 4.3 for the indexing results of three samples based on peak maximum positions obtained by FPA and analytical profile fitting, using the LSI indexing method with zero point correction (Coelho, 2003). The figure-of-merit FOM (Wolff, 1968) is generally better for FPA-based profile fitting. As identical sets of peaks had been used, the differences in FOM is exclusively due to the smaller deviations $\emptyset |\Delta 2\theta|$

	FPA			APF			μ
	FOM	$\emptyset \Delta 2\theta $	ZE	GOF	$\emptyset \Delta 2\theta $	ZE	
PbSO ₄	132.0	0.0036	-0.0073	91.4	0.0070	-0.0135	166.97
Al_2O_3	431.8 660.4	0.0024	-0.0303	160.5	0.0047	-0.0355 -0.0517	31.74

Table 4.3 Indexing results for the IUCr CPD Round Robin data of PbSO₄ (Hill, 1992), Y_2O_3 , and Al_2O_3 (Madsen *et al.*, 2001). FOM: figure-of-merit (Wolff, 1968), $\emptyset |\Delta 2\theta|$ average, absolute difference between observed and calculated peak positions 2θ , ZE: zero point error; μ : mass absorption coefficient

between the calculated and observed peak maximum positions. As the FPA generally improves the description of profile asymmetry and reduces parameter correlation, peak maximum positions are determined more accurately, particularly for small peaks and peak overlaps. It is also seen, that the calculated zero point errors are systematically different between FPA and analytical profile fitting, and are also a function of the specimen absorption coefficient (the smaller, the larger the difference). The different zero point errors obtained are due to 2θ deviations caused by geometrical instrument and specimen contributions, which are intrinsically corrected by the FPA, as seen in Figure 4.34. This leads to the determination of physically meaningful zero point (or sample height) errors by FPA, representing both misalignment and sample presentation/preparation errors. With analytical profile fitting all effects leading to line shifts are not separated.

With the FPA, the excellent line profile shape description as well as the improved determination of peak positions lead to a higher indexing success rate and FOMs, as well as more accurate lattice parameters in indexing, Pawley, Le Bail, and Rietveld procedures.

4.3.3.5 Quantitative phase analysis

Quantitative phase analysis is an application area, which is particularly characterized by peak overlap problems, dependent on the number and structural complexity of the crystallographic phases found in the specimen. The situation is similar to that discussed in Section 4.3.3.2 (single line fit of the "5 fingers" of quartz, Figure 4.31a,b), and relates to the number of profile parameters required to individually characterize the line profile shapes of all present phases, particularly in areas of strong peak overlap.

This is illustrated in Figures 4.35a,b and 4.36a,b for a cement clinker, NIST RM 2686. Figure 4.35a,b show the extreme overlap of the main calcium silicate phases "C3S" and "C2S". In full analogy to the "quartz 5-fingers problem" (Figure 4.31a,b) classic analytical profile fitting will generally fail to reliably distinguish between the individual intensity contributions of both phases (represented by the bold lines in Figure 4.35a,b) due to parameter correlation. In Figure 4.36a,b, the individual instrument contributions (based on FPA) to the line profile shapes is shown for both phases. In accordance with Table 4.2, only five refineable profile parameters were required to describe and correctly quantify all five



Figure 4.35 Quantitative analysis of the NIST RM 2686 cement clinker. The bold line represents the intensity contributions of "C3S" (a) and "C2S" (b). Figure copyright Bruker AXS.

phases, while with classic analytical profile fitting up to 35 parameters would be required to achieve a comparable quality of fit, which is not feasible in practice.

Indeed, before the year 2000, quantitative Rietveld analysis has not been performed routinely in the cement industry for both research as well as production control due to refinement instabilities and erroneous results obtained from classic analytical profile



Figure 4.36 As in Figure 4.35, but with the bold line representing the respective instrument parts of the intensity contributions of "C3S" (a) and "C2S" (b). Figure copyright Bruker AXS.

fitting. With the introduction of convolution-based profile fitting in combination with instrument function constraints as a routine method, the cement industry is currently the fastest growing application area for quantitative Rietveld analysis.

In the meantime, quantitative Rietveld analysis is also emerging, for example in the minerals and mining industries, with much more complex phase mixtures to be quantified.



Figure 4.37 Quantitative Rietveld analysis of a gold mine waste rock with 12 phases. Figure copyright Bruker AXS.

As an arbitrary example, the successful quantitative Rietveld analysis of a gold mine waste rock is shown in Figure 4.37 (Raudsepp, M. pers. comm.).

Based on a FPA-based instrument function, 12 refineable profile parameters were required to describe and quantify all 12 phases present. With classic analytical profile fitting, up to 84 refineable profile parameters would be required, which puts analysis of such materials outside of the application range of this method.

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Chapter 5 Introduction to Non-Laboratory Radiation Sources

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5.1 Introduction to non-laboratory radiation sources

Increasingly available beam time at centralized synchrotron and neutron sources, coupled with consistent improvements in beam quality and detectors has facilitated the rapid expansion of powder diffraction capabilities. Routine access to these sources has led to significant advances in data quality and has expanded the potential application for high-resolution measurements, time-resolved/*in situ* studies, elucidation of magnetic structure, and in locating hydrogen in materials. In the first part of the chapter, we outline and describe the qualities of modern synchrotron and neutron sources focusing particularly on the relevant beam qualities and practical considerations for experimental measurements. The latter part of the chapter is dedicated to the description of modern instrumentation found at user facilities, including examples of the applications of the instrumentation to problems not tenable on laboratory instruments.

5.1.1 Synchrotron radiation

5.1.1.1 Introduction to synchrotron radiation and how it is generated

Synchrotron radiation is the electromagnetic radiation emitted when a charged particle, such as an electron or positron, traveling at relativistic speeds (i.e., approaching the speed of light) follows a curved path with large radius. The production of synchrotron radiation can be characterized by several discrete steps; starting with the production and acceleration of electrons, and followed by the injection of electrons into a circular storage ring (see Figure 5.1 for an overview of a synchrotron). Electrons are generated from a cathode, similar in effect to a cathode ray tube (CRT). The electrons are then accelerated through a linear accelerator to speeds approaching that of the speed of light (>99.999%), and thus possess enough energy to be considered relativistic. After the electrons leave the linear accelerator they then typically enter a booster synchrotron. They are further accelerated in the booster synchrotron with electric fields generated by radio frequency (rf) cavities that increase the energy to values typically between 1 and 8 GeV after which they are injected into the storage ring. As the electrons orbit within the storage ring they are constantly emitting radiation tangentially to their path as they are accelerated around the ring. The relativistic



Figure 5.1 Overview of a third-generation synchrotron illustrating the major components necessary for generation of synchrotron radiation.

particle emission is concentrated into a tight forward radiation cone that is tangential to the storage ring. It is from ports in the storage ring that the synchrotron radiation is utilized in scattering, imaging, crystallographic, and spectroscopic studies. Magnetic fields are used to maintain the electrons in a circular orbit within the storage ring. Bending magnets steer the electron beam in a circular orbit, while additional magnets (e.g., quadrupole and sextupole magnets) preserve a stable orbit for the electrons within the storage ring.

There are several beam parameters that are worthwhile noting which have some effect on the overall beam quality one can expect during a scattering experiment. The stored beam current is typically expressed in milliamperes. It defines the total number of electrons in the storage ring, and has values that are typically between 50 and 500 mA, and defines the total number of electrons in the ring. The energy of the electrons in the storage ring has values typically between 100 and 8 GeV. The energy of the ring is closely correlated with the spectral distribution, rings that operate in the 100 MeV range producing vacuum ultraviolet while rings that operate in the 2-8 GeV range produce significant fluxes of hard X-rays. The number and size of the electron bunches define the time structure of the beam. Every bunch of electrons has a defined length, and it is as these bunches pass the storage ring ports that X-rays are observed in the experimental stations. As a result of discrete electron bunches orbiting the ring, the X-rays are actually pulsed on the timescale of nanoseconds. The beam size and emittance are characteristics of deviations in the orbit of the electrons. The storage ring emittance is a parameter that describes the size of the electron beam in position within the ring (in momentum phase space). The *radius of curvature* of the electron trajectory, ρ , is determined by the action of the bending magnets and is not related to the actual physical dimensions of the ring. The beam lifetime describes the slow decay of the electrons in their orbit. The major factor limiting the beam lifetime is the collision of electrons with residual gas atoms, and thus the vacuum in the storage ring becomes an important operational parameter. A notable advance in synchrotron operations at modern facilities is the inception of *top-up* operations. During top-up

operations, the storage ring is filled continuously and thus the ring operates at a constant current. During top-up operations, a ring can produce X-rays at constant current without interruption for days.

5.1.1.2 The properties of synchrotron radiation

The prime motivation for using synchrotron radiation in scattering experiments is that it provides significantly more intensity (many orders of magnitude) than standard laboratory X-ray tubes. However, it is important to first define several common terms that more accurately describe the properties of synchrotron radiation. Three terms are principally used to describe the properties of the X-ray beam (Helliwell, 1998; Mills *et al.*, 2005):

- Flux = photons s⁻¹ $(0.1\% \delta \lambda / \lambda)^{-1}$
- Brightness = photons s⁻¹ $(0.1\% \delta \lambda / \lambda)^{-1}$ mrad⁻²
- Brilliance = photons s⁻¹ (0.1% $\delta \lambda / \lambda$)⁻¹ mrad⁻² mm⁻²

Here, mrad² refers to the radiation solid angle delivered from the source and mm² the source cross-sectional area. Flux, brightness, and brilliance are quoted based on a fixed bandpass of radiation, that is, the term $0.1\% \delta\lambda/\lambda$. This bandpass is characteristic of the energy width of a monochromatic X-ray beam from a standard double-crystal monochromator similar to that found at most powder diffraction beamlines. A machine parameter that is closely related to brilliance is the beam emittance, thus there is a drive to decrease beam emittance on new sources (such as the proposed National Synchrotron Light Source II, at Brookhaven National Laboratory in Upton, New York) to ultimately increase the brightness of the beams generated from the devices described in Section 5.1.1.3. The radiation produced at a synchrotron is linearly polarized in the plane defined by the ring, and is elliptically polarized outside of this plane. The elliptically polarized X-rays are important in certain specialized techniques such as measurements of magnetic Compton scattering.

5.1.1.3 Radiation sources at a synchrotron (bending magnets, wigglers and undulators)

Second-generation sources were built to both optimize and utilize the radiation generated at bending magnets, which are the magnets used to steer the electron beam in a closed circular orbit (see the expanded section of the ring lattice shown in Figure 5.1). There are several characteristics common to bending magnets which are worthwhile noting. Bending magnets produce a fan of radiation that diverges significantly in the horizontal direction from the point it exits the ring while being tightly collimated in the vertical direction. The radiation covers a wide spectral range and is high in intensity. Because the vertical divergence of the beam is significantly smaller than the horizontal direction, scattering experiments performed with bending magnet radiation tend to favor scattering in the vertical direction.

Emission spectra that differ significantly from that obtained from bending magnets can be obtained from insertion devices, a term which includes both wigglers and undulators. These devices are installed in the straight sections of storage rings. An insertion device consists of a periodic array of magnets, and must be carefully designed to minimize perturbations to the electron beam orbit. The benefit of insertion devices is that the magnetic fields in the



Figure 5.2 Schematic of an undulator illustrating the orientation of the magnets in a straight section of a storage ring.

devices can be significantly stronger than those in bending magnets (a parameter largely dictated by the storage ring magnetic lattice). Using a periodic array of magnets, most insertion devices "wiggle" the beam multiple times. A single magnet with the directions of its poles oriented perpendicular to the electron beam will cause an acceleration of the electron beam perpendicular to the direction the electrons are traveling in the storage ring. However, an array of magnets with alternating pole directions will cause the oscillation of the electrons, again perpendicular to the direction in which they are traveling. Figure 5.2 shows a diagram of the magnet structure of an undulator. Each change of direction of the electrons as they are subsequently perturbed by magnets with opposing pole directions causes the generation of synchrotron radiation collinear to the direction the electrons are traveling. A simple schematic picture of the movement of the electrons through a straight section containing an insertion device is a simple sine function. As the electrons in the ring traverse each peak and valley, synchrotron radiation is emitted. A simple analogy can be drawn between the curvature experienced at each peak and valley and that of a bending magnet; however, the cumulative effect of each change in direction is additive in the total intensity of the beam emitted from an insertion device.

Insertion devices provide highly collimated beams of X-rays, particularly when compared to bending magnets, and thus produce beams of significantly improved brilliance. These highly collimated beams are not often used in conjunction with focusing optics in powder diffraction measurements, which would act to further increase divergence of the beam at the sample position. Wigglers and undulators differ in their magnetic lattices. As a result, wigglers produce a broad spectrum of radiation similar to bending magnets whereas undulators make use of the interference effects to produce wavelengths concentrated around several wavelengths. The energy of the selected wavelengths is commonly adjusted and optimized for each experiment by adjusting the spacing (i.e., the "gap") between the upper and lower magnet arrays.

5.1.1.4 Evolution of synchrotron sources

The *first-generation* synchrotrons were built as high-energy physics research facilities, and it was from one of these such facilities that the discovery of synchrotron radiation was made in 1947 at the General Electric Laboratories in Schenectady, New York (Elder *et al.*, 1947, 1948). Initially, the first synchrotrons had to be modified to enable access to the radiation

that was being emitted. In the 1970s the first electron storage rings were built, and these eventually were followed by dedicated facilities for scattering from synchrotron sources.

Initially, the utilization of synchrotron radiation for scattering experiments was performed parasitically on machines originally built for high-energy physics. As the utility of synchrotron radiation for study of materials was proven, there was an increasing push to build dedicated synchrotrons optimized for production and utilization of the synchrotron radiation. The first of these so-called *second-generation* sources to come online was the Synchrotron Radiation Source (SRS) at Daresbury Laboratory in the UK in 1981 and this was followed later that year by the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in Upton, NY. Not long after the SRS and NSLS, other second-generation sources were commissioned including the Alladin ring at the University of Wisconsin Synchrotron Radiation Center, the Photon Factory at the KEK Laboratory in Tsukuba, and the BESSY Facility in Berlin. In addition to new purpose-built synchrotrons for scattering, first-generation sources were converted; here the Stanford Synchrotron Light Source (SSRL) is probably the most notable, as it has continued evolving into a third-generation source.

The second-generation sources were built to optimize radiation emitted from bending magnets. The push toward smaller, more intense beams, made conditioning the ring using wigglers and undulators more attractive. Many of the second-generation sources had limited straight section in which such devices could be accommodated and the push in the early 1990s was to develop synchrotrons optimized with straight sections for utilization of insertion devices. These facilities are *third-generation* synchrotrons.

The development of synchrotron sources is not stagnant and *fourth-generation* sources are on the horizon. These fall into two classes, namely free-electron-lasers (FEL) and energyrecovery-linacs (ERLs). Several FELs have been constructed and the concept is proven. Compared to previous sources, FELs use long/straight linear accelerators to accelerate electron bunches into long undulator sections. FELs produced coherent beams of radiation that are significantly more brilliant than third-generation sources. There are several caveats to FELs, first and foremost these facilities do not support a large number of experimental endstations and are predominately single beamline facilities used for fast time-resolved studies. Second, the time averaged flux is highly dependent on the repetition rate of the accelerator. A second proposed concept for a fourth-generation source are ERLs. The ERL concept is principally being investigated by Cornell University and the Jefferson Laboratory. The basic concept of an ERL is that it recovers the energy of an electron that has circulated the storage ring to accelerate the next electron into the ring. A simple view of this process is that as an electron circumnavigates a storage ring it loses energy, this energy can be recovered in a linac and reutilized by the next electrons accelerated into the ring. Once decelerated to low energy the electrons are then directed to the beam dump, thus every electron only makes a single trip around the ring. This concept is currently under active development at CHESS, the Cornell University synchrotron.

5.1.1.5 Synchrotron sources today

With the inception of the first second-generation sources almost 30 years ago, a large number of additional synchrotrons have come online around the world as national user facilities (Brown *et al.*, 2006). Many experiments are uniquely possible at synchrotrons and



Figure 5.3 Nuclear reactions: fission and spallation.

often the data quality cannot be matched with laboratory-based instrumentation. The need for ready access to synchrotron data has pushed its continued growth, as evidenced by the newly commissioned Diamond synchrotron in the United Kingdom and the Canadian and Australian Synchrotrons. The reader is referred to the *Resources* section at the end of the chapter for more information on modern synchrotron facilities.

5.1.2 Neutron sources

Neutrons are elementary subatomic particles, which along with protons are the main components of atomic nuclei. Free neutrons, for neutron beam research, are liberated from atomic nuclei through either of two nuclear processes: *fission* in research reactors and *spallation* in accelerator-driven spallation neutron sources (see Figure 5.3). Subsequent moderation of the energy of newly liberated (highly energetic) neutrons, yields slow (i.e., thermal) neutrons suitable for neutron scattering and diffraction purposes. Particular experiments and samples may be better suited to instruments at a steady-state reactor source or a pulsed spallation source and the particular experimental advantages of each source will be discussed later.

Although compared to X-ray radiation sources, modern neutron sources suffer from low flux; their unique properties and interaction with matter make neutrons a valuable probe for condensed matter studies. While recent technological advances in modern reactor and spallation facility design has improved available neutron flux, to a rough approximation, there is greater photon flux from a candle than neutron flux available at the most intense neutron source. In practice this means that compared to X-ray diffraction experiments, neutron diffraction experiments are typified by greater sample volumes (\sim 1–50 mL), larger beams (e.g., 4 × 1 cm), and longer counting times (minutes to hours to, in some circumstances, days).

5.1.2.1 Neutrons from nuclear fission

In reactors, nuclear fission is induced when a nucleus captures a free neutron of comparable energy, becomes unstable and then splits into two smaller fragments that carry considerable kinetic energy (\sim 160 MeV total). Subsequently, an average of $2\frac{1}{2}$ neutrons are emitted from

these highly excited fragments. In practice, suitable *fissile* nuclei are generally limited to ²³⁵U or ²³⁹Pu. Of the $2\frac{1}{2}$ neutrons released per fission event: ~1 neutron goes on to initiate a further fission after slowing down to (lower) energies at which the fission cross-section is large; ~ $\frac{1}{2}$ neutrons are captured or absorbed; and the remaining ~1 neutron is available for external scattering processes.

This self-sustaining chain reaction yields a continuous flux of neutrons providing a steady-state neutron source. With a considerable energy release, this reaction is also the basis of nuclear power generation.

5.1.2.2 Neutrons from spallation

The term *spallation* refers to the multi-collision sequence of nuclear reactions, initiated by the interaction of high-energy particles with heavy nuclei, which generates a large number of neutrons (Harvey, 1959; Serber, 1947). In spallation neutron sources, short pulses of high-energy particles (protons) from an accelerator are collided with a thick target of dense high-mass-number material (e.g., W, Ta, U, Hg) generating highly excited heavy nuclei. Various particles (neutrons, protons and pions) are ejected from the collision, and these are of sufficiently high energy to collide with and excite further nuclei. Excited nuclei shed energy by "evaporating" particles, predominately neutrons, until too little energy remains to propagate this process. In practice, an average of 20–30 neutrons are generated by each incident proton (of \sim 1 GeV energy), with the neutron yield increasing approximately linearly with the mass number of the target material and energy (Carpenter *et al.*, 1999; Fraser *et al.*, 1965).

Accordingly, accelerator-driven spallation sources provide a pulsed source of neutrons with the yield depending on the target, proton energy, number of protons per pulse and the repetition rate of the pulses incident on the target (20–60 Hz). While the integrated neutron flux from a pulsed source is less than that from a steady-state reactor source, the time structure associated with the neutron pulses may be exploited such that a significant proportion of the available energy spectrum can be used for scattering experiments based on *time-of-flight* methods.

5.1.2.3 Thermalization and moderators

The energy of the neutrons as-liberated by both fission and spallation processes (~ 2 MeV) are too high to be directly applicable to scattering or diffraction studies. Ideally, diffraction studies require neutron wavelengths of the order of the inter-atomic spacing of interest (several meV). Accordingly, the energy spectrum of the as-liberated neutrons must subsequently be adjusted (lowered), within *moderators* which are arranged around the source (see Figure 5.4). These contain a volume of material, of defined temperature. Through a series of elastic collisions source neutrons are slowed down and enter into thermodynamic equilibrium with the moderator material – a process known as *thermalization* (see Figure 5.4). As such, the average neutron kinetic energy approaches that of the surrounding particles, that is, energies useful for neutron scattering. The average energy of the emerging thermalized neutrons depends on the temperature of the moderator and by varying the temperature of the moderator material, the neutron energy spectrum can be tuned (raised


Figure 5.4 Neutron moderators and the thermalization of neutrons.

or lowered) to different values than implied by room temperature and, hence, optimized for particular scattering applications.

Thermalization with a room temperature moderator material yields neutrons of average energy \sim 25 meV, referred to as *thermal neutrons*. Typically, thermal moderators include liquid water (H₂O or D₂O).

A neutron *cold source* has a special moderator maintained at cryogenic temperatures to yield cold neutrons of average energy 5 μ eV. These typically consist of a volume of liquid hydrogen, H₂ or D₂, at a temperature of 20–30 K. Most reactor and spallation sources include a cold source, which yields lower energy, long wavelength neutrons ideally suited for studying large unit cell (i.e., biological) materials, small angle scattering and magnetic scattering.

Similarly, a neutron *hot source* enhances the intensity of available higher energy, *hot neutrons* (\sim 0.2 eV). Here, the moderating material (graphite) is self-heated by fast neutrons and gamma radiation from the source to temperatures of \sim 2000°C (2300 K). These are well suited for high real space resolution diffraction measurements, that is, measurements to high momentum transfers *Q*, for example, necessary for pair distribution function analysis. Hot sources are only relevant at reactor sources, for example, at the High Flux Reactor at the ILL.

The most effective moderator materials consist of light nuclei, of comparable mass to the neutron, for optimal energy transfer. Ideally they also have low neutron capture cross-section. Typical materials include liquid H_2O , D_2O , H_2 , D_2 , Be or graphite.

In reactors, moderators play an additional role in the neutron generating fission chain reaction. The as-liberated neutrons are also too highly energetic to be easily captured by the fissile nuclei. As such moderators are required to slow down neutrons to energies at which they are more likely to induce a fission event and propagate the chain reaction. In practice, moderator material for this purpose is incorporated in the core, as a pool of liquid water (H₂O or D₂O), which also serves to cool the core and dissipate heat generated by the fission process. Further moderators and reflectors (e.g., D₂O) surrounding the core serve to redirect thermal neutrons towards the core to initiate further fission events.

In pulsed spallation sources, for instrumentation that is primarily based on time-of-flight methods, there is the additional constraint that the neutron pulses remain short within the moderator, preserving the time resolution. Accordingly, moderators at spallation sources are lined with highly absorbing materials to exclude lower energy neutrons which have been in the moderator too long (Carpenter, 1973).

Particular neutron scattering instruments will use neutrons from a specific moderator, or source, with neutron guide tubes transferring the thermalized neutron beams to the instrument.

5.1.2.4 Modern research reactors

The earliest nuclear reactor, "Chicago Pile-1", was built on a racquet court at the University of Chicago by a team of scientists led by Enrico Fermi and on December 2, 1942, the first artificial, self-sustaining, nuclear chain reaction was initiated. CP-1 consisted of layers (or a pile) of uranium metal and uranium oxide pellets embedded in and separated by graphite moderator blocks, with Cd-coated, strongly absorbing control rods to control and quench the chain reaction. Shortly after demonstrating the feasibility of the reactor source, CP-1 was dismantled and rebuilt as Chicago Pile-2 (CP-2) west of the University, at Argonne National Laboratory. There, multidisciplinary work elucidated the process of fission. This led to the construction of Chicago Pile-3, the world's first heavy-water-moderated reactor, followed by Chicago Pile-4, a fast neutron breeder reactor, and Chicago Pile-5, a research workhorse. CP-5 was in operation for 25 years from 1954 to 1979, providing neutrons for experiments on the structure and behavior of materials.

Modern research reactors (a schematic diagram is shown in Figure 5.5) contain of a core consisting of fuel and neutron adsorbing control rods with a "swimming pool" of liquid water (light or heavy) which acts as both moderator and coolant. This is surrounded by massive radiation shielding of borated concrete and steel. The energy produced by each



Figure 5.5 Overview of a neutron reactor.

fission event largely appears as heat in the reactor fuel and surroundings. Reactors are designed to have "under-moderated" cores such that fast neutrons enter the moderator so the maximum flux of thermal neutrons is \sim 15 cm from the core, at the nose of the beam tube which transfer neutrons to the instruments.

Compared to power reactors, research reactors require more highly (fissile 235 U isotope) enriched uranium, consume less fuel, operate at lower temperatures and produce less fission products. The use of natural (0.7% 235 U) or low enriched uranium with inherently low concentration of the fissile 235 U nuclei requires a heavy water, D₂O, which has lower neutron capture cross-section as core coolant and moderator. Greater 235 U enrichment of the core provides a number of distinct advantages, allowing for a smaller core, that is, source, higher power density, and light water (H₂O) as core coolant and moderator.

5.1.2.5 Modern spallation sources

The first proof-of-principle demonstration of pulsed neutron generation based on the spallation concept was ZING-P (the ZGS Intense Neutron Generator-Prototype) at Argonne National Laboratory in 1972. An overview of a spallation source is shown in Figure 5.6. As for many spallation facilities, this source was based on a pre-existing accelerator facility built by the particle physics community, ZGS (Zero Gradient Source). This prototype facility was later upgraded to (now decommissioned) ZING-P' with the replacement of the initial lead brick target by W and depleted U targets. Subsequent spallation sources have used solid tungsten, tantalum and depleted uranium targets and more recently liquid mercury targets. Currently operating spallation sources include:

- IPNS, Intense Pulsed Neutron Source, Argonne National Laboratory, USA (1981–2008)
- KENS, KEK, Japan (from 1980)



Figure 5.6 Overview of a spallation neutron source.

- ISIS, Rutherford Appleton Laboratory, UK (from 1985)
- LANCE, Los Alamos Neutron Science Center, Los Alamos National Laboratory, USA (from 1977)
- SNS, Spallation Neutron Source, Oak Ridge National Laboratory, USA (from 2007)
- JSNS, Japanese Spallation Neutron Source, J-PARC, Japan (under construction)

While the energy, and correspondingly heat, released per neutron is low for spallation compared to reactor sources, the rate of heat removal from the solid target is still the limiting factor in the neutron flux. Spallation sources currently being commissioned, SNS and JSNS, are based on a continuously circulating liquid mercury target, with an improved ability to dissipate heat and to withstand shock effects, all without radiation damage issues.

5.2 Synchrotron radiation instrumentation

The experimental instrumentation at synchrotron sources is constantly evolving and improving, however a survey of instruments used for powder diffraction at synchrotrons yield many similarities amongst the most productive instruments. Below we describe key experimental components to a beamline, focusing on a general description of what one would expect to encounter should they choose to pursue experiments at a synchrotron.

5.2.1 Conditioning the beam (monochromator and focusing optics)

The radiation originating from the synchrotron source is polychromatic (i.e., a broad spectrum of many wavelengths) and must first be conditioned before being used for diffraction experiments. Several key components will be discussed including (1) the basic concepts of monochromator design and (2) focusing optics, which act to condense the beam down into smaller spot sizes near the sample position. This section focuses on instrumentation that would typically be encountered during synchrotron powder diffraction measurements.

5.2.1.1 X-ray monochromators

There are two commonly encountered geometries used for X-ray monochromators at synchrotron sources, Bragg and Laue. Bragg monochromators utilize the reflection of X-rays off the surface of flat single crystals (i.e., reflection geometry) to select a single wavelength of X-rays. In most designs, two crystals are used, common examples are the (111), (220), and (311) reflections of silicon single crystals. The first crystal acts to select the wavelength (i.e., energy) of the X-rays, which is a function of the *d*-spacing of the reflection of the crystal being used in the monochromator, and its angle relative to the axis of the X-ray beam. The second crystal redirects the X-ray beam such that it is collinear with the original beam. This is the basis of the double crystal monochromator (DCM). DCMs allow a range of energies to be utilized for experiments. A drawing of a DCM from a bending magnet beamline at the APS is shown in Figure 5.7. Because of the pair of parallel crystals and the offset and distance between the crystals can be adjusted, the X-ray beam does not significantly change position in the experimental setup as energy is changed. This arrangement allows access to



Figure 5.7 Diagram of a double crystal monochromator, and a diagram of an actual monochromator design taken from a bending magnet beamline at the APS.

a wide range of X-ray energies without the need to move large experimental components at the beamline. When two separate crystals are used, they are often dynamically aligned using electronic feedback and piezoelectric actuators. The use of two independent crystals has the benefit that a wide energy range can be accessed as the crystals can be moved further apart when higher energy X-ray beams are desired, and also to maintain the same offset of the monochromatic beam relative to the white beam.

Another commonly encountered alternative design uses "channel cut" crystals. These crystals have both reflecting surfaces cut from a single piece of Si. While the two faces are inherently parallel and need not be subsequently aligned to each other, there are a couple of drawbacks; including a restriction in energy range dictated by the size of the silicon crystal. These drawbacks are a simple matter of geometry. If we consider the spot on the crystal face which is incident in the source beam fixed, then the position of the deflected beam on the second crystal face is dependent on the angle of the monochromator. Hence it is easy to see that there will be energies where the beam would not intersect the second diffracting face. User demand at sources has dictated that a wide energy range is readily accessible at instruments, and thus DCMs are typically favored at powder diffraction beamlines.

The other commonly encountered X-ray monochromator utilizes Laue crystals. This arrangement has the crystal oriented such that the diffracted beam is transmitted through the crystal; therefore, the design is best suited for high-energy X-rays. The application of two Laue crystals allows access to a wide spectral range of energies similar to the Bragg DCM. However, a single Laue crystal can also be used to obtain a monochromatic beam. The use of a single diffracting crystal causes the diffracted beam to be at some fixed angle from the white beam, and is usually arranged such that the monochromatic beam is deflected horizontally. Experimental stations that use only a single Laue crystal operate at a fixed energy, or multiple fixed energies if multiple crystal orientations are used. Both the double

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Laue crystal (Shastri *et al.*, 2002) and single Laue crystal versions (Rutt *et al.*, 2001) are commonly encountered at synchrotron.

An important factor governing the design of monochromators is the consideration of heat load generated by the source. Any change in temperature of the monochromator crystals or components will ultimately result in an energy shift of the monochromatic beam delivered to the experimental station. A bending magnet can produce beams with 300 W of power. Circulating water is sufficient to cool components on bending magnet beamlines. However, an undulator beam can produce a heat load in excess of 2000 W. As a result of the significant heat generated by absorption of X-rays by the silicon crystal in the white beam, monochromators on undulator beamlines need to be cryogenically cooled using circulating liquid nitrogen (Lee et al., 2000). Liquid nitrogen is not used just as a means to remove heat, but the heat transfer through silicon improves significantly at cryogenic temperatures (Mills, 1997). The thermal conductivity (k) changes from 1.48 W cm⁻¹ K⁻¹ at 300 K to 13.4 W cm⁻¹ K⁻¹ at 80 K (Mills, 1997). Single crystals of diamond can also be used in place of silicon in monochromators on undulator beamlines. Diamond crystals can be water cooled due to improved heat transfer at room temperature $(15-20 \text{ W cm}^{-1} \text{ K}^{-1} \text{ at } 80 \text{ K})$, significantly reducing engineering requirements, although suitable crystals are expensive and are not readily available.

5.2.1.2 Focusing optics

To counteract the effect of beam divergence from the source, focusing optics are used to redirect the beam to the point closer to the location of the sample, often multiple tens of meters from the source. There are multiple types of focusing optics available, among those the most commonly encounterd are mirrors, zone plates, sagitally bent crystals, and compound refractive optics. These can be used singularly or are often combined as each type has certain advantages for specific applications. Mirrors are widely used at synchrotron beamlines. Reflectivity of the surface is obtained at grazing angles. At energies used for scattering this means angles typically less than a few degrees. Commonly silicon single crystals, up to a meter in length, are used as mirrors and often have coatings (e.g., of platinum, ruthenium etc.) for operation at different energies. The second utility of mirrors (in addition to focusing) is the rejection of higher-order harmonics from the monochromatic beam. For example, because of the broad spectrum of the X-ray beam, the (333) reflection must be considered as diffracting along with the (111). Silicon crystals can also be bent to obtain focusing at the sample position and often the second crystal of the monochromator can also be bent to obtain horizontal focusing. An important consideration in using bent crystals is ensuring that they bend in a single radius, and thus focus in a single direction. Sagittally bent crystals (i.e., those bent in a single direction) are often used as the second crystal in DCMs to focus the beam horizontally on bending magnet powder diffraction beamlines.

Zone plates and compound refractive optic are probably the least commonly encountered focusing optics in powder diffraction measurements. Zone plates are circular diffraction gratings that consist of alternating transparent and opaque rings. While they produce a highly focused beam near the sample position with relatively short focal distances, they are not easily tunable over wide energy ranges and must therefore be manufactured for the desired narrow energy ranges. They are typically encountered in imaging rather than scattering experiments.

5.2.2 Diffracted beam optics

Diffracted beam optics are often typically used to improve resolution, by effectively acting as receiving slits, or to remove other scattering artifacts arising from either the sample (e.g., X-ray fluorescence or Compton scattering) or the sample environment. With regard to powder diffraction, the primary motivation of analyzer crystals is to improve resolution in the measured pattern. Typically, analyzer crystals (often perfect Si crystals or Ge) are used in the plane of scattering, and thus collimate a single value of 2θ (Hastings *et al.*, 1984). However, they can also be used to deflect the scattered beam perpendicular to the plane of scattering (i.e., horizontally). While not typically encountered, this horizontal arrangement has the advantage of improving the rate at which measurements can be made because the horizontal crystal can be combined with a position-sensitive-detector to record a range of 2θ values simultaneously (Beno and Knapp, 1993). The increase in count rate is unfortunately accompanied by degraded resolution, however, a particular advantage of this approach is that it efficiently eliminates Compton scattering and fluorescence from the measured intensity and is therefore ideally suited to anomalous scattering measurements (Beno *et al.*, 1995).

5.2.3 Examples of applications and classes of instruments

5.2.3.1 Unique applications of synchrotron radiation to powder diffraction

Synchrotron radiation provides an intense source of X-rays of tunable wavelength from ~ 0.1 Å to ultraviolet wavelengths. These characteristics enable experiments not readily feasible with a laboratory source. Diagrams of experimental setups commonly encountered at synchrotrons are shown in Figure 5.8.

Resonant anomalous scattering. The tunable nature of X-rays at a synchrotron source enable measurements near absorption edges. By carefully tuning the X-ray energy to, and just below an absorption edge, additional element-specific contrast can be obtained and used for accurate determination of site occupancies on chemically disordered crystallographic sites.

High-resolution measurements. One of the principle motivations for many powder diffraction measurements at synchrotron sources is the improved resolution that can be obtained. These measurements often prove crucial in correctly indexing patterns for structural solution.

Measurements to very small d-spacing. The availability of X-rays with short wavelengths (<0.2 Å) enable measurements to very small d-spacing $(\sim0.1 \text{ Å})$. When applied in Rietveld analysis such data can improve determination of occupancies and thermal parameters. Such measurements are also finding widespread use in studies applying the pair-distribution-function approach. The PDF approach recovers data in real space of a radial distribution function of atom–atom correlations.



Figure 5.8 Schematic examples of synchrotron instrumentation for high-resolution measurements with analyzer crystals (top) and measurements with two-dimensional area detectors (bottom).

Strongly absorbing materials. The penetrating power of short wavelength X-rays enable penetration through otherwise strongly absorbing samples, and also helps minimize the need for extinction and absorption corrections.

Complex highly absorbing sample environments. As with strongly absorbing samples highenergy X-rays offer a means of penetration through complex sample environments such as Paris–Edinburgh high-pressure cells.

In-situ/time-resolved measurements. The high intensity of synchrotrons enables the collection of complete diffraction patterns with a high degree of rapidity. Measurements in the millisecond range are now readily feasible.

5.2.3.2 High-resolution powder diffractometers

High-resolution diffractometers typically utilize crystals in the diffracted beam (i.e., analyzer crystals) to effectively collimate the scattered beam. Initial difficulties with high-resolution measurements at synchrotrons using analyzer crystals centered around developing accurate descriptions of peak shape for the pronounced asymmetry observed at low diffraction angles (Hastings *et al.*, 1984). One of the most productive high-resolution facilities on a second-generation source was the X7A beamline at Brookhaven National Laboratory. This beamline used a channel cut monochromator with no focusing optics to deliver X-rays to the sample. A single analyzer/point counter was used alternatively with a PSD which enabled more rapid measurements with only a marginal tradeoff in resolution.

Modern high-resolution powder diffractometers have evolved to use multiple analyzers to ultimately increase the rapidity of measurements. An early example of this was demonstrated at the Photon Factory (Toraya *et al.*, 1996), and currently most high-resolution instruments at third-generation synchrotrons utilize multiple analyzers/detectors (Fitch, 2004). The



Figure 5.9 Example of synchrotron powder diffraction data from an instrument using a crystal analyzer and that using a two-dimensional imaging plate detector.

diffractometers currently under construction at the Advanced Photon Source, Diamond, and the Australian Synchrotron will also employ multi-analyzer systems.

High-resolution diffractometers are often sought after for the dramatically improved resolution they provide over laboratory sources, which can prove crucial for the accurate indexing of complex crystal structures. Recently, these studies have been extended to complex molecules of biological interest (Pagola *et al.*, 2000). Another realm that powder diffraction methods are entering and which is still in its infancy is the application to protein crystallography (Von Dreele, 2007).

5.2.3.3 Two-dimensional and position-sensitive detectors

The other arrangement common at synchrotron powder diffraction beamlines are the use of either two-dimensional (2D) area detector or linear position-sensitive detectors (PSD) in place of the single point counter common 20 years ago. A comparison of the data obtained from high-resolution and 2D detector setups are shown in Figure 5.9. These detection schemes allow rapid collection of full data sets, though a significant tradeoff is a marked decrease in resolution from that obtained with analyzer crystals. The arrangement of beamline components is identical to that of high-resolution beamlines from the source up to the position of the sample. A common arrangement at beamlines specializing in powder diffraction measurements is to operate either in a high-resolution mode or 2D detector/PSD mode based on the need of the experiment.

There are examples of beamlines which specialize in measurements using area detectors, such as the X7B beamline at the National Synchrotron Light Source at Brookhaven National Laboratory which uses a 2D IP detector to measure full powder patterns. The use of area detectors allows full data sets to be collected simultaneously with exceptional statistics. These

are used to collect either full Debye–Scherrer rings or large portions of the rings. The data can be radially integrated from the center of the rings to yield powder diffraction patterns of intensity as a function of angle (Hammersley *et al.*, 1996). The application of these types of beamlines lies in the studies of materials under *in situ* conditions. Typical diffraction patterns can be collected quite rapidly, on the order of seconds, and is typically limited by the time it takes the detector to readout rather than the X-ray flux on the sample. A variety of *in situ* experiments that are possible only when rapid data collection is possible, and here we only mention a couple of the large number of potential applications. Heterogeneous catalysts are often studied *in situ* to directly observe and monitor changes to the structures of active catalysts (Chupas *et al.*, 2001; Kim *et al.*, 2003). The ion exchange of zeolites can be monitored to elucidate the mechanism of transport (Celestian *et al.*, 2004). Currently, measurements with time resolution in the range of milliseconds are readily achievable and current limitations are not attributable to lack of X-ray intensity but rather detectors that can measure and read data at fast rates.

One-dimensional linear detectors are also encountered in powder diffraction measurements as a means to increase data collection rates. One notable example of a beamline specializing with this arrangement is the Australian diffractometers at the Photon Factory. This instrument uses multiple image plates in a Debye–Scherrer geometry. The image plate is shielded such that they measure a thin strip (up to 320° total coverage) and can be translated to measure subsequent samples (Garrett *et al.*, 1995).

New developments will be driven by detector development, and several notable advances are worth mentioning with regard to powder diffraction. Hybrid pixel detectors are a notable advance in that readout times can be as short as 2 ms (Basolo *et al.*, 2007). Along these lines, the application of amorphous silicon area detectors, developed for use in medical imaging, also allow fast readout for powder measurements using high-energy X-rays (Chupas *et al.*, 2007).

5.2.3.4 High-energy X-ray scattering

A unique capability at synchrotrons, the application of which offers several experimental advantages, are the availability of high-energy X-rays. Although somewhat subjective, here we define high-energy X-rays as those with energies greater than ~60 keV and wavelengths shorter than ~0.2 Å. High-energy X-rays allow high penetration through otherwise strongly absorbing samples, and minimize errors and the corrections necessary for extinction and absorption. The high penetrating power is also ideal for measuring samples that are normally strongly absorbing, or for penetration through thick sample environments such as the 10 mm thick gasket, these gaskets are common in Paris–Edinburgh high-pressure cells (Chapman *et al.*, 2007). Furthermore, high-energy X-rays offer the ability to access large values of momentum transfer, Q ($Q = 4\pi \sin \theta/\lambda$).

The availability of high-energy X-rays has greatly expanded the pair-distributionfunction (PDF) technique (Egami and Billinge, 2004). The accessibility of high Q also enable accurate measurements of the total structure factor S(Q) to values larger than 40 Å⁻¹. PDF measurements recover structural information in real space by Fourier transform of the reciprocal space. This yields information in the form of distribution atom–atom correlations, with the ultimate quality and resolution of the data determined by the range of Q measured. In comparison to the potential of high-energy X-rays, a laboratory source using a copper tube source can only measure to an absolute maximum value of $Q \sim 8 \text{ Å}^{-1}$. PDF experiments are an unique application of high-energy X-rays (and neutron scattering), and have only recently been extended to *in situ*/time-resolved measurements due to the combination of both high-energy X-rays and 2D detectors (Chupas *et al.*, 2004, 2003).

Another elegant example that used the high penetrating power to apply resonant scattering approaches at the K-edges of lead and bismuth to determine site atom distributions in the potential thermoelectric candidate is $Pb_5Bi_6Se_{14}$ (Zhang *et al.* 2005). This study combined the use of high-energy resolution optics development with the need for resonant anomalous scattering measurements using high-energy K-edges. The absorption of X-rays by the sample near the L-edges made resonant scattering measurements intractable due to the presence of both lead and bismuth. The only alternative was in using the K-edges even though there is significantly less contrast provided by the L-edges. Relative to high-resolution measurements, the application of high-energy X-rays to problems in powder diffraction is a relatively young niche. With dedicated high-energy beamlines coming online, such as the dedicated PDF beamline (11-ID-B at the Advanced Photon Source), an increased growth in this area should be expected.

5.2.3.5 Energy dispersive, micro-diffraction and spatially resolved measurements

Currently, energy dispersive measurements are probably the least common of the different instrumental setups encountered at synchrotrons. These experiments are performed with the broad spectrum of X-rays available in a white beam at a synchrotron. Typically, a single energy resolved spectra is recorded with a solid state detector. Because the energy resolving detector is held at a fixed and defined diffracting angle, the Bragg reflections appear as peaks as a function of energy. These experiments are commonly encountered in high-pressure multi-anvil experiments where there is little angular access to the scattering from the sample. Recently this approach has been combined with angular-dispersive measurements to ultimately yield spectra similar to that obtained from standard monochromatic measurements (Wang *et al.*, 2004). However, the main disadvantage to this approach is detector dead time and the possibility of radiation damage to the sample. Standard intrinsic germanium solid state detectors can take a maximum of ~300 000 counts per second, and this is easily achievable with monochromatic beams, thus one must consider carefully the need and potential benefits in applying energy dispersive approaches.

An elegant recent example of the application of energy dispersive diffraction, which makes use of its unique properties, has been in the spatially resolved powder diffraction measurements of cylindrical cement paste samples to characterize the progress of the sulfate attack on the mineral components (Jupe *et al.*, 2004). Spatially resolved diffraction patterns were obtained from well-defined volumes by using a horizontal beam size of 50 μ m and a vertical beam size of 500 μ m. The detector was mounted at fixed scattering angle (2 θ) of approximately 2°. The samples were then rastered through the beam and thus the sample on the surface was examined separately from the material which was buried within the paste. By using this approach Jupe *et al.* were able to resolve the effect of sulfate attack on the surface and examine its migration into the bulk of the materials. In addition to furthering the understanding of an important applied problem, this work illustrated several important consequences of working on an undulator beamline. First, they noted that the gap of the

undulator has to be opened such that the intensity was decreased so that the detector did not saturate. Second, they illustrated the need to taper the undulator to broaden out its spectrum such that the spectral distribution of the beam did not adversely affect their analysis.

5.3 Neutron diffraction instrumentation

5.3.1 Neutron scattering

Neutrons are uncharged subatomic particles with spin $\frac{1}{2}$ magnetic moment, mass ~ 1 and both wave- and particle-like properties; all characteristics which make neutrons particularly valuable probes for studying condensed matter.

5.3.1.1 Neutron interactions

Neutrons are scattered from materials *via* short-range interactions with the atomic nucleus rather than with the electron cloud as occurs for X-rays. Accordingly, the neutron scattering power or *scattering cross-section* of an atom is not strongly related to the number of electrons. While X-ray scattering strength increases smoothly as the square of the atomic number (i.e., number of electrons), the total neutron cross section for scattering and adsorption varies irregularly with the isotope of a given chemical element.

This variability in neutron scattering cross-section can be used to advantage in different types of experiments:

Light atoms. Neutrons often ideally suited to probe light low Z elements (e.g., H) for which X-ray scattering is relatively insensitive.

Neighboring elements. The neutron scattering contrast between neighboring elements in the periodic table, which have virtually identical X-ray scattering cross-sections, allows them to be distinguished.

Isotopic substitution. Isotopes of a chemical element can have substantially different neutron scattering powers and, as such, isotopic substitution can be used to label chemically distinct components of a material.

Null scattering. The ratio of different isotopes can be chosen in proportions such that the net coherent scattering factor is zero. This is possible for elements for which there are isotopes with negative scattering cross-sections, for example, H/D. Using this approach, particular atomic sites in the sample can be made "invisible" to neutrons, thereby simplifying a structural problem. A similar general approach can be used to generate null scattering materials, for example, TiZr alloys.

As the nucleus can be considered to be a point scatterer, there is no angular dependence of the scattering cross section. By contrast, the scattering cross section for X-rays, which interact with the diffuse electron cloud, decreases at high angles.

The neutron spin- $\frac{1}{2}$ can interact with unpaired electrons in sample, an interaction which is of similar strength to the nuclear scattering, permitting both atomic and *magnetic structure* to be simultaneous explored.

With no net charge and relatively weak and short-range interaction with nuclei, neutrons are *highly penetrating* in most materials. This allows large/bulk sample volumes to be wholly probed as well as permitting the use of complex sample environments such as cryostats, furnaces, and pressure cells.

5.3.1.2 Relevant materials

The irregular variation of the neutron scattering and absorption cross-sections can be used to an advantage in designing sample environments, beam optics, and detectors.

Vanadium is a null scatterer with no Bragg peaks. That is, it has a near zero coherent scattering cross-section. Thin vanadium "cans" are conventionally used as sample holders which sit in the direct beam without contributing to the measured Bragg peaks. The significant incoherent scattering from a solid vanadium rod is used to measure the energy spectrum of the incident beam for normalization.

Aluminum possesses low coherent and incoherent neutron scattering cross-sections and low absorption. As a relatively strong and ubiquitous material it is used for sample environment/well windows (e.g., on a displex), heat shields, and as structural components (e.g., in gas high-pressure cells).

TiZr is a null scattering alloy occasionally used in sample environments.

Boron is strongly adsorbing in the natural isotope abundance. Strongly absorbing boron containing materials, such as boron-infused waxes, concretes and glasses, are used for shield-ing, collimation, beam stops, neutron guide substrates and masking sample environments. The boron ¹⁰B-neutron absorption reaction is the basis of many neutron detection devices.

Cadmium and *gadolinium* are strongly adsorbing and are used in collimation and to mask sample environments. This is particularly convenient with the possibility of preparing special paints based on the oxides. The ¹⁵⁵Gd-neutron absorption reaction is involved in foils for neutron imaging.

Lithium (⁶*Li*) and *helium* (³*He*). Neutron absorption reactions involving these isotopes are used in neutron detection devices.

Nickel, and in particular ⁵⁸Ni, has a high neutron scattering cross-section. Polished nickel surfaces are highly reflective for neutrons and are used in neutron guides and mirror optics. The high coherent scattering cross-section also makes metallic nickel the traditional sample of choice for characterizing neutron scattering instrumentation.

5.3.2 Neutron diffraction

As for other diffraction probes, neutrons incident on a sample are scattered and the scattered intensity measured as a function of scattering angle and probe wavelength/energy. This intensity data is related to the atomic (and magnetic) structure and can subsequently be analyzed in terms of various structural models. Schematic diagrams of neutron powder diffraction instruments are shown in Figure 5.10.

5.3.2.1 Constant wavelength neutron diffraction

Powder diffraction instruments at a steady-state reactor source generally use a *constant* wavelength (CW) neutron beam (Hewat, 2006). The monochromatic neutron beam of



Figure 5.10 Schematic examples of CW neutron powder diffraction instruments.

known wavelength irradiates the powder sample and the intensity of the scattered neutrons is measured as a function of scattering angle 2θ . The intensity can be measured by step-scanning a small point detector in 2θ or by using a multiple detector array or large PSDs covering the same 2θ range. The principle underlying constant wavelength neutron diffraction is directly analogous to monochromatic X-ray powder diffraction at laboratory and non-laboratory sources.

5.3.2.2 Neutron time-of-flight diffraction methods

While the integrated neutron flux from a pulsed spallation source is less than that at a steadystate reactor source, the application of neutron *time-of-flight* (*TOF*) methods has distinct advantages: allowing a significant segment of the neutron energy spectrum to be used; reducing backgrounds, allowing sample environment with restricted scattering geometry to be used (Jorgensen *et al.*, 1989).

Neutron time-of-flight methods, generally applied at spallation sources, make use of the time structure of the pulsed neutron beam to allow the unmonochromated "white" beam to be used. Pulses of the polychromatic beam irradiate the sample. The intensity of the scattered beam is measured by detectors at fixed angles, recording the time at which each scattered neutron arrives at the detector. Neutrons in a given pulse are generated by the spallation process initiated by a single proton pulse. They leave the source simultaneously and travel the same path (distance) source to sample to detector. As such, the time at which an individual neutron within the pulse arrives at the detector (i.e., the neutron time-of-flight) correlates to the neutron velocity and, accordingly, the neutron energy/wavelength.

Thus, a single detector at fixed scattering angle measures a complete diffraction pattern as a function of the neutron time-of-flight (or wavelength, or *d*-spacing) for each neutron

pulse. In practice, many detectors arranged in banks can be placed at different scattering angles allowing many patterns to be measured simultaneously to reduce counting times. As the complete diffraction pattern is measured at each fixed detector position, TOF neutron diffraction is highly compatible with complex sample environments where, only limited openings for the scattered (and incident) beam may be possible. This is particularly relevant where considerable collimation of the scattered beam is required to minimize or eliminate the contribution of the sample environment to the measured scattering intensity. For example, the He pressure cell used at SEPD, IPNS.

The spallation source yields a continuous distribution of moderated neutron energies, that is, wavelengths/velocities, with the intensity of the incident polychromatic beam varying as a function of neutron energy. As such, the incident spectrum for a given instrument must be measured and used to normalize the diffraction pattern to allow analysis of peak intensities. In practice, the spectrum is measured with a null scatterer with no coherent (Bragg) diffraction, typically a vanadium rod.

A number of factors contribute to the (time) resolution of the diffraction pattern obtained from neutron TOF:

- The uncertainty in the moderation time which is wavelength dependent.
- The time bin width of the detector.
- Source to sample (to detector) distance, that is, flight time.
- Beam divergence, that is, difference in neutron paths.

Higher resolution instruments are further from the source, with a longer flight path. At HRPD, ISIS only every 5th neutron pulse is transmitted. Independent of time resolution, the sharpest diffraction peaks appear in backscattering geometry $(2\theta > 90^\circ)$. With no angular dependence of neutron scattering (and no fall off at high angle as for X-rays) neutron backscattering geometries are optimal.

Another consequence of using a spallation source is that the energy spectrum naturally includes high energy, that is, hot neutrons. These short wavelength neutrons are advantageous in measurements which require access to large values of momentum transfer, Q. Measurements can be easily made to a maximum Q of ~50 Å⁻¹, which proves vital for total-scattering Pair-Distribution-Function studies (Dove *et al.*, 2002; Egami and Billinge, 2004).

5.3.3 Beam conditioning

Neutrons emerging from a moderator source require further conditioning for diffraction experiments.

5.3.3.1 Choppers (TOF diffraction)

Beam choppers act like shutters, controlling the transmission of radiation from the source to the instrument. They consist of a rotating disk with neutron transmitting openings and opaque (strongly neutron absorbing or scattering) segments. At spallation neutron sources, choppers synchronized with the neutron source frequency are essential to normal operation.

 T_0 -choppers block the high-energy neutrons and gamma radiation from the spallation event (T_0) that precedes the pulse of moderated neutrons, thereby reducing background and damage to the sample.

Frame overlap choppers condition the neutron beam to prevent fast neutrons in a pulse from overlapping or overtaking the slow neutrons from the preceding pulse and vice versa. It selects a window of neutron energies (velocities) from each pulse to prevent such overlap. For larger source to sample (to detector) distance, the overlap between subsequent pulses is increased and a narrower energy window is required. Alternatively, a broader energy window from every second (or higher order) pulse may be used.

A third type of chopper, a *selector chopper* selects neutrons of a defined energy band.

At steady-state reactor sources, the principal purpose of choppers is to create a pulsed neutron source for the application of TOF methods.

5.3.3.2 Monochromators (CW diffraction)

Constant wavelength neutron diffraction studies require single wavelength beams and, as such, the divergent white beam from the moderator source must be monochromated before scattering from the sample.

Bragg reflection from single crystals represents the most widely used approach to select a well-defined wavelength from the continuous wavelength source beam. Based on Laue diffraction, the Bragg diffraction condition is only satisfied for a single wavelength and given reflection angle. While a perfect crystal is most highly selective, reflecting the smallest spread of wavelengths, it also has the lowest reflectivity, yielding the lowest neutron flux. Given the limited available flux at neutron sources, a less perfect mosaic monochromator crystal is often favorable. This provides a higher energy band pass and higher neutron flux. In practice, a $0.2-0.5^{\circ}$ angular range provides reasonable reflected intensity and matches the divergence of the beam. Typical neutron monochromators are based on plastically deformed (i.e., mosaic) Ge, Si, or Cu crystals or pyrolytic graphite – materials with a large scattering length, high density, low absorption, and good crystal quality.

5.3.3.3 Neutron guides

Neutron guides are highly internally reflective, evacuated, hollow tubes which transfer neutrons in high efficiency from the source (i.e., a moderator) to the instrument. This includes transferring neutrons large distances to areas of low background, that is, a separate experimental building or *guide hall*. Individual guides may be capable of servicing more than one instrument.

Neutron guides consist of adsorbing boron glass plates assembled into rectangular crosssections of $\sim 20 \times 50$ mm dimensions. The inner surface is coated with a thin layer of Ni (or more efficiently ⁵⁸Ni) to form a super mirror based on the principals of total internal reflection. Neutron guides may be slightly curved, such that there is no direct line of sight to the source, and such that only slow neutrons which fulfill conditions for total internal reflection, are transmitted. This reduces background radiation including that from fast neutrons and gamma radiation.

5.3.4 Neutron detection

For thermal neutron detection, scintillation counters or gas counters are typically employed. In general, gas counters have a longer dead time after a detection event compared to scintillation detectors which are the detector of choice for instruments with a high event rate at the detector.

Scintillation counters consist of a scintillator coupled with a photomultiplier. Neutrons are absorbed in the ⁶Li or ¹⁰B-based scintillator, inducing the emission of energetic charged particles which excites the atoms of the working medium causing fluorescence. This fluorescent radiation is measured with a photocathode-photo multiplier system.

In *gas counters*, helium enriched with ³He, or BF_3 enriched with ¹⁰B, is placed in a metal cylinder with a thin wire anode. A high voltage is applied between the anode and the cylinder (cathode). As a neutron is absorbed, fast charged particles are generated. These charged particles are accelerated in the electric field and generate further charged particles through collisions with the gas molecules in an avalanche effect. This is converted into an electrical pulse at the anode or cathode.

Microstrip neutron detectors (Oed, 1988) offer a variation on the classic tube set up. Here, a grid of strips, held at alternating potential, is applied to an insulating substrate. A charged particle, produced in the gas volume above this substrate, is accelerated in the electric field producing an avalanche effect which is detected as before. This approach allows the production of large PSDs without "blind areas" as occur between detector tubes (Clergeau *et al.*, 2001).

A fundamental challenge in neutron detection is discriminating between neutrons and other types of radiation from the source such as high-energy photons (gamma rays) which unlike alpha and beta particles are not eliminated by physical barriers. In scintillation devices, neutrons and background radiation are discriminated electronically based on pulse height and/or the pulse shape typical of the radiation type. In gas counters, a "proportional counter" mode allows neutrons and photons to be electronically distinguished according to peak height.

Converter foils of a few micron thickness such as based on ¹⁵⁵Gd can be used to form neutron detecting films, image plates, and CCD devices with primarily limited to applications in imaging.

5.3.5 Applications of neutron powder diffraction

Neutron scattering has been used to address problems that are typically difficult or intractable with X-ray scattering. Neutron powder diffraction is widely used to locate light atoms in materials, for example, hydrogen in materials used in hydrogen storage or oxygen in superconducting oxides. The availability of contrast that is not possible with X-rays is also useful in other applications such as determining the occupancies of close neighbors on the periodic table (e.g., Mn and Ni). Neutron powder diffraction also has a unique niche in the determination of magnetic structures.

5.4 Resources

User facilities

- U.S. Department of Energy Scientific User Facilities information is available at http://www.er.doe.gov/bes/BESfacilities.htm
- General information regarding synchrotron and free electron laser sources is available at http://www.lightsources.org

X-ray scattering resources

The online version of the X-ray Data Booklet which contains useful information regarding absorption edges and techniques is available at http://xdb.lbl.gov

Neutron scattering resources

- Neutron scattering lengths and cross sections is available at http://www.ncnr.nist.gov/ resources/
- General information about neutron scattering including software, facilities and conferences can be found at http://www.neutron.anl.gov

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Chapter 6 Phase Identification and Quantitative Methods

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6.1 Introduction

Probably the two most common questions for the user of laboratory powder X-ray diffraction are "what's in my sample?", and "how much of it is there?" Consequently, the qualitative analysis of a new sample is often the first step for a researcher. Analysts using X-ray diffraction are fortunate in that the powder diffraction patterns are almost a unique fingerprint for a particular compound. There are instances where two unrelated compounds have practically identical patterns, but it is unusual. The power of X-ray diffraction is illustrated in Figure 6.1. Each one of the phases shown has the composition TiO₂, so would be indistinguishable using techniques such as X-ray fluorescence spectroscopy or ICP that analyze the composition of a sample. Using X-ray powder diffraction it is easy to tell which one of these forms is in the sample, or even if all three are present in the sample simultaneously.



Figure 6.1 Powder X-ray diffraction patterns of three polymorphs of TiO₂; rutile, anatase, and brookite.

6.2 Sample preparation for phase ID and quantitative analysis

6.2.1 Sample-related problems and issues

Some issues regarding sample preparation, handling and sample characteristics are common to all diffraction techniques, whilst some are of particular concern for particular applications. The analyst should have some understanding of these in order to obtain accurate results from the various techniques. Simple analysis for phase ID tends to be more forgiving in terms of sample preparation and data collection, but it can't always be ignored if an accurate result is desired from a complex mixture.

6.2.1.1 Powder average

Although it may seem obvious, one requirement for powder diffraction is that the sample is a powder. This might sound like a ridiculous statement, but the random orientation of crystallites in the sample is vital to obtain reliable relative intensities in a one-dimensional "slice" through the Debye–Scherrer cones. This begs the question "when is a powder really a powder?" This question was examined theoretically in the context of X-ray powder diffraction in an important paper by Deane Smith (Smith, 1992), that was reprinted after his death (Smith, 2001). Where the sample consists of ideal spherical particles, whether a random distribution of crystallites has been achieved depends on both the particle size, and the volume of sample being sampled by the instrument. The sampling volume varies with both the diffractometer geometry and the absorption of the sample. The sample absorption is dependent on the sample composition and density.

For a single phase sample, as a general rule, crystallites need to be 1 μ m or smaller to produce a sufficient number of crystallites (Table 6.1) to approximate random powder (Smith, 2001). Most samples analyzed do not meet these standards, which limits the accuracy of any quantitative analysis. Spinning the sample does not improve the statistics greatly. Achieving a 1 μ m particle size usually requires some effort in sample preparation with some kind of milling or grinding machine. Milling can damage the microstructure of some materials (clays are particularly vulnerable) so care must be taken. Workers analyzing challenging samples frequently use a special mill produced by McCrone that was specially designed for preparing samples for XRD and XRF analysis. Poor particle statistics can have consequences for the relative intensities of the different phases, and can be a source of significant error as seen in Table 6.2

The effects of poor particle statistics become more obvious using microdiffraction techniques. Figures 6.2 and 6.3 demonstrate this, in a comparison between the data obtained

Table 6.1	Comparison of the particle statistics for samples with different
crystallite s	izes (Smith, 1992, 2001)

Diameter (µm)	40	10	1
No. of diffracting crystallites	12	760	38 000
Crystallites per 20 mm ³	5.97×10^{5}	3.82×10^{7}	3.82×10^{10}

Table 6.2 Reproducibility of intensity from the quartz (113) reflection with different crystallite size ranges (Klug and Alexander, 1974)

Crystallite size range (µm)	15-20	5-50	5-15	<5
Reproducibility of intensity (%)	18.2%	10.1%	2.1%	1.2%



Figure 6.2 (a) Two-dimensional microdiffraction frame from an as-received cement sample, with (b) the corresponding SEM micrograph. The XRD data were obtained using a 1 mm monocapillary optic on a Bruker GADDS system (CoK α).



Figure 6.3 (a) Two-dimensional microdiffraction frame from a cement sample micronized in iso-propyl alcohol for 15 min, with (b) the corresponding SEM micrograph. The XRD data were obtained using a 1 mm monocapillary optic on a Bruker GADDS system ($CoK\alpha$).

from an as-received cement sample and one that was "micronized" for 15 min in isopropyl alcohol. The diffraction rings in Figure 6.2a are very uneven and "spotty", even though a large 1 mm collimator was used. The SEM micrograph in Figure 6.2b shows the cement to have a particle size of around 25 μ m. However, the diffraction rings from the micronized sample shown in Figure 6.3a are even and do not show any of the spottiness associated with grainy samples. The SEM in Figure 6.3b confirms that the grains are much smaller, with particles of mostly 2 μ m and below. Although 20 μ m (passes through a 600 mesh

sieve) is often quoted as being sufficient for X-ray powder diffraction, the two-dimensional frame shows that samples of this nature are still very grainy from the spotty nature of the Debye–Scherrer rings.

It should be obvious that good particle statistics become increasingly difficult to obtain for quantitative analysis of increasingly complex mixtures, as theoretically, each component of the mixture must have sufficient crystallites to form a random powder. Cements are complex, multi-phase systems, so Figure 6.3 shows that it is achievable from a practical point of view even if extremely difficult in theory.

6.2.1.2 Sample thickness

Another assumption that powder diffraction makes is that the sample is "infinitely thick" at all 2θ angles. Owing to the geometry of powder diffraction, the penetration of the beam will increase with scattering angle. Consequently if a sample is too thin, intensities obtained at higher angles will be too weak. The penetration of X-rays into the sample depends on the wavelength and the linear absorption coefficient. Therefore, what constitutes a "thin" sample can vary from sample to sample. For an angle of $60^{\circ} 2\theta$, 15 µm would be "infinitely thick" for 100% dense hematite, but 50 µm would be needed for quartz. Practically, samples are almost always porous, so allowance must be made for the lower effective linear absorption. An infinitely thick sample is ideal for reliable intensities, but it is not always optimal for the purposes of phase ID. Where the linear absorption of a material is very low (e.g., organics), then the penetration in a thick sample is such that there is a peak shift from transparency. Where accurate peak positions are more important using a thin sample on a zero-background holder (ZBH, see Chapter 3.5.4) may be preferable with such samples.

6.2.1.3 Preferential orientation

Preferential (preferred) orientation can affect quantitative analysis as well as phase identification. Certain kinds of sample, for example clays, are particularly prone to preferential orientation. This is due to their anisotropic plate-like morphology, but clays are not the only materials with this kind of particle morphology as is shown by the large plate-like portlandite grains in Figure 6.4. These particles tend to orientate, as the faces tend to lie face down when mounted on the sample holder. The most common way of mounting powder samples is the so-called top-loading mount (see Chapter 3.5.4). This mounting is particularly bad with plate-like materials as pressing the sample to obtain a nice flat surface makes the orientation of the particles at the surface even worse. Another problematic morphology is needle-shaped particles, such as exhibited by wollastonite (CaSiO₃).

A number of measures can be taken to eliminate or reduce preferential orientation. The first is to micronize the sample, reducing the aspect ratio of the particles. Micronizing benefits the powder average and microabsorption, so the conscientious X-ray analyst may already micronize samples as a matter of course. An alternative approach is to spray-dry the sample to produce spherical agglomerates with a reduced tendency to orientate (see Chapter 3.5.3). Top-loading is not the only technique for preparing a diffraction sample for analysis in reflection. Back-loading is also a common approach when orientation could be an issue, and side loading is another less common alternative (see Chapter 3.5.4). Back-loading



Figure 6.4 SEM micrograph of a Ca(OH)₂ grain in a hydrated cement material showing the layered, plate-like morphology.



Figure 6.5 Design and use of a back-loading sample holder. (a) The holder shown upside-down with a ground glass slide clipped to the bottom. (b) The sample is loaded and spread evenly in the cavity. (c) The sample is gently tamped down and held in place by a glass slide fastened with nylon screws. (d) The holder is inverted and the ground glass slide removed. The final sample surface is flat with a slight texture from the ground glass slide, but has not been subjected to the compression and shear of a top-loaded sample. Photographs courtesy of Mati Raudsepp, Earth and Ocean Sciences, University of British Columbia, Vancouver, Canada.

often requires the construction of custom sample holders, but the concept is very simple, as shown in Figure 6.5. The sample is prepared up-side down with the holder laid on a slide (often having a ground glass finish as opposed to polished). The compressive and shearing forces on the surface exposed to the X-ray beam are reduced, which significantly lowers the tendency of the particles to orientate. The use of the ground glass slide induces a slight texture in the surface that is also beneficial.

Compound	LAC (cm^{-1})	
LiF	30	
SiO ₂	89	
Fe ₂ O ₃	1181	
AI_2O_3	121	
LaB ₆ (used as a NIST reference material)	1164	
Si	139	

Table 6.3 Linear absorption coefficients (LACs) for different compounds using radiation from a copper X-ray tube (1.5418 Å)

6.2.1.4 Microabsorption

A serious problem that affects most quantitative techniques is microabsorption, otherwise known as absorption contrast. There are problems where microabsorption makes the analysis of a particular dataset impossible (Scarlett *et al.*, 2002). The severity of microabsorption is a function of the particle size and the linear absorption coefficient (LAC) of the different materials. The LAC is related to both the elemental composition (Table 6.3) and the wavelength of the radiation used to obtain the data. As a general rule, compounds containing "heavy" elements (large Z) tend to have higher values for the LAC than compounds containing "light" elements. A complicating factor in this trend is fluorescence, when an element absorbs more strongly than one might expect for its Z value. This occurs when an element absorbs a particular wavelength and then re-emits it.

In the absence of a monochromator or energy-discriminating detector, fluorescence is easily identified by an increased background that tends to increase in intensity with 2θ . Elements that fluoresce with Cu radiation include iron, cobalt, and manganese. Unlike the trend with increasing Z value, the elements that will fluoresce depends upon the energy of the X-rays, and consequently what type of X-ray tube is used. The preferred option to tackling microabsorption is to change the energy of the radiation used to collect the diffraction data. This is not practical for many laboratories, but should be considered when possible for particularly severe cases of microabsorption. Table 6.4 shows the LAC for hematite (Fe₂O₃), LaB₆ and SiO₂ for different laboratory X-ray sources.

Table 6.4 shows how the absorption characteristics of three very different compounds respond to changing X-ray energies. Quartz shows the expected increase in absorption with lower X-ray energies. Hematite shows the same trend except for a severe discontinuity for CuK α radiation. This is due to the CuK α X-ray emission energy being slightly greater than the K α absorption edge of Fe. Consequently, Fe absorbs CuK α radiation very efficiently and re-emits the energy at different energies as fluorescence, greatly increasing the effective absorption of radiation from a Cu anode tube. It may seem a little strange that the absorption of LaB₆ is lower with CrK α than for Cu, Co, or FeK α . However, Figure 6.6 shows that the La L-edges are in this energy region, and that the energy of CrK α is simply too low to excite any of the L-edges. These examples show that it is wise to compare the absorption of each mixture component for the particular X-ray wavelength being used. The

Anode	Wavelength (Å)	Energy (keV)	$\mathrm{Fe_2O_3}\;(\mathrm{cm^{-1}})$	$LaB_6 (cm^{-1})$	$SiO_2 \ (cm^{-1})$
Мо	0.71	17.5	136	149	9
Cu	1.54	8.1	1181	1164	89
Со	1.78	6.9	234	1730	138
Fe	1.94	6.4	292	2133	175
Cr	2.29	5.4	464	702	283

laboratory X-ray sources. The anodes are listed in order of increasing X-ray wavelength (i.e., decreasing energy)

Table 6.4 Variation of the linear absorption coefficients for hematite, LaB₆, and guartz for the different



Figure 6.6 Linear absorption coefficient of LaB_6 with X-ray energy. Marked features on the plot include the lanthanum L1, L2, and L3 absorption edges, together with the energies of the common X-ray tubes.

assumption that absorption of a phase inevitably increases with increasing wavelength is not always a valid one.

The extent of microabsorption is related to the particle size of the phase in question. If changing the X-ray energy is not practical, another way of reducing its impact is to micronize the sample to reduce the particle size. One could argue that this should be done in any case to improve particle statistics, but it becomes essential where microabsorption may be an issue.

A theoretical approach to correcting microabsorption was published in 1945 by Brindley (1945). The so-called Brindley correction may be useful in circumstances where the microabsorption is not too severe. In addition, it makes a number of assumptions (monodisperse particle size distributions and spherical particles) that may be problematic for a particular sample. The user needs to know the particle size and packing density of each phase before the correction can be attempted. When used with care, the Brindley correction can work fairly well, but it has been shown that incorrect use of the Brindley correction can be worse than using no correction at all (Pederson *et al.*, 2002). It should become clear to the reader that all of the sample-related problems described above are linked to particle size. If a sample is prepared with micron-sized particles:

- 1 the particle statistics will be good
- 2 microabsorption should not be as big a problem
- 3 such small particles do not tend to orientate.

Conversely, the observation of significant preferential orientation should be a clue that the particle statistics are probably suspect, and that the particles are probably large enough for absorption contrast to be severe. In some circumstances, using a different instrument geometry may improve the chances of success (Mitchell *et al.*, 2006). For instance, using a capillary in transmission geometry improves particle statistics and usually eliminates preferential orientation. Microabsorption is also eliminated, but other absorption effects now have to be taken into account.

6.2.1.5 Extinction

Extinction is rarely considered in powder diffraction data but can be significant with large crystallites of highly crystalline material such as silicon or diamond. The overall effect is to lower the intensities from the diffracted material. This will not affect phase ID, but may adversely affect the results of quantitative analysis. Large single crystal silicon and diamond grains may not be common in powder diffraction analysis, but natural quartz can be of an extremely high quality. Consequently, for practical day-to-day analysis, extinction will probably be noticed most in mineral samples where large grains of high-quality natural crystalline quartz are present. Although produced from single crystal silicon, NIST standard reference silicon has been ground to a sufficiently small crystalline material and the domain sizes are in the range of $10-20 \mu$ m, substantial extinction effects have been shown in the literature (Cline and Snyder, 1983, 1987). A correction for primary extinction effects is given in Chapter 5 of Zevin and Kimmel (1995).

6.2.1.6 Surface roughness

An additional effect on low-angle intensities can come from surface roughness. This is caused by a gradient in the density of the sample from the surface to the bulk. Diffraction from the surface of the sample has a greater contribution at low 2θ angles, so the lower density leads to lower intensities at low angles. This can be a severe issue with nanoparticles due to their generally poor packing behavior. Corrections for surface roughness have been published (Pitschke *et al.*, 1993; Suortti, 1972). They are often incorporated into Rietveld analysis software, but the corrections could be applied analytically before other qualitative and quantitative techniques if surface roughness effects are suspected.

6.3 Data collection

Although often ignored, how the data are collected may also affect the relative intensities and therefore the reliability of both phase ID and especially quantitative analysis



Figure 6.7 Geometry of incident beam divergence leading to beam-overspill at low angles. With a 0.5° divergence slit and 250 mm goniometer radius, the beam length is 25 mm at 10° 2θ whilst the sample length is 10 mm. The beam length at 45° 2θ is approximately 6 mm, therefore beam overspill will occur with any peak at 10° 2θ .

(see Chapter 3.6.1). Beam overspill is usually a problem where low-angle reflections are important, or where the analyst has to make do with a very small amount of sample. Owing to simple geometric principles, the beam from a diffractometer spreads out with decreasing incident angle. In order to obtain reliable relative intensities, it is important that the entire beam is illuminating sample, or the situation will arise as shown in Figure 6.7. In this instance, the low angle reflections will be artificially weakened. Using a 0.5° divergence slit in a diffractometer with a 250 mm goniometer radius, the beam length will be 25 mm at 10° 2θ and approximately 5.7 mm at 45° 2θ . The illumination length may be calculated using:

$$L = \frac{R\alpha}{\sin\theta} \tag{6.1}$$

where R is the radius of the goniometer circle in millimeters, and α is the divergence angle in radians. The X-ray beams tend to be narrower with parallel-beam instruments, but the effect of incident angle in beam length is still there. The obvious solutions to this include using narrower divergence slits, or a bigger sample area depending on whether the analysis requires low angles, or accurate results from very short sample lengths. One approach to avoiding this problem is the use of motorized variable divergence slits (VDS) that illuminate a fixed sample length by widening with increasing 2θ angle. This also has the effect of improving counting statistics at higher angles, and potentially improves detection limits. There can be some issues at high 2θ angles related to defocusing and peak shapes, but these are not a major concern for the techniques dealt with in this chapter. However, most analysis software requires a $1/(\sin \theta)$ intensity correction as they can only deal with fixed divergence slit (FDS) data. Such a correction is vital in intensity ratio quantitative analysis methods unless experimental ratios are determined using the same conditions. Counting statistics can be important in detecting trace impurities in a sample, and the use of variable count time data collection as an alternative to variable slits can be as effective for qualitative analysis as it is for Rietveld analysis (Madsen and Hill, 1994). The variable count time approach requires longer experiment times as it uses FDS geometry, but does not create some of the artifacts present in VDS data. An issue that can relate strongly to signalto-noise is sample fluorescence. If fluorescence from a sample is likely to occur, then the



Figure 6.8 Effect of sample fluorescence from a manganese-containing sample using copper radiation. The data collected without a monochromator has a higher background, is significantly noisier, and consequently has a much lower detection limit for weaker reflections and phases.

diffractometer should be fitted either with a diffracted beam monochromator, or a decision made to use an alternative X-ray tube if it will be a regular issue. The effect of fluorescence of copper radiation with a manganese-containing sample is shown in Figure 6.8. It is pretty obvious that picking out weak reflections, for example a weak reflection at $31^{\circ} 2\theta$ due to cation disorder, will be impossible from the dataset where a monochromator was not used.

Diffractometers tasked with routine phase ID work are often heavily used, so some thought should be given to optimizing the experimental time needed to obtain the best data that is "fit-for-purpose". Phase-ID does not require the same resolution as say traditional indexing techniques, so in many instances there is little point in using step sizes as small as 0.01° or even $0.02^{\circ} 2\theta$. In a given length of experiment this simply succeeds in producing noisy data with little or no benefit to the analysis. It is usually more effective to use slightly larger step sizes (such as $0.04^{\circ} 2\theta$) with longer count times to produce data with better signal-to-noise, and therefore better detection limits. This can be seen in Figure 6.9, where both datasets were obtained in the same time. It can be seen that the data using a 0.01° step size is noisier than that using a 0.02° step size with half the count time.

6.4 Powder diffraction as a fingerprint method

The diffraction pattern of a material is usually reduced into peak positions and intensities. The positions of the lines are related to the spacings between planes in the lattice, and the intensities depend on the atoms that lie on particular sites. It is this independence of intensity and position that leads to such a wide variety of possible patterns – much like the human fingerprint. The variation of the peak positions and intensities with elements and lattice spacings (lattice parameter) are demonstrated in Figures 6.10 and 6.11. Figure 6.10



Figure 6.9 Data from a quartz stone with two different step-size/count-time combinations that took 25 s. R_{WP} values from single peak-fitting demonstrate the better data quality with the 0.02° vs 0.01° step-size, where a smaller R_{WP} corresponds to a better fit.



Figure 6.10 Calculated X-ray powder diffraction patterns for NaCl and "KCl", where the Na is changed to K whilst keeping the lattice parameter unchanged.

shows the effect of simply swapping the "heavier" K for Na in the NaCl structure. The peak positions remain unchanged as there is no change in the lattice spacings. However, there are changes in the peak intensities, most notably the peaks marked with asterisks.

Figure 6.11 shows what happens to the pattern of NaCl when the a lattice parameter (and therefore the lattice planes in the structure) is artificially increased to that of KCl. The relative intensities do not change as the elements on the sites in the structure are the same. However, increasing the a lattice parameter increases the distances between all of the



Figure 6.11 Calculated X-ray powder diffraction patterns for NaCl (a = 5.640 Å), and for NaCl with the larger lattice parameter of KCl (a = 6.278 Å).

lattice planes in the crystal structure. This increases the *d*-spacings and so shifts the peaks to lower angles. The inverse relationship between *d* and 2θ follows from Bragg's law (see Chapter 2):

$$n\lambda = 2d\sin\theta \tag{6.2}$$

In common with the fingerprint, a diffraction pattern only helps to identify the material if there is a match with a pattern that is already known. As with all such problems it is often useful to simplify the problem by reducing the data to a smaller number of data points. This was the approach taken by Hanawalt *et al.* in 1938 (Hanawalt *et al.*, 1938), who reduced the experimental patterns to tables of *d*-spacings and relative intensities (*d*–*I*). They published *d*–*I* tables for 1000 chemical substances and paved the way for the current Powder Diffraction File (PDF) which contains over 250 000 entries. The search-match approach developed by Hanawalt in 1938 (Hanawalt *et al.*, 1938) relies on using the *d*-spacings and intensities of the three strongest lines in a pattern to identify the phase. The central role played by Hanawalt and his search-match methodology (Hanawalt, 1986) is reflected in the original printed search manuals, known as the Hanawalt manuals. An alternative to the Hanawalt is the Fink system, which uses the eight lines with the largest *d*-spacings to characterize the pattern. The Fink system does not use intensities so is complementary to the intensity-weighted Hanawalt method. Search manuals for the Fink system are also published by the International Centre for Diffraction Data (ICDD).

Before the advent of computer search-match software, trying to identify phases in an experimental pattern would usually involve the manual searching of patterns using the PDF in book form (Hanawalt, 1986). It is easy to understand that identifying an unknown phase in this way can be extremely slow, and become harder with additional phases. Where a researcher is attempting to synthesize a number of related materials then some common sense could make the process easier. Data that required hand matching was often in the form of exposed X-ray film, either from a Debye–Scherrer or Guinier camera (see Section 3.2.2 in Chapter 3). When a particular group of phases were expected, making cards marked

with pen/pencil to overlay on the films could simplify phase identification greatly. However, where a sample is a complete unknown, hand matching becomes a daunting task.

The advent of computer search-match software revolutionized the process of identifying phases in diffraction patterns. The search-match software developed in complexity along with the hardware. For instance, the original version of the structure sensitive SEARCH-MATCH was only semi-automated as it used a programmable calculator (Frevel, 1982), but was later fully automated for a HP3354 computer using a version of Basic (Filsinger and Frevel, 1986).

Despite the increase in speed, complete unknowns can still produce multiple potential hits. This is where compositional information becomes extremely important, and why the combination of tools such as X-ray fluorescence spectroscopy (XRF), inductively coupled plasma mass spectrometry (ICP) and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) with X-ray diffraction is so powerful. In the search-match of an unknown, what isn't in the sample is almost as important as elements that are present, as it significantly reduces the number of possible hits. When a sample is not single phase, compositional information can also help in determining unknowns by comparing the differences in composition of the sample with the compositions of the known phases.

A seemingly trivial change in the approach of search-match algorithms has made significant improvements in the quality of the matches. The original algorithms concentrated only on matching peaks with intensities. More recently, the absence of a peak in part of the pattern has been given as much weight as the presence of one. This approach has made the matching process less sensitive to intensity errors and preferential orientation issues. Identifying the major phases in a mixture is usually not too difficult if entries are present in the Powder Diffraction File 2 (PDF2) database. Minor phases are much more problematic. Approaches based on using calculated "residual" patterns after subtracting the major phases are quite promising in this regard.

It becomes obvious that the presence of unknown systematic errors in the data could prevent a computer-based search-match from succeeding. The most common error in diffractometers is the zero-point error. This "offset" of the θ and 2θ axes from their true positions produces a linear offset in all of the peak positions. The extent of this offset should not change significantly over time, and can easily be determined *ex-situ* if necessary by use of standard materials. Zero-point errors should be almost insignificant in a well-aligned modern diffractometer, but may occur in older, poorly maintained "work-horse" diffractometers. Sample-dependent peak shifts such as sample displacement in Bragg–Brentano geometry are more difficult to deal with. They are not usually a serious problem if the sample is mounted correctly, but all too often samples are mounted in a hurry by junior researchers/students without much thought to accuracy. The peak shift in degrees given by sample displacement is given by:

$$\Delta 2\theta = -2\Delta h \frac{360(\cos\theta)}{2\pi R} \tag{6.3}$$

R is the radius of the goniometer circle and Δh is the displacement in millimeters. By convention, the positive direction is away from the center of the focusing circle; therefore, a positive Δh corresponds to a displacement of the sample down from the optimum position. For a diffractometer with a 250 mm circle, a sample displacement of 100 μ m (i.e., down) will cause a peak shift of 0.045° at 20° 2 θ . Sample displacement has a (cos θ) angular

dependence, whilst the zero-point error is independent of scattering angle, so theoretically it is possible to distinguish between them. However, data for phase ID purposes is often only taken up to $60-70^{\circ} 2\theta$. Owing to the ($\cos \theta$) dependence, this range is insufficient to easily separate zero-point error from sample displacement, so both errors can often be lumped together as one or the other. Modern search-match software is not as sensitive to systematic errors as some of the older algorithms, and can handle significant displacements (Le Meins *et al.*, 2003).

Should it be deemed necessary, options available to determine and correct the errors are to use an internal standard, or possibly cell-parameter refinement. The peak shifts from sample displacement have a known angular dependence, so refining the unit cell of the full pattern of an internal standard allows the error to be calculated. This allows the true and accurate positions of the unknown peaks to be determined. The problem of sample displacement can also have a hardware solution. Parallel-beam optics can be supplied with many modern laboratory powder diffractometers, which are insensitive to sample displacement. This makes such instruments insensitive to what would otherwise be "poor" samples (uneven, rough, displaced), so can be attractive where inexperienced users collect their own data. Parallel-beam instruments often have lower peak resolution, but as mentioned earlier, this is not a problem for phase-ID. Zero-point errors can still occur in parallel-beam instruments, but this does not change from sample to sample and can be reduced by good alignment and maintenance.

The use of non-ambient stages to study phase behavior (e.g., decomposition at high temperatures) is becoming more popular. Although most entries in the PDF2 are for materials under ambient conditions, there are a growing number that have been collected under different conditions. In addition to the thermal expansion of the unit cell, changing the temperature in a reflection measurement often induces a vertical displacement in the sample holder itself, no matter how well aligned the sample was initially. The use of parallel-beam optics can avoid this problem, but can introduce problems of their own (Whitfield, 2003). An alternative approach is the availability of motorized and computerized stages that can automatically correct the stage displacement effects with temperature. These require careful calibration, but allow the researcher to keep the good resolution of Bragg-Brentano geometry whilst nearly eliminating displacement peak shifts in the data. A more unusual alternative would be the use of non-ambient capillary measurements. Even eliminating displacement still leaves peak shifts due to thermal expansion of the sample unit cell. This means that search-match algorithms will have great difficulty in matching at higher temperatures. Where there are significant changes in the phase composition with temperature (e.g., thermal decomposition) the easiest solution may be as simple as letting the sample cool down to room temperature. The occurrence of phase transitions may complicate this somewhat, with reversible transitions (e.g., α -quartz to β -quartz) and irreversible phase transitions (anatase to rutile) both being possible.

Despite the fact that there are thousands of entries in the databases, there are still compounds that do not appear. Where the elemental composition of the sample is known, and no match can be found, it is often productive to look for analogues that do appear in the database. Such analogues are often structurally similar and have minor differences in both peak positions and intensities, but are overall very similar in appearance. Figure 6.12 shows two analogues that are both materials used in lithium batteries, LiCoO₂ and LiNiO₂. They have the same structure type and symmetry but different lattice parameters and an



Figure 6.12 An example showing the similarities and differences between two structural analogues, LiCoO₂ and LiNiO₂.

additional electron (i.e., scattering power) in changing from Co^{3+} to Ni^{3+} . In terms of X-ray powder diffraction, cobalt and nickel are practically indistinguishable so the relative intensities are almost the same. The real difference is in the lattice parameters, to the extent that a d–I search may not reveal the analogue. In this situation it is up to the analyst to use their common sense and chemical knowledge to narrow down the possibilities for a visual match. Some search-match software allows the user to manipulate the lattice parameters of a unit cell in an attempt to find a match from a similar pattern.

Different algorithms have been developed to improve the speed and reliability of the search-match process. Search-match is so central to diffraction analysis that a Round Robin was undertaken to compare software and the contribution of user skill to the process (Le Meins *et al.*, 2003).

Certain classes of materials are known for being particularly challenging both to identify and quantify. Some of the most challenging are the clay minerals. Many clays have very similar diffraction patterns and can contain structural defects such as turbostatic disorder that can severely distort certain peaks. Additionally, the presence of stacking faults can introduce peak shifts as well as broadening, in particular classes of reflection in cubic-closepacked (ccp) structures (Warren, 1969). Stacking faults often occur in both layered materials and metals. Hexagonal close-packed (hcp) structures only show anisotropic broadening with stacking faults, and no peak shifts. In both ccp and hcp structures, twinning faults produce just peak broadening behavior (Warren, 1969). Where anisotropic broadening is present relative peak heights will be changed, and it becomes particularly important to use peak integration when accurate relative intensities are required.

6.4.1 High-throughput screening

Recent advances in powder diffraction applications and instrumentation have made data overload a reality. New detector technologies mean that conventional laboratory diffractometers are now capable of collecting good-quality datasets in 20 min that previously


Figure 6.13 Raw diffraction data of tutorial data for analysis in the PolySNAP program.

may have taken hours. Instruments have been developed specifically to carry out rapid combinatorial and high-throughput XRD screening for both research and quality control purposes. High-throughput screening has revolutionized many processes in the pharmaceutical and other industries. However, to make use of all this extra data, tools are required to extract the required information at an equally rapid pace to the data collection. In a quality control environment for instance, the analyst may be looking for a simple pass or fail vs an expected result. As is often the case, new approaches have been developed to address the needs of a growing market.

The use of cluster analysis for examining powder diffraction patterns was described extensively in 2004 (Barr *et al.*, 2004a), and is now marketed in a commercial product called PolySNAP (Barr *et al.*, 2004b). High-throughput screening often involves picking out the few different samples among a large number of practically identical ones. This makes it useful for quality control where the same result may be expected; the task being to identify the "odd" ones. Handling such a job manually would be extremely tedious, so a method is required to automate this sorting process. The patterns are matched statistically for each individual datapoint. This means all features of the patterns are used, including background features as well as the absence or otherwise of a peak. Figure 6.13 shows the raw diffraction data for 21 tutorial files included with the package. The results of the analysis may be output in a variety of graphical formats as shown in the cell display of Figure 6.14a and the dendrogram display in Figure 6.14b. The PolySNAP software can process 1500 datasets simultaneously, so is truly capable of matching the rate of output from high-throughput analytical techniques. The pattern-matching algorithm is not specific to diffraction data, so data from techniques such as NMR or FTIR could conceivably be processed and analyzed.

6.5 Phase matching using the powder diffraction file – search-match routines

Qualitative analysis of powder X-ray diffraction data is a basic requirement for most users of the technique. Consequently, all instrument vendors supply software that will



Figure 6.14 Graphical displays of the PolySNAP pattern-matching analysis in the forms of (a) a cell display and (b) dendrogram display. Tutorial data and screen grabs reproduced by permission of Professor Chris Gilmore and Dr Gordon Barr, University of Glasgow, UK, and Bruker-AXS Inc, Madison, USA.

attempt to match an experimental pattern to a database of "knowns". For most researchers, the database used is the PDF produced and sold by the International Centre for Diffraction Data (ICDD). The PDF has gone through some major changes whilst evolving from the PDF1, to the PDF2, and more recently the PDF4 format (Faber and Fawcett, 2002). An example of information retrieved from the PDF2 database for NaCl is shown in Figure 6.15.

The Mineral Powder Diffraction File (Smith *et al.*, 1999) and the Pauling file are additional databases that may be used to match experimental data. In addition to experimental



Figure 6.15 The PDF2 card 5-628 for NaCl. The image is from the PCPDFWIN software (screen grab image reproduced with permission from International Centre for Diffraction Data).

powder diffraction databases, the data in full crystal structure databases may be utilized by calculating the expected powder pattern from the structure. The structural databases (Allen, 1998) include the Inorganic Crystal Structure Database (ICSD), CRYSTMET, Cambridge Structure Database (CSD), Protein Data Bank (PDB). In recent years, the PDF database has incorporated calculated patterns from a number of sources to complement the experimental patterns it contains.

In conventional search-match analysis it is usual to do some "pre-processing" before the software is asked to start the search. The background is subtracted from the experimental pattern. This produces more reliable intensity values for the matching process. It is quite common to smooth experimental data where noise is a problem, but care must be taken not to distort the peaks in the pattern too much. It must be considered that reducing noise through smoothing will do nothing to improve detection limits, whilst increasing count times during data collection will improve them.

Most modern laboratory X-ray powder diffraction data contains peaks from both the $K\alpha_1$ and $K\alpha_2$ lines, unless an optic known as a primary monochromator or an energy discriminating detector is used. Primary monochromators are usually single crystals of Ge, and produce pure monochromatic $K\alpha_1$ radiation. They are not widely used nowadays because they can severely impact the observed intensities, but many older, historical patterns in the PDF database were taken using film-based instruments (Guinier cameras) that used a primary monochromator. There are a number of such patterns that are still regarded as high-quality data in the PDF2 database. With some software it is desirable to remove



Figure 6.16 Effect of $K\alpha_2$ stripping on an experimental pattern of LaB₆ obtained using a CuK $\alpha_{1,2}$ source. The dashed line corresponds to the raw data and the solid line to the stripped data.

the K α_2 reflections before attempting the search-match, but this depends on the preferred methodology in the software package being used. Although the results of this stripping are not perfect, it may stop some older software attempting to match K α_2 peaks at high angles, and can produce more reliable *d*-spacing values across the angular range. Once the preprocessing has been done, the user can assume a wavelength equivalent to pure K α_1 for their search-match software. The effect of K α_2 stripping on a low and high angle reflection of data from LaB₆ is shown in Figure 6.16. The stripping at high angle is quite straightforward and does not affect the K α_1 reflection. However, the peak overlap of the K α_1 and K α_2 lines at low angles means that the observed peak intensity and position changes once the K α_2 contribution is removed. This could cause some problems in matching to experimental K $\alpha_{1,2}$ PDF entries depending on the software methodology.

There are many software packages available that will perform search-match on an experimental pattern. A comprehensive list of software available (including freeware, share-ware, and commercial) is given on the CCP14 website (http://www.ccp14.ac.uk/solution/search-match.htm). All of the main instrument vendors supply software capable of carry-ing out search-match using the PDF databases, which include EVA/SEARCH (Bruker-AXS), Jade (MDI/Rigaku), and X'Pert Highscore (PANalytical). Additional stand-alone programs such as Match! (Crystal Impact, Germany), and Crystallographica Search-Match (Oxford Cryosystems Ltd, UK) are also available.

The PDF2/PDF4 databases provide an indication of the "quality" of each of the entries. The highest quality patterns (indicated by a "*") are obtained on an instrument that has been demonstrated to be well aligned and had various checks performed on the data quality. The space group and refined unit cell parameters must also be given, and no unidentified peaks can be present. Various other quality marks can be assigned to samples or data that are

less well characterized, including indexed ("I") with no more than two unidentified lines, questionable, alternate, and deleted. Additional entries are indicated for calculated and non-ambient data. It is worth remembering that certain types of samples, for example, some clays, by their nature will not have the highest quality entries, but are still perfectly acceptable for search-match purposes. The higher quality patterns can also contain information such as the density of the material, color and how it was made/sourced. Densities are required to calculate linear absorption coefficients, so the PDF can be a useful resource in many regards.

A short example of a simple search-match procedure is shown in Figure 6.17 using the EVA software produced by Bruker-AXS. The sample is a straightforward mixture of corundum and rutile, and the data is a high-quality set from a well-aligned instrument. The process starts with the usual data processing in the form of a background subtraction. The EVA software does not require $K\alpha_2$ stripping of the experimental data. It is possible that some degree of smoothing may be required if the dataset is noisy, but smoothing can introduce distortions into the data and is not desirable if it can be avoided. Once the data processing is done the options for the search-match may be set. In this case the results are restricted to inorganic materials, and only high quality, indexed experimental patterns will be considered. No restrictions based on chemistry/composition have been used in this case. To simplify more complex problems, restrictions on composition are often used in terms of excluded, possible, and included elements. In this case, the top two ranked matches are indeed corundum and rutile from all of the inorganic/mineral entries in the PDF2 database.

The ranking of matches in the search-match process is usually done on the basis of some kind of Figure of Merit (FOM). The FOM in EVA/SEARCH is derived from rules based on the presence of a line where intensity exists being a bonus, and the supposed presence of a line where no intensity exists in the experimental data leading to a penalty. However, the various user-defined options/criteria have a significant affect on the outcome, so the skill of the user is still an important factor.

6.6 **Profile fitting**

Given the reliance of the *d*-spacings in the search-match process, having accurate peak positions is very desirable. "Where is the peak?" It's a simple enough question, and the obvious answer would be to say that it is at the top of the peak where the intensity is at a maximum. Strictly speaking it isn't the correct answer (see Chapter 4), but it should be accurate enough to obtain the correct result from a search-match, especially if composition information is available, to narrow the search. If the sample is a complete unknown, then having more accurate peak positions can greatly improve the chances of getting the correct result. In laboratory diffractometers, various instrumental aberrations (described in Chapter 4) shift the actual peak position away from the point of maximum intensity. If the zero-point error of the instrument is known, accurate peak positions can considerably increase the chances of picking the correct phase from the 250 000+ patterns in the PDF.

Peak fitting may also be useful in deconvoluting overlapping peaks. In simple mixtures this may not be as important, but it can provide clues as to which reflections belong to a common phase. Convolution-based peak fitting allows for the size broadening of individual



Figure 6.17 Sequence of events in a simple search-match of experimental data in Bruker's EVA software. (a) Data treatment of the as-collected data (bottom) in the form of background subtraction (top). (b) Selection of options in the search-match. (c) Result of the search-match. (Screen-grab images of EVA software reproduced with permission from Bruker-AXS Inc, Madison, WI, USA.)

peaks to be constrained. Assuming that the broadening is isotropic, a rough assumption that the crystallite size broadening of peaks from the same phase should be identical, can be a powerful tool. Such an approach can help to determine if a material is truly single phase, or consists of two closely related phases.

6.7 Assigning hkls and cell parameter refinement

Where a search-match produces a perfect match to a good-quality entry in the database, assigning *hkl* values to the various reflections is very straightforward. Where no match can be found it becomes necessary to carry out an indexing step to determine the unit cell symmetry (cubic, orthorhombic, etc.) and the lattice parameters, from which the Miller indices may be calculated. Knowing the *hkls* of the reflections indicates which reflections are related, and will move in the same direction when changing a particular lattice parameter. Indexing generally requires high-quality data, and has historically been regarded as one of the most difficult tasks in powder diffraction with low symmetry cells. A number of programs and approaches exist to tackle the problem, probably the most commonly used being the CRYSFIRE package (Shirley et al., 1980) that provides a front-end to a number of different indexing programs that use differing mathematical approaches to the problem. One of the most novel recent developments in indexing is the singular value decomposition method (Coelho, 2003) that can index extremely large unit cells is extremely quick and even suggests a possible space group. The approach has been implemented in both the commercial and academic versions of TOPAS (Coelho, 2005). The issues surrounding indexing of a powder pattern is dealt with in more detail in the chapter on structure solution (Chapter 7).

The real power of knowing the unit cell symmetry and dimensions is the ability to refine the cell parameters against the experimental data. Refinement of cell parameters has a significant advantage in the search for accurate peak positions. In refining cell parameters it is possible to determine the value of any systematic zero-point or sample displacement error that shifts the *d*-spacing values away from their true positions. The zero-point error of an instrument may be determined using standard reference materials. However, sample displacement varies from sample-to-sample. In the absence of a cell refinement, determining the sample displacement requires the use of an internal standard, which is not always desirable.

Much research on functional materials involves the use of doping to change the properties of a compound. This can result in a whole series of related materials known as a solid solution, with slightly different compositions and very similar diffraction patterns. The PDF2 database contains many such series of compositions. In many instances there is a structural phase transition from one structure type to another with changing composition, producing two different solid solution series. One method for determining which composition is correct is to determine the lattice parameters. Most substitutions produce subtle, but noticeable changes in the lattice parameters. Where the calculated pattern matches one of the known compositions, the search is then finished. However, should no exact match be found, it can still be possible to determine the phase composition from a unit cell refinement. The approach relies on Vegard's law, which states that the change in lattice parameter with composition is linear in the absence of a phase transition. Using cell parameter information on



Figure 6.18 Plot showing Vegard's law for La_{1-x} Sr_x FeO₃ between x = 0.3 and 0.6.



Figure 6.19 Raw diffraction data from Sm_{0.2}Ce_{0.8}O_{1.9} (SDC).

"end-members", it is possible to determine the composition of the unknown. An example is shown in Figure 6.18 for a region of solid solution behavior in $La_{1-x}Sr_xFeO_3$. Where an unknown sample in the $La_{1-x}Sr_xFeO_3$ series falls in this range (i.e., has the same cell symmetry) it would be possible to extrapolate the composition with some confidence.

The use of peak fitting/cell refinement can also help determine whether a sample is truly single phase. Figure 6.19 shows the raw data from a material that was claimed to be nanoparticulate single-phase samarium-doped ceria (SDC); a material used as a solid electrolyte in solid oxide fuel cells. The nominal composition was $Sm_{0.2}Ce_{0.8}O_{1.9}$ where the oxygen vacancies provide a path for oxide-ion diffusion. Indeed, the pattern shown in Figure 6.19 looks single phase, but the peak broadening exhibited by nanomaterials can obscure the presence of secondary phases. Such phases are quite possible in solid-solution systems such as SDC, if the reaction has not been properly finished, and may have a profound impact on the functional properties of the material. A closer look at the data using the TOPAS software (Coelho, 2005) tells a different story. The analysis was done using a Pawley cell refinement, but an approach using size-constrained fitting of the individual peaks can



Figure 6.20 Single-phase Pawley fit to a cubic Fm3m cell. The difference plot shows significant and systematic problems.



Figure 6.21 Pawley fit after adding a second cubic Fm3m cell to the refinement. The misfit disappears, and the lattice parameter of the second phase refines to that expected from pure CeO₂.

also be used. The difference plot from the Pawley fit shown in Figure 6.20 reveals some serious misfits in the main reflections that have the same, systematic error. Ceria is often used as a simple, cubic well-behaving material in demonstrating peak-broadening behavior in nanomaterials, so no unusual anisotropic character in the peaks would be expected. The unit cell parameter derived from the fitting is similar to those for an SDC material, but not as close as could be expected for the particular composition. Adding a second unit cell into the refinement produces an excellent fit as shown in Figure 6.21. The second cell has a unit cell parameter practically identical to undoped ceria and has a smaller crystallite size. The

multi-phase nature of the sample was confirmed by the poor properties of the material as a fuel-cell electrolyte.

6.8 Quantitative phase determination in the absence of structural information

Quantitative analysis is one of the most important industrial applications of X-ray powder diffraction, and often plays a role in quality control. Although the possibility was first suggested in 1919 (Hull, 1919), the first real-life applications of quantitative X-ray diffraction were published in 1925 by Navias (Navias, 1925) on quantifying mullite in fired ceramics, and in 1936 by Clark and Reynolds (1936). The subject of the 1936 paper was one that will be recognized by many workers today – the analysis of mine dusts for quartz. Clark and Reynolds added a fluorite standard to correct for absorption, but the mathematical relationships describing the effects of absorption on quantitative analysis weren't published until 1948 by Alexander and Klug (1948). These authors went on to describe the practice of quantitative analysis in their comprehensive book on X-ray powder diffraction (Klug and Alexander, 1974). A more modern text on the subject was authored by Zevin and Kimmel in 1995 (Zevin and Kimmel, 1995), and covers the various techniques in detail. Unfortunately it is currently out of print, but a more concise and inexpensive text published by the Mineralogical Society of America (Bish and Post, 1989) is still available.

A number of different methods have been described to carry out quantitative analysis using X-ray diffraction data over the years. Many of these are now rarely used, but in some circumstances can still be valuable tools for the analyst in particular circumstances.

The most recent developments in quantitative analysis have centered around the use of the Rietveld method which is covered in Chapter 8. However, there is still a role for the other techniques available to the analyst. One weakness of the Rietveld method is the requirement for crystal structures for each of the phases in the mixture. In an interesting example of convergence, the same least-squares minimization techniques used in Rietveld refinements are being applied to RIR techniques and analysis using observed rather than calculated patterns.

6.8.1 Spiking method

The spiking (or doping) method can be used when the analyst has a pure supply of the phase α to be quantified, and the mass absorption of α is similar to the sample matrix. It is analogous to the method of standard additions used in X-ray fluorescence spectroscopy. The method is quite general, the only requirement being that a reflection without overlaps must be visible from a phase (β) other than the one being quantified (α). The identification of phase β is not important for the quantification process. In a sample mixture containing α and β , the ratios of the intensities from a line of each phase may be obtained from equation (6.4).

$$\frac{I_{i\alpha}}{I_{j\beta}} = \frac{K_{i\alpha}\rho_{\beta}C_{\alpha}}{K_{j\beta}\rho_{\alpha}C_{\beta}}$$
(6.4)



Figure 6.22 Spiking method to derive the unknown concentration of phase α (C_{α}) by standard additions of α (Y_{α}).

where C_{α} is the concentration of α , ρ_{α} is the density of α , and $K_{i\alpha}$ is a constant for a given phase α and diffraction line *i*. After adding a mass Y_{α} of phase α to the mixture containing an unknown amount of α , the equation describing the ratio becomes:

$$\frac{I_{i\alpha}}{I_{i\beta}} = \frac{K_{i\alpha}\rho_{\beta}(C_{\alpha} + Y_{\alpha})}{K_{i\beta}\rho_{\alpha}C_{\beta}}$$
(6.5)

that can be simplified to:

$$\frac{I_{i\alpha}}{I_{j\beta}} = K(C_{\alpha} + Y_{\alpha}) \tag{6.6}$$

Plotting $I_{i\alpha}/I_{j\beta}$ vs Y_{α} for a series of additions will produce a straight-line plot, where the slope is *K*, and C_{α} is the –(intercept) as shown in Figure 6.22.

Problems will occur with this constant absorption method if the addition of phase α significantly changes the mass absorption of the sample. Approaches to applying the spiking method where the mass absorption changes significantly are detailed in Zevin and Kimmel (1995), but it becomes significantly more complicated and becomes much less attractive for routine analysis.

6.8.2 Dilution method

The dilution method differs from the spiking method, in that the added material should not constitute any of the phases to be analyzed. The material may be crystalline or amorphous, but should have a known mass absorption coefficient. Should the diluent be crystalline, measurements of the diffraction peaks are not necessary. An advantage of this approach is that measurement or calculation of the sample mass absorption (μ^*) is not necessary. It does require measurements of both the diluted and undiluted samples. Once again, the addition of material means that the method is not entirely non-destructive. The details of

the mathematics may be found in Zevin and Kimmel (1995). If M_d is the mass of the diluent and M_s the mass of the sample, the weight fraction, c_d , of the diluent is given by

$$c_d = M_d / (M_s + M_d) \tag{6.7}$$

After working through some mathematics, the concentration of the unknown phase *j* in the diluted sample is given by

$$c_j(1 - c_d) = \frac{c_j M_s}{M_s + M_d}$$
(6.8)

The mass absorption of the diluted sample is given by

$$(\mu)_d^* = \mu_d^* c_d + (1 - c_d)\mu^* \tag{6.9}$$

where μ_d^* is the mass absorption of the diluent and μ^* is the mass absorption of the sample. Solving the equations describing the original and diluted sample for the original weight fraction c_i produces:

$$Kc_{j} = \frac{I_{ij} (I_{ij})_{d}}{I_{ij} - (I_{ij})_{d}}$$
(6.10)

 I_{ij} and $(I_{ij})_d$ are the intensities of the *i*th diffraction peak of phase *j* before and after dilution. *K* is a constant which may be determined by plotting for a number of standard samples where *K* is the slope and c_j is the argument. Once *K* is known, it can be used to calculate the phase abundance in unknown samples.

The chosen diluent must meet a number of requirements. Diffraction from the diluent must not interfere with the peaks from the sample. Amorphous materials will not produce interfering Bragg reflections, but they can add significant background under the peaks of interest, which is also undesirable. The diluent should have negligible fluorescence and have a similar mass absorption coefficient to the sample of interest. Ideally, it should be easy to mix uniformly with the sample as a fine powder and be un-reactive. In order to reduce the expected errors to a minimum, the optimal dilution level occurs when the peak intensity drops to 1/3 of its original, undiluted intensity. In practical terms this means a 2:1 ratio of diluent to sample where the absorptions are similar.

A derivation of this technique can be used to reduce the variability of absorption in a range of dissimilar samples. In this approach, the diluent is deliberately chosen to have a relatively high absorption. If sufficient diluent is added, this will equalize the absorption of the samples. A consequence of large dilutions, are that the intensities from the phase to be analyzed are significantly reduced. This has an obvious effect on the counting statistics and generally requires a very strong reflection to maintain a respectable detection limit. However, where the reflection is sufficiently strong, it does allow for the quantification of a phase in diverse mixtures without the need for finding suitable standards for each sample.

6.8.3 Internal standard method

The use of standards or reference materials is one of the oldest techniques for dealing with matrix absorption problems. The basis of the method is that weight fraction of the phase of interest is a linear function of the ratio of the intensities of the standard and the phase of interest. The intensity ratio is independent of the sample absorption, although the absorption of the standard should match that of the sample to avoid microabsorption.

The concentration (C_{α}) of a phase α in the sample is a linear function of the intensity ratio with the standard phase *s*:

$$\frac{I_{\alpha i}}{I_{js}} = K \frac{C_{\alpha}}{C_s} \tag{6.11}$$

where *K* is a constant that may be determined from the slope of a plot, from a series of measurements on various two-phase mixtures of the phase of interest (α) and the chosen internal standard (*s*). Once the calibration has been carried out, the concentration of phase α in the diluted sample may be calculated by simple rearrangement:

$$C_{\alpha} = \frac{I_{\alpha i} \times C_s}{I_{js} \times K} \tag{6.12}$$

The weight fraction, C_{α} of phase α in the original sample is then given by

$$C_{\alpha} = \frac{C_{\alpha}}{1 - C_s} \tag{6.13}$$

It should be remembered that the use of peak heights instead of integrated intensities can be unreliable. The internal standard is often highly crystalline, and the ratio of peak intensities will be affected by peak broadening behavior. Using integrated intensities avoids this issue.

Microabsorption causes the linear relationship between concentration and intensity ratio to break down, invalidating the results. The presence of microabsorption effects can be detected in the calibration graph with pure phases. Should the calibration plot be non-linear then the presence of microabsorption should be suspected.

Peak overlap between the standard and sample should be avoided, and particle statistics should be considered to yield reliable intensities. The chosen standard should have strong reflections to avoid the need to add large quantities to obtain sufficient particle statistics. This normally means a high symmetry crystal structure with fine, spherical grains. The need to match the absorption of the standard to the sample led to the release of the SRM674 set of diffraction intensity standards (Hubbard, 1983).

One characteristic of the internal standard method is that the analyst does not need to quantify all of the phases in a mixture simply to quantify a single phase of interest. These additional phases may be complete unknowns or even amorphous. If the weight fractions of all the known phases are added up, the quantity of "unknown" material may be quantified by a shortfall in the mass balance from 100%.

6.8.4 Reference intensity ratio

The reference intensity ratio (RIR) method (Davies, 1988; Zevin and Kimmel, 1995) is a particular case of the internal standard approach (see Section 6.8.3), and is often one of the most accessible for the X-ray analyst. Many entries in the PDF contain the information required, and data analysis packages supplied by instrument vendors can often use the

RIR data to produce a quick, semi-quantitative result. More sophisticated, Rietveld-like full pattern matching has recently appeared, for example in the Bruker-AXS EVA software, that uses RIR values. This technique uses least squares to minimize the same R_{wp} residual as a Rietveld analysis would, but without crystal structure information.

The concept behind the most common RIR method is to provide an intensity ratio of the 100% intensity peak of a phase (I_{α}) to the 100% (113) peak (I_{cor}) of corundum in a 50:50 mixture (effectively yielding the calibration constant *K*):

$$\frac{I_{\alpha}}{I_{cor}} = K \frac{C_{\alpha}}{C_{cor}} \tag{6.14}$$

The availability of RIR values from the PDF2 or elsewhere, means that it may not be necessary to experimentally determine the calibration constant, K, depending on the accuracy required. Literature values will be perfectly adequate for semi-quantitative analysis, but greater accuracy will be obtained if the ratios are determined experimentally on the same instrument to be used for the analysis. There are some assumptions during this calibration process, which may, or may not be problematic. There is normally an assumption that the corundum and phase being referenced are 100% crystalline. An amorphous fraction in either or both will lead to error in subsequent analyses. The NIST SRM676 corundum quantitative analysis standard (Reed, 1992) has recently been recertified with an 8 wt% amorphous content (Kaiser, 2005), demonstrating how assumptions such as this may adversely impact the accuracy of results. The use of variable slits will distort the relative intensities, so an angular ($1/\sin \theta$) correction must be applied to the intensities from VDS data.

If the RIR ratios are known for each of the phases present, a "standardless" analysis may be undertaken without the addition of any corundum as an internal standard. Theoretically, any phase could be used as the reference material, but corundum was chosen for practical reasons of accessibility and tendency not to orientate in a powder. Of course, one may use a reflection other than the 100% peak where the reduced relative intensity is taken into account. This could be done for a couple of reasons. The first may be that the 100% reflection has a serious overlap with another phase. A second may be the use of multiple reflections for a single phase to produce a more reliable result. The use of multiple reflections may also ameliorate issues such as mild preferential orientation.

There is one particular disadvantage in using the standardless RIR approach as opposed to adding a known standard (corundum or otherwise). While an amorphous content may be determined using an internal standard approach, the standardless RIR technique is only sensitive to crystalline proportions and may completely miss a significant portion of the sample.

The linear absorption coefficient of corundum is quite low at 125 cm⁻¹. Many phases of interest will have significantly higher absorptions, so the results when determining an experimental RIR could be severely affected by microabsorption. SRM676 corundum has a particle size of approximately 0.5 μ m, but unless the rest of the sample is of a similar size, problems may arise. Where a standard with a higher absorption than corundum is required, the set of reference materials in NIST SRM674 or SRM674a may be a suitable alternative. This set contains a number of phases with a range of absorption coefficients, together with certified RIR values for CuK α radiation (Hubbard, 1983) (see Table 6.5).

	LAC (cm^{-1}) [CuK α]	Reference intensity ratio
α -Al ₂ O ₃	124.9	1.00
ZnO	288.0	5.43
TiO ₂	549.5	3.44
Cr_2O_3	952.1	2.16
CeO ₂	2082.9	14.1

 Table 6.5
 Linear absorption coefficients and certified RIR values for the SRM674 diffraction intensity standards (Hubbard, 1983)

6.8.5 Clay analysis

Clay analysis often requires some additional work to obtain accurate results for both qualitative and quantitative analysis. Many clay minerals have very similar powder diffraction patterns, making even a basic qualitative analysis more difficult. Some approaches are used that tend to be specific to clay analysis. The analysis of clays can be an instance where deliberately inducing preferential orientation can be beneficial. This maximizes the intensities from the basal plane 00*l* reflections that are often a key diagnostic tool. This may even involve separating the layered clay minerals from other components such as quartz to improve the orientation. Another technique involves the use of chemical treatments to selectively expand the layers of particular clay phases, so helping to pinpoint which particular one is present.

Clay minerals often have poorly defined crystal structures, sometimes making the use of the oft-preferred Rietveld quantitative analysis impractical. However, full pattern techniques can sometimes cope with effects such as preferential orientation that single line techniques struggle with. In these instances, full pattern techniques not requiring a detailed crystal structure may be preferable, as described in the following section.

6.8.6 Full pattern quantitative analysis without a structure

The technique described by Smith *et al.* (1987) for the use of full patterns is somewhat analogous to a full-pattern RIR method in that the method is calibrated using the addition of corundum to standard samples (Smith *et al.*, 1987).

The Rietveld and structureless approaches to quantitative analysis have been converging for years, with Smith (Smith *et al.*, 1988) describing the simultaneous use of calculated and observed patterns in an analysis (Smith *et al.*, 1988). The analysis of experimental patterns uses a least-squares method, minimizing the expression in:

$$\delta(2\theta) = I_{\alpha}(2\theta) - \sum_{p} M_{p} R_{p} I_{p}(2\theta)$$
(6.15)

where $I_{\alpha}(2\theta)$ and $I_p(2\theta)$ are the diffraction intensities at each 2θ interval for the unknown phase α , and each of the standard phases, p, respectively. R_p is the RIR for the phase p, and M_p is the weight fraction.

It is now possible within some Rietveld analysis software for some or all of the phases to have unknown structures. The "observed" pattern approach does not necessarily require



Figure 6.23 Quantitative analysis results for the PolySNAP tutorial data when a library of standard patterns is available. The results for MIXT_1 and MIXT_2 are now shown as pie-charts corresponding to the proportions of each phase present.

a unit cell, but the lack of a unit cell requires a very close match between the standard "observed" pattern and that in the sample. An excellent recent example using a modern Rietveld analysis package was the use of a calibrated, observed pattern for nontronite (Scarlett and Madsen, 2006) combined with calculated ones for other phases for a full-pattern quantitative analysis.

The PolySNAP software described earlier can also carry out full-pattern quantitative analysis where a library of comparison patterns is available. Figure 6.23 shows the output from PolySNAP when a library of standard patterns is available. The datafiles are the same as those for Figure 6.14. The graphical cell outputs for the analysis of MIXT_1 and MIXT_2 are now shown as pie-charts, corresponding to the quantification results. MIXT_1 is found to be a mixture of forms B, C, and E, whilst MIXT_2 is a mixture of forms A, D, and E. More detailed results can be extracted from the numerical results. A quantification of amorphous contents may also be attempted if an amorphous fraction is suspected.

6.8.7 Quantification of amorphous content

The quantification of amorphous fractions is increasingly being regarded as an important component of an overall analysis. Some techniques described above, for instance the internal standard method, allow the analyst to calculate amorphous contents by adding up the crystalline phase fractions and taking the difference from 100%. A more simplistic approach is to measure the so-called "amorphous hump". Correctly identifying the background is very important for this. An integration of this very broad peak can give an indication of the amorphous content. Indeed, in the TOPAS software package (Coelho, 2005) a single

peak added to fit an amorphous background can be used to automatically calculate the amorphous content, but any software capable of peak fitting will suffice. Amorphous content determinations tend to be very sensitive to microabsorption problems, so care should be taken to minimize them.

6.8.8 Errors

Error analysis is often a neglected aspect of quantitative analysis. Errors can accumulate from a number of factors related to the sample, data collection, and the instrumentation. Many of these factors have been discussed earlier in this chapter, and correct propagation of these errors is required to obtain a realistic understanding of the accuracy of results. The equations relating to propagation of counting statistic errors are given in Snyder and Bish, 1989. Simple approaches such as using multiple repetitions of the analysis procedure can reduce some of the errors associated with particle statistics and preferential orientation for instance, but systematic errors such as microabsorption would remain.

6.9 Conclusions

Phase ID is probably the most common application for laboratory X-ray powder diffraction, and is used by everyone from the experienced practitioner to the "greenest" undergraduate student. Such is the power of modern instrumentation, software and databases, that more often than not, the beginner will obtain the phase information that they require without a good understanding of the concepts involved. However, there are still a significant number of phase ID problems for which there is no "get out of jail free" card. In these cases, knowledge and experience, both in the practical and theoretical aspects of powder diffraction, can be key to finding the correct solution.

Quantitative analysis has always required a bit more thought on the part of the analyst, and this is still the case. Certain experimental aberrations that are given scant regard in phase ID must be addressed to obtain reliable quantitative results. In many instances, equipment vendors provide software that can assist in performing analysis using a variety of methods, and these still have their place despite the ascendance and popularity of quantitative Rietveld analysis.

It is apparent that good sample preparation is highly desirable for qualitative and especially quantitative analysis using X-ray powder diffraction. Powder average, preferential orientation and microabsorption are all related to particle size, so ensuring that the particle/crystallite sizes are small enough is usually enough to avoid their worst effects. Sample preparation is also important for X-ray techniques discussed in other chapters of this book, so is equally relevant (in some cases more so) for other applications of X-ray powder diffraction analysis.

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Chapter 7 Structure Solution

Armel Le Bail

7.1 An overview of structure solution by powder methods

Powder diffraction is generally the first-choice characterization technique applied to solid state samples in chemistry laboratories for a qualitative analysis. Most of the times, the sample is identified successfully (Chapter 6). When no known crystal structure matches with the powder pattern, and if no single crystal of suitable size can be prepared, then the challenge for a successful structure determination by powder diffractometry (SDPD) may start. The "suitable" single crystal has a minimal size that can be decreased a lot if you can employ high-energy X-ray beam (providing the crystal will tolerate it long enough without collapsing). For instance, tetracycline hydrochloride ($C_{22}H_{25}N_2O_8Cl$) was proposed as one of the two samples during the 1998 SDPD Round Robin (Le Bail and Cranswick, 2001), it was also simultaneously structurally characterized by the use of high-intensity synchrotron radiation (Station 9.8 at CLRC, Daresbury Laboratory) from a $0.04 \times 0.03 \times 0.02$ mm single crystal (Clegg and Teat, 2000), and the free refinement of all H atoms was possible (not from powder data). Conventional laboratory X-ray sources would give diffraction data too weak to be useful with such a small organic single crystal. This warning is to recall first that a single crystal study is always easier and preferable to an SDPD, when possible.

If the SDPD is decided upon, the main difficulty comes from the fact that the threedimensional information corresponding to a single crystal study is lost by a statistical average. From powders, you get one-dimensional data along the diffracting 2θ angles: imagine a sphere reduced by projection onto a circle and the circle reduced to a single line starting at the sphere center, all diffraction peaks being now along this line. As a consequence, the handicap is severe. Systematic and accidental overlapping complicate all SDPD steps: indexing, solution, and refinement, especially the latter two, because overlapping increases enormously at higher diffracting angles and indexing is mainly realized from the low and medium diffracting angle data.

7.1.1 Abundance of tools attempting to reduce the handicap

The description of the many possible ways for a successful SDPD as a complex maze is famous (in the first of two recent books dealing with this topic (David *et al.*, 2002; Pecharsky and Zavalij, 2003)). A beginner can easily be lost there, ignoring which button to press. Another possibility to describe in brief the messy SDPD topic is the logo (Figure 7.1) of



Figure 7.1 Logo of the SDPD mailing list (http://groups.yahoo.com/group/sdpd/).

the SDPD mailing list (Le Bail and Cranswick, 1999) showing a disordered stacking of software and methods: they are too many to make a quick simple decision without training. If nothing can be done without computer programs, which one to use, why, and when, are the essential questions. This chapter tries to provide advice and directions. Very different strategies will have eventually to be chosen, depending on the level of knowledge about the sample: chemical content more or less established, probable presence of defined polyhedra or of molecules of which a three-dimensional full description is available, and so on. The more the knowledge about the sample, the more complex structures can be solved with relative ease, though certainly not routinely for the more complex of them. Complexity itself does not have a simple definition in the SDPD topic, and this will be discussed.

7.1.2 Evolutions and revolutions

The recent expansion of the SDPD topic during the last 20 years is clear from the quasiexponential increase in the number of published papers (Figure 7.2). Ten or twenty years ago, there were respectively 300 or 30 published SDPDs (Le Bail, 2001b), to be compared to more than 1300 today. After a long and slow evolution during which SDPD could be realized only after the cumbersome process of extracting manually the peak intensities, and then applying classical Patterson or Direct methods, two revolutions occurred. Both have waited a decade before being really admitted. Only the references corresponding to a few landmark papers are given here, the whole bibliography, including more than 50 review papers, is available at the SDPD-Database (Le Bail, 1995). The first revolution during the years 1981–1988 corresponded to the possibility to extract quickly and automatically large quantities of peak intensities by the Pawley (Pawley, 1981) and Le Bail (Le Bail *et al.*, 1988) methods by cell constrained whole powder pattern decomposition techniques (Le Bail, 2005b). The second revolution corresponded to the birth of the so-called direct-space methods during the years 1989–1997, by Monte Carlo/simulated annealing, grid-search techniques (Deem



Figure 7.2 Cumulative histogram of the number of published SDPD papers.

and Newsam, 1989, 1992; Newsam *et al.*, 1992; Solovyov and Kirik, 1993; Harris *et al.*, 1994; Masciocchi *et al.*, 1994), applied to the location of individual atoms or molecules, and then by genetic algorithms (Kariuki *et al.*, 1997; Shankland *et al.*, 1997a; Harris *et al.*, 1998). Obviously, both revolutions have benefited from the incredible increase of the personal computer power and capabilities, as well as from the impressive resolution improvements associated with the third-generation synchrotron machines. Meanwhile, the Patterson and direct methods were adapted to the powder diffraction handicap (peak overlapping) and their efficiency was continuously improved up to now (Cascarano *et al.*, 1992; Rius, 1999, 2004; Altomare *et al.*, 2006b), including finally direct-space features as well.

The number of published papers per year, dealing with new structures determined from powder data, is now close to 200, doubling every 4 years, but this is still 200 times less than from single-crystal data: a very small crystallography niche. A full SDPD always includes the Rietveld refinement at the ultimate step (Chapter 8), but here the first D for "determination" in SDPD means the *ab initio* establishment of the atomic coordinates, excluding to obtain them by the simple recognition of an isostructural compound at the identification stage (in such a case, the Rietveld refinement is directly possible). The domain of SDPD applications is large, to all cases where suitable single crystals are lacking, including many topics of interest: characterization of pharmaceutical polymorphs, pressure-induced phase transitions, openframework materials such as zeolites, titanosilicates, hybrid materials, vitamins, proteins (exceptionally), and so on.

7.1.3 Powder diffractometry in 10, 20, or 50 years?

Nowadays, there is already an alternative route which could well be considered as a third future revolution. Results of blind tests about molecule packing prediction are available

(Day *et al.*, 2005), this approach provides series of cell candidates ranked by energy. Enumeration/prediction is also possible for some framework solids belonging to welldefined topological classes like zeolites (4-connected 3D nets) (Treacy *et al.*, 2004) and more generally to the family of N-connected 3D nets with N = 3-6 and mixed N-N' frameworks (Le Bail, 2005a). Then, the corresponding calculated powder patterns can simply be combined with search-match identification programs for "immediate structure determination," or predetermination... This is a bit of a dream and far from being generalizable yet. Some especially spectacular and lucky cases can be counted on less than the fingers of one hand (Férey *et al.*, 2004, 2005).

On the other hand, the young "charge flipping" algorithm (Oszlányi and Sütő, 2004) may become successful enough and render obsolete some of the structure solution methods described in this chapter, but it is too early to be definite. The influence of progress in computers will certainly continue. There is a clear current tendency to install multiprocessors at homes, and this is favoring algorithms based on Monte Carlo or genetic process being in use for indexing and structure solution (in direct space). Combining multiple powder patterns and/or multiple characterization tools (electron diffraction, NMR) is another trend.

Anyway, once the SDPD is decided, the first unavoidable step, if the structure prediction methodologies cannot solve your problem immediately, is to index the powder pattern. In this chapter, the practical aspects of structure solution from powder diffraction data will be shown through the application of a few selected academic open-access software to some relatively simple examples (knowledge in structure solution from single-crystal data would facilitate the comprehension).

7.2 Indexing a powder diffraction pattern: a bottleneck

Indexing is the attribution of *hkl* Miller indices (Chapter 2) to the powder pattern peaks according to a probable cell. The problem looks simple since a maximum of six parameters $(a, b, c, \alpha, \beta, \gamma)$ will completely characterize the most complex cell (triclinic) and only one parameter is required for a cubic cell. If 20 peak positions can be estimated from the powder pattern, then the problem is largely overdetermined in all cases. However, the solution is not always straightforward because of several reasons: inaccuracy in peak positions (due to zero-point error, sample misplacement, low resolution, bad crystallinity), the presence of impurities providing spurious additional peaks, the possibility to miss some large high-symmetry cells which can also be described in smaller sub-cells of lower symmetry, the fact that one of the *a*, *b*, *c* parameters can be very short if compared to the two others (dominant zone) so that the first diffraction peak involving it through the *hkl* Miller indices may not be included among the first 20 which will be exclusively *h0l* lines, for instance (if *b* is small), and so forth.

It is hard to be sure that a sample is single-phase. However, some keys for a successful indexing can be summarized: the powder pattern resolution should be maximal, avoiding too much preferred orientation; the tools used for peak position hunting and indexing should be the best on the market; the figures of merit (FoM) have to be well understood so as to be able to save time by discarding the poor quality suggestions of the indexing programs; further checking by post-indexing visualization is recommended in case of good quality multiple equivalent propositions; finally, cell-constrained whole pattern fitting has

to be the penultimate test in order to be convinced enough before attempting the structure solution (solving the structure being the ultimate proof). Fortunately, indexing powder diffraction data is one of the crystallography topics still respecting the traditional way of sharing openly academic computer programs. There are three classics: *ITO* (Visser, 1969), *TREOR* (Werner *et al.*, 1985) and *DICVOL* (Boultif and Louër, 2004) which were placed in competition with some more recently released ones through a series of benchmarks, concluding (Bergmann *et al.*, 2004) that if all programs produce excellent results with excellent data, not restricting oneself to a single indexing program can considerably increase the chances of success in the general case.

7.2.1 Starting with a simple case: Y_2O_3

The estimation of the peak positions for the Y_2O_3 conventional laboratory powder pattern (get file N°81 in PowBase (Le Bail, 1999)) is summarized in Figure 7.3 by using *WinPLOTR* (Roisnel and Rodriguez-Carvajal, 2001). The detected peaks (a task generally made by second derivative calculations) can be saved in different formats prepared for various indexing computer programs. Even if some very small peaks (having intensity <1% of the most intense) are not yet taken into account, this should allow for giving a first try



Figure 7.3 WinPLOTR saving the Y₂O₃ peak positions for an indexing computer program.

Y_2O_3								
! Wavelength, zero point and NGRID (NGRID=3: black box mode)								
1.54056 0.00	00 3							
! List of 2thet	a positions, intensity (min.=20)							
20.504 141	11.							
29.157 111	198.							
33.791 263	32.							
35.910 531	1.							
37.921 135	5.							
39.848 606	ó.							
41.700 118	3.							
43.488 881	1.							
46.889 271	1.							
48.528 421	13.							
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51.685 66.								
53.207 506	ó.							
54.697 117	7.							
56.169 404	4.							
57.614 260	03.							
59.035 563	3.							
60.433 471	1.							
61.811 194	4.							
63.178 149	Э.							

 Table 7.1
 Typical data for indexing in automated mode with *McMaille*

which will be attempted by using *McMaille* (pronounce MacMy), a recent software applying a Monte Carlo algorithm to indexing (Le Bail, 2004a). The data prepared by *WinPLOTR* for *McMaille* are listed in Table 7.1.

Running *McMaille* provides a summary of the results on the screen, reproduced in Figure 7.4. In this case, *McMaille* is working in the so-called "black box mode." Less information is exploited on areas such as peak positions, intensities, wavelength, and a null zero point (this is a global constant for the approximation of angular shift due to systematic errors from both instrumental – if misaligned – and sample – if not in the diffracting plane – effects that you should absolutely never neglect). In the black box automated mode, *McMaille* follows its own strategy: testing first the highest symmetries, down to triclinic, staying inside of some predetermined maximum limits of cell parameters and volumes, and finally it may stop before attaining triclinic cells if some high-quality solution is detected. All indexing programs have such maximal default values which the user has to know, by reading the manuals, and which he may modify if no result is obtained.

The essential points to examine in the output file of any indexing program are the FoMs, generally noted M_{20} and F_N (de Wolf, 1968; Smith and Snyder, 1979). The higher the values of these two FoMs, the more plausible are the corresponding cells. *McMaille* proposes two additional FoMs: R_p and McM_{20} . The first is equivalent to the profile R factor in Rietveld fits (Chapter 8), so that the smaller it is, the better is the fit on the pseudo-powder pattern

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Figure 7.4 *McMaille* displaying its best results for Y₂O₃.

reconstructed by *McMaille* from the peak positions and intensities. The second is defined according to:

$$McM_{20} = [100/(R_p * N_{20})] * Br * Sy$$

where N_{20} is the number of possibly existing lines up to the 20th observed line (for a primitive *P* lattice). *Br* is a factor arbitrarily set to 6 for *F* and *R* Bravais lattices, 4 for *I*, 2 for *A*, *B*, *C*, and 1 for *P*. *Sy* is a factor equal to 6 for a cubic or a rhombohedral cell, 4 for a trigonal/hexagonal/tetragonal cell, 2 for an orthorhombic cell, and 1 for a monoclinic or triclinic cell. In Table 7.2 are compared the M_{20} and F_{20} proposed without taking account of extinctions (*P* lattice) with the R_p and McM_{20} corresponding to the 10 best *McMaille* solutions for the Y_2O_3 powder pattern (they are many more than given in Figure 7.4, where only those below a specified R_p are listed for a given symmetry).

These results illustrate all the difficulty of indexing (sometimes said to be more an art than a science) which is to detect the most probable solution(s) in a list which can be long. McM_{20} appears, in this case, to be the best at separating clearly the most probable cubic *I*-centered solution, due to the consideration of both symmetry and Bravais lattice. According to (F_{20} , M_{20}) and R_p , the best solutions would be respectively Nos. 9 and 5. The *McMaille* program will not always stop as it has done here, it may well examine all symmetries down to triclinic. In black box mode, it will stop if a solution with $R_p < 0.02$ is found. In that case, an orthorhombic solution (No. 5) with $R_p = 0.015$ was detected with a very small cell volume (149 Å³), which is exactly 1/8 of the retained cubic solution. The cubic cell volume is also a multiple of many other cells in Table 7.2, and having a look

Ν	IN	FoM <i>McM</i> ₂₀	Rp	F ₂₀	<i>M</i> ₂₀	$\begin{array}{c} \text{Volume} \\ (\text{\AA}^3) \end{array}$	V/V_1	a (Å)	b (Å)	с (Å)	Bravais lattice	Symmetry
1	20	1226	0.032	145	162	1192.1	1.00	10.603	10.603	10.603	I	Cubic
2	20	401	0.023	211	230	297.9	0.25	7.4961	7.4961	5.3021	Р	Tetra
3	18	381	0.060	448	507	421.3	0.35	7.4967	7.4967	7.4967	Р	Cubic
4	18	310	0.038	289	324	344.1	0.29	8.6576	8.6576	5.3008	Р	Hexa
5	20	305	0.015	256	290	149.0	0.12	7.4985	3.7476	5.3011	Р	Ortho
6	17	207	0.066	420	478	243.2	0.20	6.1205	6.1205	7.4976	Р	Hexa
7	19	193	0.069	351	358	172.1	0.14	7.4988	7.4988	3.0601	Р	Tetra
8	18	175	0.039	198	213	421.3	0.35	7.4978	7.4978	7.4949	Р	Tetra
9	17	111	0.144	471	530	217.6	0.18	8.6575	8.6575	3.3520	Р	Hexa
10	18	97	0.038	226	246	210.7	0.18	7.4957	5.3022	5.3006	Р	Ortho

Table 7.2 Figures of merit as produced by *McMaille* for the 10 most probable Y_2O_3 cell candidates, sorted according to the largest *McM*₂₀ (the best solution according to the different FoM are in bold)

IN: Number of indexed lines.

 V/V_1 : Ratio of the cell volumes of the Nth proposition in the list by the first.

at the volume ratio is generally highly informative. The ultimate decision has to be made by the user, always. A high-level training in crystallography will help a lot to make this correct decision. In this case, solutions with small R_p are proposed in cubic ($R_p = 0.032$), hexagonal ($R_p = 0.038$) and tetragonal ($R_p = 0.023$) and if *McMaille* had not stopped at the orthorhombic symmetry ($R_p = 0.015$), it would have provided cells also in monoclinic and triclinic symmetries, probably with even lower R_p values.

Are all lines indexed? In black box mode, whatever the number of lines given, *McMaille* will work only by using the first 20 lines, and has a default tolerancy of three unindexed lines. The number of not indexed lines is provided (parameter Nind in Figure 7.4). All lines are indexed in cubic, tetragonal and orthorhombic (Nind = 0). Further verifications would have to be made in manual mode, and also by using other indexing computer programs. Will any attempt be that "easy"? Certainly not. Indexing is really a bottleneck. *McMaille* prepares a file for a Rietveld-like fit (a .prf file) for the best solution which you can see by using *WinPLOTR*. The plot corresponding to the cubic cell is shown in Figure 7.5. The vertical bars note all lines that should be there if the lattice was primitive (*P*). A lot are lacking in this case corresponding to the extinction condition h + k + l = 2n.

Some computer programs perform automatically every SDPD step (indexing, space group suggestion, solving the structure, refining, producing Fourier difference map), like *EXPO* (indexing with *N*-*TREOR* (Altomare *et al.*, 2000)): you may decide to use these programs first, and if they fail already at the indexing step, you may go back to some standalone computer programs.

7.2.2 A case a bit more difficult: τ -AlF₃

Computer programs for hunting the peak positions are numerous (see session 2 of the open-access SDPD Internet Course (Le Bail *et al.*, 2001)), academic (*WinPLOTR*, *PowderX*,



Figure 7.5 WinPLOTR displaying the McMaille best cell for Y₂O₃.

etc.) or commercial (EVA, Highscore, Jade, etc.). Let us try now PowderX (Dong, 1999) on the τ-AlF₃ powder pattern (Le Bail *et al.*, 1992) (get file No. 1 in PowBase (Le Bail, 1999)). It is corrected for a large zero-point error (0.3°) due to the fact that the sample was dusted on the sample holder for avoiding preferred orientation (remember that you should never try to index without having defined the zero point). Dusting a sample on the holder through a sieve allows for reducing preferred orientation effects. But since this enlarges the peak widths, it is not recommended at the indexing stage: press slightly the sample for a better resolution (no such problem with synchrotron parallel beam or capillaries). Typical excellent minimal peak FWHM (full width at half maximum) are, for well crystallized compounds: 0.04–0.06°(2 θ) for conventional laboratory instruments (CuK α) and 0.005–0.01°(2 θ) for third-generation synchrotron sources. Note that a 0.02° FWHM at a synchrotron source with a 0.7 Å wavelength is equivalent to 0.04° in your lab with a copper target. The zero-point correction can be done before indexing by two methods: mixing a reference compound with the sample or using the harmonics technique. Let us consider that you know how to do these "simple" things. If not, see sessions 2 and 3 of the SDPD Internet Course (Le Bail et al., 2001).

The τ -AlF₃ conventional powder pattern as seen with *PowderX* after removing the background, stripping $K\alpha_2$, and peak search is displayed in Figure 7.6. You might also play with the zero-point correction system detecting harmonics inside of *PowderX*. Remove those weak peaks with intensity <1% of the most intense one, keeping the first at low angle. Peaks at low angles are essential even if they are weak. Start *McMaille* and see the results. Cells with R_p close to 5% appear in tetragonal, orthorhombic, monoclinic, you may stop the calculation by typing *K* (large character), and then think ... which cell is the good



Figure 7.6 Peak position hunting with *PowderX* for τ-AlF₃.

Table 7.3 Figures of merit as produced by *McMaille* for the five most probable τ -AlF₃ cells (the best solution according to different FoM are in bold)

N	IN	FoM <i>McM</i> ₂₀	Rp	F ₂₀	M ₂₀	Volume (Å ³)	V/V_1	a (Å)	b (Å)	с (Å)	Bravais lattice	Symmetry
1	19	276	0.134	18	16	2991.5	1.00	14.409	14.409	14.409	I	Cubic
2	19	160	0.062	14	11	2989.3	1.00	14.427	14.427	14.362	1	Tetra
3	19	111	0.091	11	10	2987.0	1.00	14.393	14.393	14.419	1	Tetra
4	19	110	0.076	77	70	747.3	0.25	10.201	10.201	7.1818	Р	Tetra
5	19	74	0.058	76	67	373.6	0.125	5.1025	5 10.196	7.1816	Р	Ortho

IN: Number of indexed lines.

 V/V_1 : Ratio of the cell volumes of the Nth proposition in the list by the first.

one in Table 7.3? Again there are several possibilities. Remember that high symmetry cells can be proposed in a lower symmetry. In that case, the tetragonal cell with smallest volume (747 Å³) seems to have chances to be the correct one. *McMaille* produces files with .ckm extension which can be read by the *Chekcell* program (Laugier and Bochu, 2003), which may help to decide by visualization. All of the cells with the highest FoMs have volumes multiple of 374 Å³, corresponding to the orthorhombic cell No. 5 in Table 7.3. The use of *Chekcell* allows to compare, Figure 7.7. At this stage, it is difficult to really decide, however, two of the three first large cells have large R_p values, so that there is a chance that the cell



Figure 7.7 Examining using *Ckekcell* the list of most probable τ-AIF₃ cells from *McMaille*.

would be tetragonal subcell with parameters a = 10.2 Å and c = 7.2 Å (No. 4 in Table 7.3), giving success to the traditional M_{20} and F_N FoMs this time. One intense impurity line was obvious to the chemist (this is α -AlF₃), explaining that never more than 19 of the 20 selected lines are indexed (it should have been removed, indeed). Whole profile fitting (Pawley or Le Bail methods) would provide some more convincing argument (a perfect fit) and would allow to decide for some space group possibilities.

7.2.3 C₁₄H₁₂O₄ synchrotron data – even more difficult?

The synchrotron powder pattern for dimethyl-2,6-naphthalenedicarboxylate (Kaduk and Golab, 1999) (file No. 89 in PowBase (Le Bail, 1999)) was recorded at the X3B1 beamline, $\lambda = 1.15023$ Å. Let us come back to *WinPLOTR* for the peak position extraction. In principle, synchrotron data corresponds to parallel beamline so that the zero point is null. This time the file is saved for *TREOR*, increasing the limit of the FoM to be 50. Because this is synchrotron data, you may expect high FoMs. Beginners may be tempted to retain 60 or more lines, but this would be an error. Using more than 20 may even obscure the results since ambiguities in the *hkl* attribution increase at large diffracting angles. *TREOR* can be executed inside of *WinPLOTR*, resulting in the screen shot of Figure 7.8. With that indexing software, seeing the statement "YOU HAVE GOT AN INTERESTING RESULT !!!" is given only if M_{20} is obtained better than your specifications (or than a default value) which was 50 here, it may announce a correct solution. *TREOR* runs much faster than *McMaille*. It is

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better to apply it first. In that case, $M_{20} = 131$ is immediately convincing enough for going to the next step (whole powder pattern fitting).

7.2.4 Tetracycline hydrochloride – synchrotron data

For this Round Robin sample (Le Bail and Cranswick, 2001) (file No. 17 in Powbase (Le Bail, 1999)) measured at $\lambda = 0.692$ Å, let us try again *WinPLOTR* and save the results for *DICVOL04*. This program is generally much faster than *McMaille* but is a little bit longer than *TREOR* for low symmetries (monoclinic and triclinic), so, the recommendation would be to start with *TREOR*, then to use *DICVOL04*, and finally *McMaille* if no convincing result is obtained. *ITO* brings generally no more interesting cell candidates. The sample was in a capillary, explaining the amorphous component seen in Figure 7.9. *DICVOL04* produces an orthorhombic cell with $M_{20} = 94$ which is again sufficiently convincing for going directly to the next SDPD step. With more than 2218 Å³, this cell may have escaped to a search by some programs having volume default values generally limited to 2000 Å³. A simple way to deal with large cells (proteins for instance) without changing the default values of the



Figure 7.9 Activating *DICVOL04* in *WinPLOTR* for indexing the tetracycline hydrochloride synchrotron powder pattern.

indexing programs is to give a fictitious wavelength being 2, 5, or 10 times smaller than the true one. Then, the resulting cell parameters will be 2, 5, or 10 times smaller that the actual ones.

7.2.5 Indexing final recommendations

Not obtaining results with *TREOR*, *DICVOL04*, or *McMaille*, you may consider trying with *CRYSFIRE* (Shirley, 2003), a package adding several other programs to them. Consider also to use *N*-*TREOR* (either standalone or inside of *EXPO*) instead of *TREOR*. Visit the Indexing Benchmarks Web pages (Le Bail, 2004b) comparing the performances of many indexing programs (including commercial ones), and see why using *ITO* may not be very interesting. Once a convincing cell is obtained, it is advisable to have a new look at the crystal structure databases in order to see if some compounds having escaped to the search-match step are not more or less fitting (isostructural compounds with different-enough cell parameters). Data quality remains the most important factor in indexing, and great care should still be invested in recording the powder pattern. Obtaining both the highest resolution and the highest accuracy should be the primary aim, since in general all programs are likely to yield an obvious solution with high FoM for such data.

7.3 Space group determination, intensities extraction

From the (generally) 20 or more peaks considered at the indexing stage, one may obtain a suggestion for a Bravais lattice, but the space group determination needs more efforts. At this step, a cell-constrained whole pattern decomposition should be performed. It would provide more confidence into the indexing results and allow to see more clearly if some extinction rules are really present, by performing further statistical automated analysis of the reflection intensities or careful visual examinations by an expert in crystallography. Many techniques were used up to now in order to extract intensities with the target to refine a crystal structure from powder diffraction data (Le Bail, 2005). Before the availability of personal computers, the simplest method consisted in weighting the intensities by hand. This was possible for isolated reflections. Peaks were cut out of the printed paper representation (selecting the largest possible scale), by using scissors, and then the weight of the pieces of paper were measured, with a balance. Alternatively, the peak surfaces were carefully measured by a planimeter, a funny surface integrator for which you needed good eyes and dexterity. You could really solve simple problems from intensities extracted by these methods. In a sense, you already extracted inaccurate intensities in precedent paragraphs, because intensities are a by-product of peak position estimation software. But extraction of "accurate" intensities is the subject of this paragraph, using specific computer programs performing a whole profile analysis. If this was done in the past without cell constraint (fitting peaks individually), the dominant approach is now to use the cell parameters as a constraint for the estimation of the angular reflection positions.

7.3.1 Whole pattern refinement with cell constraint

The revolution came with the Pawley method as described in a paper entitled *Unit-cell* refinement from powder diffraction scans (Pawley, 1981). The main purpose was to refine cell

parameters from the whole pattern; however, the possibility to use the extracted intensities as the starting point for the application of direct methods was clearly offered by the author. Similar to the Rietveld method (Rietveld, 1969), the Pawley method was not recognized as a revolution for a long time. In the *Pawley method*, profiles are analytical, their width is constrained to follow a Caglioti law (Caglioti et al., 1958) with the three refinable parameters U, V, W as defined in most of the Rietveld-derived computer programs (Chapter 8). The main difference compared to the Rietveld method is that the intensities are themselves considered as refinable parameters. Slack constraints are introduced for stabilization of the intensities of those reflections overlapping exactly or too closely. So, the reflection positions are constrained from the knowledge of cell constants. The cell parameters are themselves least-squares - refined during the process if the user chooses to do so. Taking the case of a powder pattern with 1000 reflections as an example, the number of parameters to be refined when applying the Pawley method is close to 1010 (the 1000 intensities + one to six parameters for the cell + the zero point + one or two profile shape parameters + the U, V, W). This leads to a pretty matrix which should be reversed in the refinement process (and consider 10010 for the 10000 reflections of the dreamed synchrotron pattern). Indeed, the version available in 1987 was limited to a maximum of 300 reflections. The user had to cut the data into several pieces for some complex crystal structures. Current versions have been improved.

A quite different process was proposed and applied in 1988 (Le Bail et al., 1988). The algorithm proceeds by iterations of the Rietveld decomposition formula (which evaluates the so-called " $|F_{obs}|$ " used in any of the Rietveld programs in order to propose the Bragg reliability factor $R_{\rm B}$ and $R_{\rm F}$ and to allow for Fourier difference map calculations) so that the only parameters refined are the cell and profile parameters (a dozen parameters maximum whatever the number of reflection intensities to be extracted). The starting proposition corresponds to a set of reflections as determined by the cell and space group, to which are allocated arbitrarily the same structure factor amplitude values (say $|F_{calc}| = 100$.). The new extracted " $|F_{obs}|$ " become the $|F_{calc}|$ at the next iteration. With so few parameters to refine, the method is quite fast, stable and efficient. Those reflections which are strictly overlapping are naturally equipartitioned by the process. Efficiency does not mean exactness. One cannot pretend recovering the information definitely lost in powder diffraction as the data is reduced to one-dimension. " $|F_{obs}|$ " is given within quotes to indicate that they are not really observed since they are estimated by a process which makes them to depend on the $|F_{calc}|$: they are biased in both Rietveld and Le Bail methods. Nowadays, various modifications of the Pawley and Le Bail methods are in use, representing the main approaches for extracting structure factors from a powder pattern.

Trying to define the space group, when not using an automated system, one has to perform first an intensity extraction selecting a primitive space group without extinction in the symmetry considered. If the cell looks orthorhombic, that first whole pattern fitting will be made with the *Pmmm* space group, or with P2/m if monoclinic, P4/mmm if tetragonal, and so on. If a Bravais lattice different than *P* was suggested by indexing, then this will be checked very fast, for instance if a *C*-centered lattice was suggested for an orthorhombic cell, realizing the whole pattern fitting either in *Pmmm* or in *Cmmm* will produce fits with similar quality, that is similar R_p and R_{wp} reliability factors (same definition as for the Rietveld method), otherwise, if the Bravais lattice is not *C*, the profile *R* factors will seriously increase. The fit will only be slightly better in *Pmmm* than in *Cmmm*, because the additional peaks in the former will accidentally improve the global fit at some places, but a careful visual examination will confirm that no additional peak is really there. The process is tedious, checking by categories (*h*00, 0*h*0, 00*l*, *hk*0, *h*0*l*, 0*kl*, etc.) if an extinction rule can be established. Generally, some ambiguity will remain, pointing finally at several possible space groups.

7.3.1.1 Intensity extraction and space group determination for Y_2O_3

At this stage, the cell No. 1 in Table 7.2 looks quite convincing. The best is then to extract the intensities by a whole pattern fitting for each of the space groups remaining in competition. A meticulous examination of the angular ranges where there should be extinction is required. Extraction is realized here by the Le Bail method as implemented in the Rietveld *FULLPROF* computer program (Rodriguez-Carvajal, 1993). Other academic Rietveld or standalone software which can carry out such Le Bail fit calculations are *GSAS*, *RIETAN*, *MAUD*, *LHPM*, *WinMprof*, *EXPO*, *EXTRACT*, *PowderCell*, *AJUST*, and so on (see the CCP14 web site). Accidental or systematic overlap do not simplify the space group evaluation job. In that case, the true space group *Ia*-3 is suggested after the observation that there could be the extinction rule (0kl : k, l = 2n). But the suggestion is made only after a fit in the *Im*-3*m* space group (Table 7.4) and only from the 310 and 730 reflections because the 330, 510, 530, 550, 710 all have systematic overlap (note that the intensity equipartition

in the <i>la</i> -3 final space group)							
No.	h	k	Ι	20	"I _{obs} "		
1	2	0	0	16.706	4.9		
2	2	1	1	20.497	295.2		
3	2	2	0	23.711	0.8		
4	3	1	0	26.558	1.1		
5	2	2	2	29.146	2509.9		
6	3	2	1	31.540	12.4		
7	4	0	0	33.781	606.5		
8	3	3	0	35.897	62.3		
9	4	1	1	35.897	62.3		
10	4	2	0	37.911	26.8		
11	3	3	2	39.838	152.5		
12	4	2	2	41.690	23.4		
13	4	3	1	43.477	107.6		
14	5	1	0	43.477	107.6		
15	5	2	1	46.886	71.9		
16	4	4	0	48.521	1111.3		
17	4	3	3	50.116	29.8		
18	5	3	0	50.116	29.8		
19	4	4	2	51.674	7.1		
36	7	3	0	67.170	1.1		

Table 7.4 Intensities extracted by a Le Bail fit in the Im-3m space group from the Y₂O₃ powder pattern (in bold the reflections forbidden in the Ia-3 final space group)

No.	Space group	Rp	R _{wp}	Number of <i>hkl</i>
1	lm-3m	19.8	25.5	324
2	I4/mmm	11.7	15.2	875
3	I4/mmm	14.3	18.1	875
4	P4/mmm	7.91	11.7	476
5	Pmmm	11.4	15.4	465

Table 7.5 Differentiating possible cells by cell-constrained whole powder pattern fitting for τ -AlF₃ (best solution in bold)

applies for these reflections with the same $h^2 + k^2 + l^2$ summation). The couples or profile reliabilities (R_p and R_{wp} in %) obtained with the Pm-3m, Im-3m, and Ia-3 space groups were respectively (8.58, 11.7), (8.65, 11.7), and (8.65, 11.7), and this was inconclusive. This shows how the manual estimation of the possible space group can be tedious, and requiring good knowledge of the extinction rules. Moreover, any automatic estimation would not have been really more efficient.

7.3.1.2 τ -AlF₃

From the five cells in Table 7.3, the Le Bail fits made by using space groups without extinction are at that time much more explicit. The R_p and R_{wp} couples are given in Table 7.5. Then, finding if there are some special extinctions, one may suspect h + k = 2n for hk0 (Table 7.6) but this needs the visual inspection to verify if the 300 and 410 reflections are existing or not (Figure 7.10), however, they are very close to other intense reflections. Once their absence is more or less established, the P4/nmm or P4/n space groups become probable and a new Le Bail fit in P4/nmm confirms that the R_p and R_{wp} (7.70 and 11.4%) do not increase.

7.3.1.3 C₁₄H₁₂O₄

Lower symmetries may sometimes lead to more obvious interpretations than high symmetries for which several space groups will frequently correspond to the same extinction rules. For instance, the series of 16 indistinguishable space groups *P*3, *P*-3, *P*312, *P*321, *P*3*m*1, *P*31*m*, *P*-31*m*, *P*-3*m*1, *P*6, *P*-6, *P*6/*m*, *P*622, *P*6*m*m, *P*-6*m*2, *P*-62*m*, and *P*6/*mmm* represents one of the worse situation for a SDPD!

One of the most common errors by newcomers in crystallography is to search only for extinctions corresponding to standard space groups. In this way, one will find possibly $P2_1/c$ (h0l, l = 2n), but will fail to identify $P2_1/n$ (h0l, h+l = 2n) or $P2_1/a$ (h0l, h = 2n), being other descriptions of the same space group No. 14. In the case of $C_{14}H_{12}O_4$, trying P2/m or $P2_1/c$ produces similar relative good fits (Figure 7.11), whereas trying $P2_1/a$ or $P2_1/n$ allow to reject immediately these hypothesis (because intense lines are not taken into account in the calculations, leading to very big R values). Nevertheless, the fit quality with the best hypothesis is not that good ($R_p = 17.0, R_{wp} = 17.3\%$) and a more careful examination reveals that there is a strong anisotropic broadening (Chapter 4), another plague on the SDPD route.
No.	h	k	1	20	"I _{obs} "
1	1	1	0	12.284	23.9
2	0	0	1	12.334	96.0
3	1	0	1	15.100	4701.0
4	2	0	0	17.406	2992.9
5	1	1	1	17.442	1680.1
6	2	1	0	19.480	0.0
7	2	0	1	21.389	10585.4
8	2	1	1	23.121	8507.5
9	2	2	0	24.713	2190.5
10	0	0	2	24.814	527.3
11	3	0	0	26.238	148.9
12	1	0	2	26.333	5999.3
13	3	1	0	27.684	4763.2
14	2	2	1	27.707	4999.7
15	1	1	2	27.775	3231.
16	3	0	1	29.086	5335.8
17	3	1	1	30.408	462.6
18	2	0	2	30.471	1613.2
19	3	2	0	31.660	2.0
20	2	1	2	31.741	11.7
21	3	2	1	34.096	300.3
22	4	0	0	35.231	7.4
23	2	2	2	35.304	156.3
24	4	1	0	36.353	12.6
25	3	0	2	36.424	286.8
26	3	3	0	37.445	2.4
27	4	0	1	37.463	3.6

Table 7.6 Intensities extracted by a Le Bail fit in the *P*4/*mmm* space group from the τ -AlF₃ powder pattern (in bold the reflections forbidden in the *P*4/*nmm* final space group)

7.3.2 Probabilistic approaches for the space group determination

Visual inspection may lead to ambiguous results about the presence or absence of reflections, producing a list of possible space groups. Probabilistic approaches were developed for space group automatic estimation. Intensities and their correlation matrix extracted via the Pawley method were used through a procedure based on a Bayesian probabilistic approach (Markvardsen *et al.*, 2001) to check the probability of each extinction group compatible with the crystal system under consideration. Another approach uses the statistics of the normalized intensities, as extracted by the Le Bail method) (Altomare *et al.*, 2004a). It is found that in general, only a small number of extinction symbols are relatively highly probable and a single extinction symbol is often significantly more probable than any other. However, experts have the tendency to verify by themselves the suggestions of these



Figure 7.10 The Le Bail fit of the τ -AlF₃ conventional laboratory powder pattern by using *FULLPROF* and the *P*4/*mmm* space group, showing the possible (*hk*0, *h* + *k* = 2*n*) extinction rule.



Figure 7.11 The Le Bail fit of the $C_{14}H_{12}O_4$ synchrotron powder pattern by using *FULLPROF* selecting the $P2_1/c$ space group.

automated approaches. The efficiency of these algorithms depends a lot on the quality of the intensities extracted by a Pawley or Le Bail fit. The quite important weakest lines themselves depending on careful background estimation, from a high-quality pattern (not too noisy, etc.). For a recent thorough discussion about the extraction and use of correlated integrated intensities with powder diffraction data, see Wright (2004) and references therein.

With one or several space group hypotheses at hand, the next SDPD step can be undertaken, structure solution *stricto sensu*.

7.4 Classical (Patterson and direct) methods of structure solution

The so-called classical methods are those applied most frequently to single-crystal data, with increasing efficiency since more than 30 years: the Patterson or direct methods (Giacovazzo, 1992). When these methods are applied to powder data, the extracted intensities are required, so that the overlapping handicap is back. Without paying special attention to this problem, things are just like if you try to study a very bad "single" crystal, totally affected by merohedral twinning and even more. In practice with powder data, the exact overlapping of two reflections leads to the following proposal: the two reflections are given the same " $|F_{obs}|$," this is the so-called equipartition. Of course, this choice is obviously false, however this is the most acceptable proposition we can do at this stage. Three main approaches were developed, trying to overcome the overlapping problem:

- 1 Removing as far as possible the dubious equipartitioned data. This may work if no more than 50% of the data are removed up to $d_{(hkl)} = 1$ Å for the direct methods, or up to 80% with Patterson method if only a few heavy atoms have to be located. With this approach, the same software as those generally used for single-crystal structure solution (*SHELX* (Sheldrick, 1990), *SIR* (Burla *et al.*, 2005), *MULTAN* (Declerq *et al.*, 1973), etc.) can be directly applied to such "cleaned" powder data.
- 2 Restricting the possible solutions by applying relations between structure factors derived from direct methods and the Patterson function: enforcing the positivity of the electron distribution map, the positivity of the Patterson function (David, 1987; Jansen *et al.*, 1992; Estermann and David, 2002).
- 3 Multiplying the number of direct method solution tests made on different datasets obtained by modifying randomly the original equipartition (Altomare *et al.*, 2001). This increases the chances for success, and is possible because of the very short computing time needed for realizing one direct method solution test with the current algorithms and computers.

It would be preferable to eliminate reflections according to the degree of overlap as a percentage of the diffracting-angle-dependent-FWHM rather than to use a fixed proximity value. However, the *OVERLAP* software (Le Bail, 1988) simply eliminates a reflection if it has a neighboring one at less than δ (°2 θ). If the application of the direct and/or Patterson methods is unsuccessful with the complete dataset, then the game consists in applying them to reduced datasets with $\delta = 0.01$ and then 0.02, 0.03, 0.04° (2 θ), and so forth.

The choice of the method (direct or Patterson) is suggested by the presence or not of "heavy" atoms. There is no difference here with the strategies recommended for a singlecrystal study. The optimal conditions for determining a structure from the direct methods (when the initial model for starting a refinement will be larger than 2 or 3 independent atoms) correspond to a dataset going up to 1 Å resolution ($2\theta \max \sim 100^{\circ}$ for a Cu $K\alpha$ wavelength). No more than 50% of the reflections corresponding to this resolution should be discarded by the above OVERLAP program if one expects some significant result by the direct methods. Frequently, the structure is determined by using the whole dataset. This may be considered amazing when the number of false structure factors is as high as 50% or even more. One can think that the false structure factors are randomly false (by the equipartition process) so that the direct methods process, which consists in searching for order, is not affected a lot. The consequence of random errors will be to increase a background above which the peaks associated with the order may still be located. It will be however more and more difficult to find these order-related-peaks when the true information is more and more diluted. Let us see some simple applications.

7.4.1 Patterson method for Y_2O_3

The Patterson method, also called the "heavy-atom" method, is especially suited for the finding of a few heavy scatterers from X-ray diffraction data (but see how the Patterson method may have some revenge in Burla *et al.*, 2006). The yttrium large atomic number suggests that this method would work with Y_2O_3 . From the 201 intensities extracted in the *Ia-3* space group, the *SHELXS* computer program is applied. The instruction file is short (Table 7.7), the longer part consists in the list of symmetry cards (still no automatic recognition of the space group by its Hermann–Mauguin notation in the academic version).

In a first test, all the 201 reflections are used, in spite of the large errors due to equipartition of strictly overlapping reflections. This results in a suggestion for two independent yttrium atom positions (Table 7.8). The trained crystallographer eye should first look at the peak intensity (or atom number = at. no.) and at the minimum distances between atoms for being convinced of the seriousness of a solution. This supposes to have some knowledge in the usual crystal chemistry in the system under study.

Indeed, using the *OVERLAP* software for removing the reflections closer than $0.02^{\circ}(2\theta)$, only 19 peaks are not eliminated (<10%), but this is again sufficient for obtaining exactly the same result with the two yttrium positions. At this step, the Rietveld method is applied, and we may discard the oxygen atom *SHELXS* propositions. The cell and profile parameters established at the Le Bail fit are kept fixed. The two yttrium atoms are inserted in the *FULLPROF*.pcr file, and only the scale factor is adjusted in a first step. Then a few Rietveld refinement cycles are done with more parameters (the *z* coordinate of atom Y1, and one common isotropic thermal *B* factor for both Y atoms), the Rietveld *R* factors decrease to $R_p = 30.9$, $R_{wp} = 40.1$ (background removed), $R_B = 28.1$, $R_F = 11.8\%$. A Fourier difference map is then performed. This can be done either by using the tools associated with *FULLPROF* (the *GFOURIER* software) or *SHELXL* (or else). One clear peak on the Fourier difference map is located at distances close to 2.3 Å from the Y atoms, in general position, corresponding to 48 equivalents, completing the Y₂O₃ formula. Adding this oxygen atom to the Rietveld refinement allows to complete the structure (still not refining the profile

 Table
 7.7
 SHELXS
 shortest
 instruction
 file
 for
 the

 Patterson
 method

 </

TITL Y2O3 D8-Bruker
CELL 1.5406 10.6048 10.6048 10.6048 90.0 90.0 90.0
ZERR 1 0.0010 0.0010 0.0010 0.0000 0.0000 0.0000
LATT 2
SYMM $x + 1/2, -y + 1/2, -z$
SYMM $-x, y + 1/2, -z + 1/2$
SYMM $-x + 1/2, -y, z + 1/2$
SYMM y, z, x
SYMM $-y + 1/2, -z, x + 1/2$
SYMM $y + 1/2, -z + 1/2, -x$
SYMM $-y, z + 1/2, -x + 1/2$
SYMM z, x, y
SYMM $-z, x + 1/2, -y + 1/2$
SYMM $-z + 1/2, -x, y + 1/2$
SYMM $z + 1/2, -x + 1/2, -y$
SFAC Y O
UNIT 32 48
PATT <- command prescribing the Patterson method
HKLF 3
END

 Table 7.8
 Results from the SHELXS automated Patterson solution for Y2O3

Name	At. no.	X	у	Z	SOF	Mini	mum dist	ance
							Self first	
Y1	41.7	0.5000	0.7500	0.4999	0.5000	3.75		
Y2	41.2	0.2500	0.7500	0.2500	0.1667	5.30	3.75	
O3	9.9	0.3758	0.8758	0.6242	0.3333	3.75	2.29	2.31

parameters), decreasing the *R* factors to $R_p = 8.84$, $R_{wp} = 11.7$ (background removed), $R_B = 2.45$, $R_F = 1.88\%$. It would be time then to refine all parameters together (see Chapter 8).

The large insensitivity of the Patterson method to the elimination of up to 80% of the data (even more in this case) explains the success of early SDPDs on simple structures based on the presence of a small number (1 or 2) of independent heavy atoms. For more than 2 independent atoms, the Patterson method begins to have difficulties with data disturbed by overlapping problems. However, the tetracycline test sample structure could be solved by the Patterson method ("seeing the Cl atom and a few others") during the SDPD first Round Robin, a kind of "tour de force" which can be realized sometimes by experts.

Colution 1

Heavy-a	atom assignm	ents:						
,	x	У	Z	SOF	Height			
Y1	0.4873	0.0000	0.2500	0.5000	504.1			
Y2	0.7500	0.2500	0.2500	0.1667	459.8			
Atom	Peak	X	у	Z	SOF	Di	stances a	nd angles
Y1	0.	0.4873	0.0000	0.2500	0.500	0	Y2	3.846
						0	1	2.221
						0	2	2.380
Y2	0.	0.7500	0.2500	0.2500	0.167	0	Y1	3.846
						29	1	2.297
						56	2	2.285
1	233.	0.3795	0.1292	0.3747	1.000	0	Y1	2.221
						22	Y2	2.297
						34	1	2.698
2	161.	0.6256	-0.1256	0.1256	0.333	0	Y1	2.380
						0	4	2.991
						7	Y1	2.380

Table 7.9 Direct methods results by *SHELXS* for Y_2O_3

7.4.2 Direct methods for Y_2O_3

Do the direct methods also work well in this simple case? There is only a little change in the *SHELXS* instruction file, replacing the command line "PATT" in Table 7.7 by a line "TREF." Results are shown in Table 7.9. The answer is yes, and even the oxygen atom is located better than with the Patterson method in that case. This is why most crystallographers generally first use the direct methods nowadays, even if there are some heavy atoms: they will appear at the top in the list of suggested atom positions, anyway. A 29-independent-atoms structure, β -Ba₃AlF₉, was solved in 1993 (Le Bail, 1993) after the finding of the 7 independent heavy Ba atoms by the direct methods from X-ray data, whereas the structure could not be solved by the Patterson method. However, the direct method would not work in the Y₂O₃ case on the dataset reduced to less than 10% by the *OVERLAP* software.

There is a gap between the peak heights of the two Y atoms in Table 7.9 (504 and 460) and the height of the next peaks (233, 161) supposed to be possible oxygen atoms. Such gaps allow for the atom attribution. The last peak in the list with height 161 being an artifact.

7.4.3 Direct methods for τ -AlF₃

By using the space group P4/nmm, 447 " $|F_{obs}|$ " were extracted up to 145°(2 θ). The cell volume suggested 16 formula units per cell. For inorganic compounds, the deduction of

Peak	Atom	X	у	Z	SOF
334.	Q1	0.2500	0.2500	0.0918	0.1250
328.	Q2	0.2500	0.2500	0.5857	0.1250
323.	Q3	0.5848	0.2500	0.6704	0.5000
259.	Q4	0.5000	0.0000	0.0000	0.2500
150.	Q5	0.6181	0.0512	0.1667	1.0000
149.	Q6	0.6287	0.1287	0.5000	0.5000
130.	Q7	0.3750	0.1250	0.0893	0.5000
124.	Q8	0.2500	0.2500	0.3612	0.1250
123.	Q9	0.2500	0.2500	0.8440	0.1250
105.	Q10	0.2500	0.0550	0.5910	0.5000
92.	Q11	0.7500	0.2500	0.7668	0.2500
78.	Q12	0.5137	0.1789	0.7389	1.0000
65.	Q13	0.5836	0.2500	0.5163	0.5000
55.	Q14	0.7500	0.0979	0.1772	0.5000
48.	Q15	0.3975	0.2500	0.3970	0.5000

Table 7.10 Direct methods results from *SHELXS* for τ -AlF₃

an approximate number Z of motives per cell is made on the basis of a volume of the order of 16–20 Å³ for a fluorine or an oxygen atom. Clearly, the direct methods are adequate for τ -AlF₃ because Al³⁺ and F⁻ are isoelectronic (no heavy atom). The finding of half the independent atoms would not be sufficient for starting a Rietveld refinement in such a case very similar to an organic structure problem characterized by the presence of light elements only. Almost the whole structure has to be found by the direct methods if one expects to succeed in the structure determination. The brute force consisting in the *SHELXS* application to the whole dataset gave a list of 15 atom sites (Table 7.10). Examining this list by a structure drawing program (*STRUPLO*, Fischer, 1985) revealed that the 11 first atom sites described completely a new MX₃ corner-sharing 3D octahedral network (Figure 7.12). With such a complete model, the final Rietveld fit is then straightforward.

7.4.4 Limits

The ability of direct methods to solve large organic problems from powder data depends mainly on the resolution. With third-generation synchrotron sources, and FWHM <0.01°(2 θ), the possibilities have extended since the "old times." Twenty years ago, based on some 500 Å³ structures solved in the *P*-1 space group, with FWHM ~ 0.12°(2 θ), corresponding to ~25 atoms in general position, ~75 refinable atomic coordinates, ~1000 extractable "|*F*_{obs}|," one could extrapolate to other crystal systems and with higher resolutions, this gives at ~0.01°(2 θ) FWHM: 300 atoms in general position, 900 refinable atomic coordinates, ~12 000 extractable "|*F*_{obs}]," 6000 Å³ in triclinic or up to 576 000 Å³ for a *F*-centered cubic cell (passing from 2 equivalent general positions to 192). But this



Figure 7.12 First vision (with *STRUPLO*) of the τ -AlF₃ structure after application of the direct methods: all octahedra are there, detected par the automatic polyhedra recognition of the drawing program.

estimation of feasibility limits is for inorganic compounds showing intense peaks even at $150^{\circ}(2\theta)$ ($\lambda = 1.54$ Å) whereas organics have few if any diffracted intensity after 90° or even $60^{\circ}(2\theta)$. Moreover, most of the time, the selected wavelength at synchrotron sources is close to 0.7 Å, and the sample may not be so well crystallized, introducing intrinsic line broadening, and so on, so that the above limits correspond to maximal values rarely attained by using Patterson or direct methods. We will see later that these limits are no longer valid with the direct space methods if applied to molecular compounds.

If the classical single-crystal programs can attain such limits, then the computer programs especially designed for dealing with powder data should be able to perform even better. The best known of these computer programs are *EXPO* (Altomare *et al.*, 2004c, 2006a), *XLENS* (Rius, 2004; Rius-Palleiro *et al.*, 2005), *SIMPEL* (Jansen *et al.*, 1993). *EXPO* integrates *EXTRA* (Altomare *et al.*, 1995), a program addressed to full pattern decomposition (Le Bail method) and *SIRPOW* (Cascarano *et al.*, 1992), which applies direct methods for solving crystal structures. The package exploits supplementary amount of information which become available during the phasing process: the preferred orientation, the pseudotranslational symmetry, the positivity of the electron density, the positivity of the Patterson function, a well oriented and positioned fragment. Such an information allows theoretically to improve the pattern decomposition in *EXPO*. Similar or different approaches are provided with *XLENS* and *SIMPEL*. These three computer programs have been applied to numerous successful SDPDs, however, they never participated in the SDPD Round Robin comparisons.

7.4.5 Strategy for structure completion after Patterson or direct methods

Retaining an atom site as proposed by the Patterson or direct methods is a question of common sense according to the sample knowledge. You may not have the exact formulation but you should know the composition of the magic pot at the synthesis stage. It is the examination of the inter-atomic distances which allows you to accept the model or not. It may be useful to transfer the atomic coordinates of your model into a program more specialized in inter-atomic distance calculations and eventually in a structure drawing program recognizing automatically polyhedra rings. When you believe having obtained a sufficient starting model, a way to continue is to test this hypothesis by using a single-crystal structure refinement program (SHELXL for instance) applied to your " $|F_{obs}|$." Even if the model was obtained from the full dataset, it will be better to refine it on a reduced dataset (apply the OVERLAP software with $\delta = 0.02^{\circ}(2\theta)$ or more, depending on your data resolution and on your problem size). A model which corresponds to a reliability R less than 40–35% begins to be interesting with SHELXL, a fortiori if peaks extracted from the Fourier difference map make sense. If the peaks pass the test of inter-atomic distances credibility, they are added to the model as atoms and new refinements and Fourier synthesis are done (do not be too sure of your sample composition, time and again errors are produced or new reactions take place: Cl atoms enter sometimes in fluorides by the chloride flux method, for instance, although this rarely occurs). Once it has become impossible to extract more information from the " $|F_{obs}|$ " set (reduced) as resulting from the Pawley or Le Bail fits, and if the model seems coherent, it is time to apply the Rietveld method. The initial model may not be complete but it should be sufficient for starting this Rietveld refinement. New " $|F_{obs}|$ " have to be extracted at the end of these refinements, they will still be biased, but much better than those obtained from the initial Pawley or Le Bail fits. The initial model may be very incomplete, leading to high starting R_p and R_{wp} values. In such a case it is advisable to not refine the profile parameters at all, keeping them at the values corresponding to the best Pawley of Le Bail fits, in order to avoid divergency. The extraction of new " $|F_{obs}|$ " at the last Rietveld refinement cycle and their new injection into SHELXL (or any single-crystal refinement program you may select) will allow to go further if a new Fourier synthesis reveals new sites. The process has to be repeated up to complete satisfaction. Results which should be submitted for publication are those of the last refinement by the Rietveld method. Never consider the SHELXL result as the final one, the Rietveld method is the only recognized method for powder data refinement!

7.4.6 Most difficult structures solved before 1999 by the classic methods

The "complexity" of a structure at the final Rietveld refinement stage is related to the total number of independent atoms (C1) (not to the cell volume), or more exactly to the number of refinable atomic coordinates (Nc). The difficulty to solve using the classic methods depends on the number C2 of independent atoms which have to be located first, forming a starting model sufficient to find then the rest of the structure by Fourier difference map. In the case of an organic compound, if you do not know the molecular formula exactly, the

minimum starting model is close to the total number of independent non-hydrogen atoms. For an inorganic compound, this may be considerably less. For instance, for solving the structure of La₃Ti₅Al₁₅O₃₇ (Morris *et al.*, 1994), the structure considered by the authors themselves as the most complex ever solved in 1994, with C1 = 60 independent atoms in the *Cc* space group, Nc = 170 refined atomic positions, it was necessary to locate first only C2 = 5 heavy atoms (La, Ti), the 55 remaining atoms could then be deduced from the subsequent Fourier difference maps. Complexity/difficulty regarding the Rietveld method is thus quite different from the complexity/difficulty regarding the structure solution step. The list of most complex structures, having $C2 \ge 10$ and solved before 1999 by the direct methods, when less than 300 SDPD papers were published, is given in Table 7.11. All were determined from extracted intensities either by the Pawley or Le Bail methods, on which the direct methods from the various computer programs discussed above were applied. The

Formula or name	S.G.	С1	Nc	С2	Radiation	Reference
$2(C_6H_5NH_3) \cdot Mo_3O_{10} \cdot 4H_2O$	Pnma	27	70	18	XC12	Lasocha et al., 1995
Chlorothiazide-I	<i>P</i> 1	23	48	17	Sync	Shankland <i>et al.,</i> 1997b
α-NaCaAlF ₆	P2 ₁ /c	18	54	17	XC12	Le Bail <i>et al.,</i> 1998
$K_2 Ti Si_3 O_9 \cdot H_2 O$	$P2_{1}2_{1}2_{1}$	16	48	16	XC12	Dadachov and Le Bail, 1997
$Ti_2O(PO_4)_2(H_2O)_2$	P-1	19	57	15	XC12 +	Salvado <i>et al.,</i> 1997
					S + N	
$Ti_2O(PO_4)_2(H_2O)_2$	P-1	15	45	15	XC12	Poojary <i>et al.,</i> 1997
$C_{24}H_{16}O_7$	P-1	47	141	14	S	Knudsen <i>et al.,</i> 1998
$Bi(H_2O)_4(OSO_2CF_3)_3$	P2 ₁ /c	29	87	14	XC1	Louër <i>et al.,</i> 1997
SiO ₂ (ITQ-4)	I2/m	14	37	14	S	Barrett <i>et al.,</i> 1997
γ -Zn ₂ P ₂ O ₇	Pbcm	14	35	14	XC1	Bataille <i>et al.,</i> 1998
$Ti_3(PO_4)_4(H_2O)_2 \cdot NH_3$	P-1	14	36	14	XC12	Poojary <i>et al.,</i> 1997
β -VO(HPO ₄) · 2H ₂ O	P-1	18	54	12	XC12	Le Bail <i>et al.,</i> 1989
Li ₆ P ₆ O ₁₈	P2 ₁ /n	15	45	12	XC12	Ben-Chaabane <i>et al.,</i> 1998
Cr ₈ O ₂₁	P-1	15	42	12	XC1 +	Norby <i>et al.,</i> 1991
					S + N	
$(UO_2)_3H_2(HO_3PC_6H_5)_4 \cdot H_2O$	P212121	50	150	11	XC12	Poojary <i>et al.,</i> 1996
HP ₄ N ₇	P2 ₁ /a	11	33	11	S	Horstmann <i>et al.,</i> 1997
τ-AlF ₃	P4/nmm	11	17	11	XC12	Le Bail <i>et al.,</i> 1992
$Zr_2(NaPO_4)_4 \cdot 6H_2O$	<i>P</i> 1	32	93	10	XC12	Poojary and Clearfield, 1994
$(NH_4)_2Ti_3O_2(HPO_4)_2(PO_4)_2$	P21	25	74	10	XC12	Poojary et al., 1997
$Na_2Ca(HPO_4)_2$	P21	13	38	10	XC12	Ben Chaabane <i>et al.,</i> 1997
α -(NH ₄) ₂ FeF ₅	Pbcn	10	21	10	XC12	Fourquet et al., 1989

 Table 7.11
 Structures corresponding to the largest number of atoms (C2) located by direct methods from powder data, before 1999

S.G. = space group.

C1 = number of independent atoms.

Nc = number of refined atomic coordinates. C2 = number of independent atoms in the direct methods initial model.

Radiation: XC12 = X-ray conventional CuK α_{12} ; XC1 = CuK α_1 ; S = synchrotron, N = neutron.

Formula or name	S.G.	С1	Nc	С2	Radiation	Reference
T ₃ R ₃ Zn-human insulin	R3	1630	4893	MB	S	Von Dreele <i>et al.,</i> 2000
Sapo-40	P2/n	62	182	9	XC12 + S	Estermann et al., 1992
La ₃ Ti ₅ Al ₁₅ O ₃₇	Сс	60	178	5	S + N	Morris et al., 1994
Thiothixene	P21	59	177	GOM	S	David <i>et al.,</i> 1998
$Rb_{44}K_4[Si_{96}Zn_{24}O_{240}] \cdot 48H_2O$	P4 ₂ /ncm	59	170	Zeo	S	McCusker et al., 1996
$(UO_2)_3H_2(HO_3PC_6H_5)_4\cdot H_2O$	P212121	50	150	11	XC12	Poojary <i>et al.,</i> 1996
Capsaicin	P2 ₁ /c	49	147	GOM	S	David <i>et al.,</i> 1998
$C_{24}H_{16}O_7$	P-1	47	141	14	S	Knudsen <i>et al.,</i> 1998
$C_{60}Br_{24}(Br_2)_2$	<i>P</i> -1	44	42	MB	S	Dinnebier et al., 1995
$(CH_3(CH_2)_{16}COO)_2Ca \cdot H_2O$	P2 ₁ /c	42	126	MB	S	Lelann and Berar, 1993
Promazine hydrochloride	P2 ₁ /c	41	123	GOM	S	David <i>et al.,</i> 1998
$[(CH_3)_2NH_2]_4Mo_6O_{20} \cdot 2H_2O$	P21	38	113	6	XC12	Toraya <i>et al.,</i> 1984
$(PEO)_3 LiN(SO_2 CF_3)_2$	P2 ₁ /c	37	111	MC	XC1	Andreev et al., 1997
Y _{17.33} (BO ₃) ₄ (B ₂ O ₅) ₂ O ₁₆	Ст	32	62	9	XC12	Lin <i>et al.,</i> 1997
$Zr_2(NaPO_4)_4\cdot 6H_2O$	<i>P</i> 1	32	93	10	XC12	Poojary and Clearfield, 1994
C ₁₁ H ₁₄ N ₆	<i>P</i> -1	31	93	MPP	XC1	Karfunkel <i>et al.,</i> 1996
$S_6C_{24}(T_6)$	P2 ₁ /a	30	90	G	XC12	Porzio <i>et al.,</i> 1993
$Bi(H_2O)_4(OSO_2CF_3)_3$	P2 ₁ /c	29	87	14	XC1	Louër et al., 1997
$Ga_2(HPO_3)_3 \cdot 4H_2O$	P21	29	86	2	S + N	Morris et al., 1992
β-Ba ₃ AlF ₉	Pnc2	29	74	7	XC12	Le Bail, 1993
$[Si_{32}B_4O_{72}][N(CH_3)_4]_4$	P2 ₁ /a	28	84	MB	S + XC1	Gies and Ruis, 1995
C ₁₀ H ₁₆ O	Cmcm	27	81	11	S	Mora and Fitch, 1997
$2(C_6H_5NH_3)\cdot Mo_3O_{10}\cdot 4H_2O$	Pnma	27	70	18	XC12	Lasocha <i>et al.,</i> 1995
$(AIPO_4)_3 \cdot (CH_3)_4 NOH$	P2 ₁ 2 ₁ 2	26	70	6	XC12	Rudolf et al., 1986
$S_5C_{20}(T_5)$	P2 ₁ /a	25	75	G	XC12	Porzio et al., 1993

Table 7.12 The SDPD most complex structures at the Rietveld refinement step, before 1999, with largest number of independent atoms $C1 \ge 25$ and refined atomic coordinates Nc

S.G. = space group.

C1 = number of independent atoms.

Nc = number of refined atomic coordinates.

C2 = number of independent atoms in the direct methods initial model.

MB = molecular building, GOM = global optimization method, Zeo = zeolite special modeling, MC = Monte Carlo, MPP = molecule packing prediction, G = guessed.

Radiation: XC12 = X-ray conventional $CuK \alpha_{12}$; $XC1 = CuK \alpha_1$; S = synchrotron, N = neutron.

most complex had only C2 = 18 atoms. Since that time, things have changed a lot, with the higher resolution synchrotron data.

The SDPDs with the highest number of independent atoms C1 before 1999 are listed in Table 7.12. Most were solved by using synchrotron data. They are to be considered as the most complex at the Rietveld refinement stage. Indeed, the ratio N_{hkl}/P (=reflection number)/(number of refined parameter) may lead to the necessity to use constraints and stereochemical restraints. A more recent SDPD (2000) corresponding to a protein (Von Dreele *et al.*, 2000), still a winner today according to the criterion C1, was placed at the head of the list and is a typical example of the difficulty associated with low N_{hkl}/P values (=2927/4893 in this case, leading to the use of 7981 stereochemical restraints).

In 1992, the "most complex structure" (according to C1) with only 29 independent atoms (compare to 4893 for the protein) was published in *Nature* (Morris *et al.*, 1992), just because it was powder data, needing both synchrotron and neutron experiments. Since these (heroic) times, more complex structures (the protein excepted) according to both C1 and C2 criteria have been solved with more or less ease.

In Table 7.12 are given some structures determined by methods other than the conventional ones (*C*2 not given). Probably, those large structures would not have been solved by the classical approach of the Patterson or direct methods if it had been necessary to locate almost all the independent atoms for obtaining the starting model allowing for a first refinement. We will see in the next paragraph that a new complexity/difficulty criterion is now necessary for such structures, solved by the "direct space" approach, because in spite of the large number of independent atoms, that protein structure was as easy to solve as a structure with one heavy atom by the Patterson method. Of course, the limits extend as well a lot more again, almost up to those corresponding to single-crystal data, if you are able to extract more information (reducing the overlapping handicap) by methods enlarging the number of correct data by taking advantage of special thermal effects, texture, as discussed later.

7.5 Direct space methods of structure solution

Chemical knowledge is indispensable to the application of the direct space methods since they consist in placing atoms, either independent or as a whole molecule, or both mixed, at some positions in the cell, generally wrong positions at the beginning of the process, and moving them by translations as well as rotations for molecules or polyhedra, and permutation times to times between individual atoms, up to obtain a satisfying fit to the powder pattern or to a mathematical representation of it. Going from wrong starting atomic positions to the final grossly correct ones is made by a general process called global optimization (GO) which can be realized by different but eventually similar procedures: Monte Carlo (MC), Monte Carlo with simulated annealing (SA) and/or with parallel tempering (PT), genetic algorithm (GA). These processes present a similarity in the use of random number sequences: atoms and molecules realize a random walk. The decision to keep the moves (etc.) depends on the fit to the powder data.

Sometimes the "direct-space methods" (not to be confused with the direct methods) are called "global optimization methods" or "model building methods," and even sometimes "real space methods." "Direct space" was the definition retained in the pioneering papers (Deem and Newsam, 1989, 1992; Newsam *et al.*, 1992). "Direct space" as opposed to "reciprocal space" has an adequate crystallographic structural meaning, and should be preferred to "real space," which, opposed to "imaginary" would call to mind both real and imaginary parts of the diffusion factors. "Global optimization" has a larger sense and designates the task of finding the absolutely best set of parameters in order to optimize an objective function, a task not at all limited to crystallography.

We are now at the limits of the most recent developments in SDPD. Some special methods may have been applied to quite a small number of real problems, and sometimes to none.

There are very few programs easily available in the public domain, the majority are either commercial or are distributed confidentially. Most computer programs are able to work indifferently on molecular systems or extended solids or hybrid compounds.

7.5.1 DoF, flexibility, limitations, and software

Irrespective of the number of atoms, a molecule can be located easily in a cell, as a rigid body, corresponding to 3 positional (x, y, z) and 3 orientational (Θ, Φ, Ψ) degrees of freedom (DoF), by checking the fit quality on, say, the first 30 or 50 peaks of the diffraction pattern. But the number of DoFs will increase by one for every added free torsion angle, and more complications arise if several independent molecules have to be located altogether or/and if water molecules or chlorine/sulfur/and so forth atoms are involved. For inorganic compounds, in principle an atom in general position corresponds to 3 DoFs (the 3 xyz atomic coordinates), however, crystal-chemistry rules may allow to guess if some defined polyhedra are to be expected. An octahedron for instance, instead of corresponding to $7 \times 3 = 21$ DoFs when described by the atomic coordinates (if all atoms were in general positions), can be translated and rotated as a whole polyhedron, corresponding to only 6 DoFs. Most of these computer programs are also able to start from a complete set of independent atoms, at random at the beginning, and then will try to find their positions, moving them while matching to the data (in that case, the number of DoFs is equal to Nc in the previous subsection). Combinations of (several) molecules (or polyhedra) together with independent atoms are of course possible. Searching for the structure of tetracycline hydrochoride ($C_{22}H_{25}N_2O_8Cl$) in the $P_{21}2_12_1$ space group, one would have to determine the number of independent molecules nM, the number of torsion angles nT, the number of atoms to be added separately (the chlorine atom here) nA, and the total number of DoFs would be nM(6 + nT) + 3nA, in case of the additional individual atoms occupying a general position. Even if more complex structures may have been solved since that time, Table 7.13 gives a good idea about the direct-space computer programs possibilities in 2002.

The computer programs having provided solutions to the SDPD Round Robins were DASH (1998), FOX, and TOPAS (2002). Ever since, more computer programs have appeared (ORGANA (Brodski *et al.*, 2005)). Two computer programs more specifically dedicated to zeolites were not included, these are ZEFSAII (Falcioni and Deem, 1999), and FOCUS (Grosse-Kunstleve *et al.*, 1997). Moreover, software like EXPO (direct methods) or FULLPROF, MAUD (Rietveld computer programs) (etc.) are offering now some direct-space features. It can be noticed that the direct-space methods can be applied through fitting to the atomic pair distribution function (PDF), however, if this is done with three-dimensional models, then the diffuse scattering present in the PDF will not be accounted for, as it is not when fitting to the powder pattern by the Rietveld method.

For those direct-space computer programs fitting to the whole profile, this supposes that the Pawley or Le Bail methods were used at the stage of estimating the profile parameters, since these programs do not search simultaneously for the best structure and profile parameters, the task would be too heavy and uncertain. Anyway, some programs tend to become able to do more than structure solution, become more or less complete packages including peak hunting and indexing capabilities and final Rietveld refinement.

Drogram pame	Acrace	Paf	6	Data	Evamula	Loc L	Dof
	////	NGI.	2	Cata	rvanipre	5	. MGI.
DASH	U	David et al., 2006	SA	Ч	Capsaicin	16	David <i>et al.</i> , 1998
EAGER	A	Harris et al., 1998	GА	WP	Ph ₂ P(O)(CH ₂) ₇ P(O)Ph ₂	18	Kariuki <i>et al.</i> , 1999
ENDEAVOUR	U	Putz <i>et al.</i> , 1999	SA	_	Ag_2PdO_2	45	Schreyer and Jansen, 2001
ESPOIR	0	Le Bail, 2001a	MC	_	Gormanite	54	Le Bail <i>et al.</i> , 2003
FOX	0	Favre-Nicolin and Cerny, 2002	SA/PT	WP	Al ₂ (CH ₃ PO ₃) ₃	24	Edgar <i>et al.</i> , 2002
OCTOPUS	A	Harris et al., 1994	MC	WP	Red fluorescein	7	Tremayne <i>et al.</i> , 1997
POWDERSOLVE	U	Engel <i>et al.</i> , 1999	MC	WP	Docetaxel	29	Zaske <i>et al.</i> , 2001
PSSP	0	Stephens and Hug, 2002	SA	_	Malaria pigmentβ haematin	14	Pagola <i>et al.</i> , 2000
SAFE	۲	Brenner et al., 2002	SA	WP	$C_{32} N_3 O_6 H_{53}$	23	Brenner et al., 2002
SA	۲	Andreev <i>et al.</i> , 1997	SA	WP	(CH ₂ CH ₂ O) ₆ :LiAsF ₆	79	MacGlashan <i>et al.</i> , 1999
TOPAS	U	Coelho, 2000	SA	WP	Caffeine anhydrous	93	Stowasser and Lehmann, 2002
Arcess. C – commerc	ial with acad	demic nrices () – onen access A – cont	act the auth	Ore			

Table 7.13 Selection of programs (alphabetical order) applying direct-space methods for the structure solution from powder diffraction data, with one of the most complex problem (maximum DoF), or typical structure, suggested by the authors themselves, and solved before 2002 (by courtesy of Yuri G. Andreev)

Ref: two references, one for the program publication and the other for the example. GO = global optimization, MC = Monte Carlo, SA = MC + simulated annealing, PT = paralleltempering, GA = genetic algorithm. Data: P = Pawley, L = Le Bail, I = integrated intensities, WP = whole pattern.

DoF = degrees of freedom corresponding to the example.

There are essentially three ways to deal with powder data overlapping in the direct-space programs:

- 1 The powder pattern itself (at least a part of it) is calculated for each tested position of the model inside the cell, and compared to the raw data. This is the method retained in the *OCTOPUS* program, for instance, and others. There is no need to extract the structure factors. Reconstituting the raw data may be computer-time-consuming.
- 2 The extracted " $|F_{obs}|$ " are used, but a pseudo-pattern is regenerated from them and compared to a pattern generated from the $|F_{calc}|$. This allows saving time since no background, Lorentz polarization, asymmetry (etc.) has to be calculated. This method is used in the *ESPOIR* program exclusively, up to now.
- 3 A fitness function is defined, including the extracted " $|F_{obs}|$ " and calculated structure factors, together with the correlation function. This function is used to decide which molecule will "survive." This is the method built in the *DASH* program (extraction by the Pawley method), and also in *PSSP* (extraction by the Le Bail method).

7.5.2 Molecular compounds

The starting molecule, supposing that it is known either by NMR characterization or because the compound is coming from a controlled synthesis, may be obtained from the usual databases of crystal structures or molecules. Depending on the programs automatization level (not all programs are able to cope with special position recognition during the moves, allowing changes in the number of equivalent atoms, like *FOX* does), some questions may have to be examined at the very beginning of the building of the starting model: will the atoms/molecules be at general or special positions, does an inversion center need to be placed inside of the molecule? In such a case, the starting model will have to be only half the molecule, or it may be preferable sometimes to decrease the symmetry to a sub-group, for instance, and if this is done, the intensities should of course be re-extracted in the new selected space group if the software is working on extracted " $|F_{obs}|$." Some programs require the description of the molecule by internal coordinates according to the *Z*-matrix format, other programs have automated systems finding where the connections can be rotated (torsion angle).

Applying direct space methods requires generally much less data than direct methods. Five intensities per degree of freedom may be sufficient, so that a simple molecule structure with 6 DoFs can be solved by using the first 30 reflections of the powder pattern. However, big organic or organometallic problems can be completely solved only if one disposes of a maximum of knowledge about the molecular formula together with the most excellent data. Very complex molecules will present more serious difficulties at the Rietveld structure refinement stage: the ratio of the effective number of structure factors with the number of atomic coordinates to refine may be as small as 3 or less (because there is soon no accurate intensity on the powder pattern at resolution d < 1.5 Å), so that the model needs to be constrained/restrained. This may lead to difficulties to locate some additional water molecules, or to be absolutely sure that there is not any misunderstanding somewhere which could explain why the Bragg factor $R_{\rm B}$ is going to be sometimes as large as 10 or 15%. No need to say that some proposed H atom positions will be dubious. You will have to know



Figure 7.13 Comparison of the molecular structures obtained from global optimization by *DASH* and from the final Rietveld refinement.

"how much is too much," or your manuscript will be rejected (by a good reviewer). No size limit to the structure solution here, the limit comes from the correctness of the guess: if the starting model is partly false, a minimum R will be attained, but the structure will be erroneous to some extent.

7.5.2.1 Tetracycline hydrochloride

It is interesting to recall how the structure of tetracycline hydrochloride was solved by the direct-space method during the 1998 SDPD Round Robin. A model for the molecule was taken from the tetracycline hydrate in the Cambridge Structural Database (TETCYH10 entry), removing the water. The tetracycline fragment as well as the Cl atom were positioned at random in the cell and an optimum position was searched (Figure 7.13) by simulated annealing using the *DRUID* (now renamed *DASH*) program against the 100 first structure factors extracted by the Pawley method from the synchrotron data. There is something curious between the starting and final model. The main move is that the O2 and N1 atoms in the TETCYH10 model have rotated by 180° along the C2-C3 axis. The H atoms did not move a lot between the initial and final model. An additional hydrogen atom should have been found for building the complete structure, O2 in the hydrate becoming an OH, this hydrogen was not located. Interviewed on this question, the Round Robin participant said that this is probably due to tiredness because of a night of hard work. Anyway, this is a good example to see how difficult it may be to complete an SDPD of a molecular compound by the direct-space method.



Figure 7.14 The direct space computer program ESPOIR solving the bethanechol chloride structure.

7.5.2.2 Bethanechol chloride

Bethanechol chloride, a cholinergic agent, is a synthetic ester which is structurally and pharmacologically related to acetylcholine. It was the sample case selected during the establishment of the indexing benchmarks (Bergmann *et al.*, 2004), because several unindexed powder patterns were available inside of the ICDD-PDF (if the molecular formula was known, the crystal structure was not, or at least it remained unpublished). Once indexed, the crystal structure was easily determined by using *ESPOIR* (Figure 7.14) starting from the Cartesian coordinates of the bethanechol chloride $C_7H_{17}CIN_2O_2$ known molecule (introduced without the Cl and H atoms) (6 DoFs) and the Cl atom (3 additional DoFs). The fit is quite good with R = 0.074 after test 3 on the first 50 reflections of the powder pattern. In that case, a test represented 75 000 attempted random rotations, 25 000 random translations of the molecule, plus 100 000 moves of the Cl atom (of which 31, 17, and 11 events were accepted, respectively). Twenty such tests were decided, because sometimes the random walk may finish in a false minimum. Such calculations need a few minutes with a PC.

7.5.3 Inorganic compounds: polyhedra or independent atoms

We have seen that the direct methods (and Patterson) could find hardly more than 20 atoms for the initial structure model before 1999 – but the more recent literature was not analyzed

completely. In direct-space methods, it is also possible to solve structures by considering independent atoms. Software are more or less efficient at doing such attempts, depending on their ability to cope with special positions or not. FOX can do it in an automated way, ESPOIR needs for an initial guess of special positions which could be occupied, or at least needs for the relative numbers of atoms in each site. For solving the Y₂O₃ structure with ESPOIR, you have to test several combinations, including the correct one with two Y atom sites, one with 24 and the other with 8 equivalents. In the case of τ -AlF₃, the number of different guesses for the finding of the relative proportions of the 11 independent sites of Table 7.10 renders the task extremely tedious (it would be interesting to see if FOX, with its facility to manage special positions, would really be as efficient as the direct methods in such a case). The ideal situation is encountered with space groups not having any special position. ESPOIR was capable to solve the mineral gormanite crystal structure (Le Bail et al., 2003) from a synchrotron powder pattern, in spite of the presence of three impurities representing \sim 10% of the total intensity of the pattern (a frequent problem with mineralogical samples) in the P-1 space group, locating 18 atoms from the first 500 hkl (54 DoFs). Not only moves but also permutations are realized in such a case (not practiced when considering independent molecules). The direct space software working with the whole pattern, are not all able yet to cope with the presence of known impurity contributions, so that the intensity extraction was necessary here.

Reducing the number of DoFs by enforcing the presence of polyhedra gives more chances and pushes the complexity limits far away. One has to be careful with the assumptions, testing several possibilities. As an example, participant 2 solved the 2002 SDPD Round Robin sample 2 structure $(Sr_5V_3(F/O/OH/H_2O)_{22})$, Figure 7.15) (Le Bail and Cranswick, 2003) with *FOX* in the following way: either 3 tetrahedra VO₄ and 5 cubes SrO₈ or 3 octahedra VO₆ and 5 cubes SrO₈ were rotated and translated (48 DoFs in both cases). Both models have



Figure 7.15 Projection of the 2002 SDPD Round Robin sample 2 structure of $Sr_5V_3(F/O/OH/H_2O)_{22}$ along the *b*-axis.

yielded the same correct positions for the cations. The positions of anions were determined by a third modeling using free atoms. Participant 7 solved this sample 2 structure with *TOPAS* by putting into the cell 30 independent atoms (no constraint/restraint) at random positions, locating them by simulated annealing.

7.5.4 Hybrid compounds

Because of the ability of direct-space methods to determine the position of molecules of unlimited size with only 6 DoFs, the race for the publication of the most complex structure ever determined by SDPD is over (almost). Complexity can be defined in several ways: cell volume has to be weighted by the symmetry and Bravais lattice; a number of independent atomic positions C2 in the initial model was a better criterion for inorganic structures solved by direct methods; the number of DoFs is now pertinent for the direct-space methods, and also maybe the number of independent objects (molecules together with polyhedra and/or individual atoms). The solution of the structures of hybrid metal organic frameworks imposes to the direct-space computer programs to manipulate simultaneously several such objects. The 2002 SDPD Round Robin sample 1 with the $Al_2F_{10}[C_6N_4H_{20}]$ formulation (Adil et al., 2007) gave the occasion to the software developers to compete in a relatively complex case, due also to the poor quality of the powder pattern (conventional laboratory X-ray, with large FWHM and the presence of an impurity). Participant 2 solved the structure by using FOX according to the following strategy: structural units location in direct space by simulated annealing in the parallel tempering mode. Three independent entities (two AlF₆ octahedra and the $C_6N_4H_{20}$ molecule) were allowed to rotate and move in the P2/c space group, corresponding to 18 DoFs (Figure 7.16). The final refinement was made by using the FULLPROF software. Much more details are given by the participants at the SDPDRR-2 Web site (Le Bail and Cranswick, 2003). Participant 7 solved this structure by using TOPAS according to the following strategy: molecule location in direct-space, simulated annealing, structure determination using step intensity data, starting with 3 "rigid" bodies (including



Figure 7.16 The 2002 SDPD Round Robin sample 1 structure of $Al_2F_{10}[C_6N_4H_{20}]$, as determined by using *FOX*.

2 for AlF₆ octahedra). For the $C_6N_4H_{20}$ molecule, 3 rotational and 3 translational DoFs and 4 torsion angles were used. This (and in the previous subsection) illustrates the possible different strategies which may be chosen depending on the scientist and depending on the software.

7.6 Structure prediction and powder diffraction

The words "structure prediction" may represent quite different situations, from partial to full prediction, and this is a bit confusing. On the partial side are the techniques for molecular packing prediction: the molecule is known, the prediction of the packing of the molecules is attempted by various techniques, producing different cells corresponding maybe to existing or realistic polymorphs ranked by energy. Also partial predictions are the extrapolation of established geometrical characteristics for the enumeration of all possibilities (exclusive corner-sharing tetrahedra in zeolites, or corner-sharing octahedra, or mixed polyhedra). At the "full prediction" side are the *ab initio* quantum mechanics methods exerted with more or less approximations. Prediction may be considered now as the ultimate chance to solve a structure when everything, including powder diffraction, failed. However, in a near future, structures, properties and synthesis predictions should allow for a definitive human mastering of the solid state.

7.6.1 Molecular packing prediction

Progress in this topic are discussed in a series of papers reporting the results of blind tests (Day et al., 2005). The techniques and software will not be fully described here, the packing is realized generally through energy considerations and tests are made on selected space groups (the less than 20 most frequent space groups for organic compounds). Lists of possibilities are then sorted by energy rank. Though there is no need of a powder pattern for the building of the models, the confirmation in a real case, where no single crystal is available in principle, would have to be realized by comparison with a powder pattern (a priori unindexed, otherwise, the list of predicted models could be shortened from the cell parameters). Beside these blind tests, some successes are already on the front of the scene for some organic pigments, polymorphism, and so forth, for which it is possible to provide only a small list of selected references here (Karfunkel et al., 1996; Panina et al., 2007; Schmidt et al., 2005, 2006; Price, 2004; Kiang et al., 2003; Van Eijck and Kroon, 2000; Filippini et al., 1999; Karfunkel et al., 1993). Moreover, the question of the selection of the best structure candidate by comparison with powder diffraction data, because the predicted cell parameters may substantially differ from the actual ones, is leading to the establishment of some new index of similarities (Hofmann and Kuleshova, 2005).

7.6.2 Inorganic crystal structure prediction

It is enlightening to cite shortly a few of the computer programs and methods producing predictions in the inorganic world. *CASTEP* uses the density functional theory (*DFT*)

for ab initio modeling, applying a pseudo-potential plane-wave code (Payne et al., 1992). The structures gathered in the database of >1000000 hypothetical zeolites (Treacy *et al.*, 2004; Foster and Treacy, 2003) are produced from a 64-processor computer cluster grinding away non-stop, generating graphs and annealing them, the selected frameworks being then re-optimized with the General Utility Lattice Program, GULP (Gale, 1997) using atomic potentials. Recently, a genetic algorithm was implemented (Woodley, 2004) in GULP in order to generate crystal framework structures from the knowledge of only the unit cell dimensions and constituent atoms (this being closer to structure determination than to prediction), the structures of the better candidates produced are relaxed by minimizing the lattice energy, which is based on the Born model of a solid. A concept of "energy landscape" of chemical systems is used by Schön and Jansen (2001a,b) for structure prediction with their computer program G42. Another package, SPuDS, is dedicated especially to the prediction of perovskites (Lufaso and Woodward, 2001). The AASBU method (Automated Assembly of Secondary Building Units) (Mellot-Draznieks et al., 2000, 2002) is used in Cerius2 (Cerius2, 2000) and GULP in a sequence of simulated annealing plus minimization steps for the aggregation of large structural motifs. This list of software is finally small owing to the fact that structure and properties prediction is obviously an unavoidable part of our future in crystallography and chemistry. From these approaches, if zeolites are excluded, the number of inorganic crystal predictions of new probable structures is of the order of a few dozens of compounds, including still unknown varieties of carbon, sodium chloride, AB₂ compounds (etc.). Approaches can be elementary up to highly sophisticated (ab initio), the latter option being still computer time consuming. On the elementary side, the new GRINSP (Geometrically Restrained INorganic Structure Prediction) code (Le Bail, 2005a) for the building of N-connected 3D nets (N = 3, 4, 5, 6, and binary combinations) allows for the exploration of single or mixed frameworks, extending the domain of possible investigations. From the GRINSP predictions was built the Predicted Crystallography Open Database (PCOD), including >60 000 silicates, phosphates, sulfates, fluorides, and so on (Le Bail, 2003). The powder patterns calculated from the PCOD were included into the P2D2-1 (Predicted Powder Diffraction Database version 1) so as to enable identification by search-match (Chapter 6). The GRINSP predictions include 6-connected 3D nets so that the τ -AlF₃ structure is among the predicted entries with less than 1% error on the cell parameters (Le Bail and Calvayrac, 2006). If the P2D2-1 had existed in 1992, then this new aluminum fluoride crystal structure would have been directly solved at the identification stage (Figure 7.17).

7.6.3 Hybrids

If more than 1 000 000 zeolites are predicted when \sim 150 zeotypes are actually known, what will be the total number of predicted inorganic compounds? We certainly need for better ways to eliminate most of the false structure candidates, but it seems that we will be submerged soon by billions of structures. Moreover, molecular structures, on their side, will also provide billions of models, so that predicted hybrids very probably will be even much more. Solving one complex hybrid structure by prediction seems to be extremely fortunate. Indeed, this was the case for two giant structures solved by combined targeted chemistry and computational design (Férey *et al.*, 2004, 2005). Both correspond to two super-zeolites



Figure 7.17 Positive identification of τ -AlF₃ by search-match against the PPDF-1, from the Predicted Crystallography Open Database, with the *EVA* software.

(MTN-analogous) built up from super-tetrahedra made from hybrid stuff which had to be guessed before the prediction. Both have cubic cells with large volume (380 000 and 702 000 Å³, S.G.: *Fd*-3*m*, 68 and 74 independent non-hydrogen atoms). Will such exploits become routine now? Probably not very soon.

7.7 Structure solution from multiple powder patterns and multiple techniques

Going closer to single-crystal-like data means that it will be possible to solve (and then refine) more complex structures than from a single powder pattern. All effects which can modify more or less intensities and/or overlapping are thus potentially interesting.

The first idea is to combine X-ray and neutron patterns, providing more different data (intensities varying according to the X-ray and neutron scattering factors) for the solution of the same problem. Also, one can produce multiple neutron powder patterns from isotopically substituted samples. Exclusively from neutron, complete SDPDs are scarce, with the exception of magnetic structure determination (Rodriguez-Carvajal, 1993) which may use magnetic intensity extraction and simulated annealing at the solution stage. The scarcity is



Figure 7.18 La₂W₂O₉ structure completed by *ESPOIR*, finding nine missing oxygen atoms from neutron data, with distance restraints to the imposed (already obtained from X-ray) La and W atoms.

mainly a consequence of low-resolution data obtained at neutron powder instruments compared to synchrotron or even laboratory X-ray experiments. The undisputable advantage of neutrons was largely employed for the characterization of the copper superconductors, for instance, giving always higher quality results on questionable oxygen atoms than any X-ray data. However, strictly speaking of structure solution, neutrons are mainly used for complementing X-ray results, allowing to answer specific questions like the location of light atoms such as H/D for organic compounds or O, F, Li (etc.) atoms for compounds containing very heavy X-ray scatterers (Bi, W, Pb, etc.). An example is α -La₂W₂O₉ (Laligant *et al.*, 2001) for which the W and La atoms could be located from the X-ray powder pattern, but not the oxygen atoms. The cell is triclinic, pseudo-cubic, but in spite of the considerable overlapping (see Figure 7.18), precluding any success by the direct methods, the nine independent oxygen atoms could be located by the direct-space Monte Carlo process in *ESPOIR* from the first 150 extracted intensities. In that case, a likely [WO₄] tetrahedra hypothesis failed, the compound exhibits a mixture of [WO₆] octahedra and [WO₅] trigonal bipyramids sharing corners.

Obvious other possibilities for the recording of multiple powder patterns are the use of texture (preferred orientations) (Lasocha and Schenk, 1997; Baerlocher *et al.*, 2004) or of anisotropic thermal expansion (Brunelli *et al.*, 2003) or of X-ray anomalous dispersion

(Prandl, 1990, 1994; Burger *et al.*, 1998) effects. Computer programs written and available for dealing with such multiple datasets are not numerous.

The combination of multiple techniques may as well, of course, extend the complexity limits associated with a single powder pattern. The techniques of choice to be combined with powder diffraction are electron microscopy (Gramm *et al.*, 2006) and solid state NMR (Middleton *et al.*, 2002; Harper *et al.*, 2006). However, given the single powder pattern measurement ease with a conventional laboratory diffractometer, it is probable that the multiple patterns/techniques approaches will not become the dominant procedure before a long time, at least for the simplest cases.

7.8 Conclusion

From the user point of view, the most interesting SDPD computer program is an integrated package able to perform all the steps (indexing, intensity extraction, space group estimation, structure solution, structure completion and even Rietveld refinements) with efficiency (press-button-solving). On the commercial side are *TOPAS* (Bruker), *Materials Studio* (Accelrys), or to a lesser extent *DASH* which is combined with *DICVOL* and applies the Pawley method. On the academic side are *EXPO* (combined with *N-TREOR*), *MAUD* or packages driven by a graphical user interface like *WinPLOTR* (calling *ITO*, *TREOR*, *DIC-VOL*, *McMaille*, *FULLPROF*, and more), *PowderX*. These suites may have some weaknesses, for instance, offering only one indexing program, or requiring a pure sample, or not providing complete Rietveld possibilities, or being able to perform well either the Patterson and direct methods or some of the direct-space ones, but not both approaches, and so forth. Anyway, the trend is now clearly toward more complete and automated systems (Altomare *et al.*, 2004b), this may allow to continue to decrease the training level in crystallography at universities. However, where automation fails, a well-trained crystallographer should succeed.

The answer to the question "What is a complex structure solved from powder diffraction nowadays?" could be: regarding the current efficiency of the various powder diffraction methodologies, a complex structure is simply a structure not yet solved. The level of complexity has moved enormously during the past 20 years, since methods have so largely progressed, and continue to progress. The direct-space methods revolution had the consequence that we can solve structures too large for being refined without restraints/constraints from a single powder pattern by the Rietveld method. We may also estimate that a structure is "complex" if it needs more than 50 DoFs at the structure solution stage, which may then correspond to an unlimited number of atomic coordinates refined at the last Rietveld step. Routine can be considered as attainable for less than 20 DoFs, if the powder pattern resolution is not too bad. The crystallographer skills have a role to play here, making the difference between a sample going back in a drawer for a long time, or a structure being finally published. This is a rather poor introduction to the next chapter, but the larger structures attainable at the structure solution step, which may sometimes correspond to 10 times more atomic coordinates than reflections, will produce monsters without some precautions at the Rietveld stage, to the point that the advice "make energy minimization, not Rietveld refinement" was recently given (Smrčok et al., 2007).

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Chapter 8 Structure Refinement

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8.1 An introduction to Rietveld refinement

Crystal structures are determined using structure factors, the amplitudes of which are derived from the measured integrated intensities of diffraction peaks. A serious disadvantage of powder diffraction compared to single-crystal techniques is that the three dimensions of diffraction information are compressed into the one-dimensional powder pattern. This "overlap problem" ultimately limits the amount of structural information obtainable from a powder pattern. Except in very simple cases, it is not possible to determine accurate integrated intensities of enough diffraction peaks (and thus structure factor magnitudes) to solve and refine a crystal structure in the routine fashion of conventional single-crystal techniques.

In a single-crystal experiment, the unit cell and space group are determined, the intensities of many diffraction peaks (reflections) are measured, and converted into structure factor magnitudes. Phases are derived using Patterson, direct methods, or other techniques, and a set of fractional atomic coordinates, displacement coefficients, and occupancies (the model) is derived. The model is then refined using non-linear least-squares techniques (Prince, 1994). The progress and quality of the refinement is monitored by several statistical quantities, the most important of which is the weighted *R*-factor:

$$\sum_{hkl} w_{hkl} \left(|F_o| - k |F_c| \right)^2$$
(8.1)

in which the sum is carried out over all measured reflections, F_o is the measured structure factor, F_c is the structure factor calculated from the model, k is a scale factor, and w is the weight of the reflection (generally $1/\sigma^2(F_o)$).

In developing what is now known as the Rietveld method (Rietveld, 1967, 1969), Hugo Rietveld had two great insights. One is that the individual data points in a powder pattern are equally valid least-squares quantities as structure factor magnitudes:

$$\sum_{i} w_i (y_{oi} - y_{ci})^2 \tag{8.2}$$

in which y_{oi} is the observed intensity at the *i*th data point, y_{ci} is the calculated intensity at that point, and *w* is a weight $(1/\sigma^2(y_{oi}))$. The sum is carried out over all points of the powder pattern. The second insight is that the intensities in a set of overlapping peaks could be partitioned according to the intensities calculated by the model. It is easier to measure the intensity of a point in a powder pattern than it is to measure a structure factor amplitude, but it is harder to calculate the intensity at that point. In addition to the normal structural parameters – atomic positions (fractional coordinates), occupancies, atomic scattering factors, displacement coefficients, lattice parameters, and symmetry – we need to include many "global" parameters such as incident intensity, concentration, background, diffuse scattering, extinction, absorption, preferred orientation, multiplicity, the Lorentz-polarization factor, the profile shape function, surface roughness, specimen displacement, and specimen transparency. All of these bits of diffraction physics can affect the intensity at a point in a powder pattern, and so need to be understood and modeled. Some of the parameters can be highly correlated. The Rietveld method was developed originally for low-resolution neutron diffraction data. Development of functions to describe X-ray peak profiles and enough computer power to carry out the refinements delayed widespread adoption of the Rietveld method until the mid-1980s.

We might consider the Rietveld method the opposite of "garbage in, garbage out." We can get the maximum information out of a diffraction pattern by putting in as much as we know about structure and diffraction physics. Effective use of the method requires a fair amount of knowledge and experience. An advantage of the Rietveld method is that ideal specimens are fairly rare; the method can account for all of those non-idealities encountered in real life in a physically meaningful way. Although originally developed to refine structures using powder data (a starting model is required), the information which can be derived from the global parameters is often more important in day-to-day applications. I do virtually all of my routine data processing by the Rietveld method.

8.2 Statistical and graphical measures of a refinement

There is no single measure of the quality of a Rietveld refinement. Applying the method successfully requires interacting with the raw data in a much more intimate fashion than most of my analytical colleagues. This interaction requires looking at a variety of measures, including statistical (Toby, 2006), graphical, and chemical.

Many statistical measures of the quality of a Rietveld refinement have been proposed, but none of them are suitable as the sole measure. Since we are trying to fit a model to data (never the other way around!), all of the measures ultimately try to assess the differences between the observed and calculated data points in the pattern.

The Rietveld algorithm minimizes the weighted sum of the differences between the observed and calculated profile points. The most straightforward statistical measure is the square root of the quantity minimized scaled by the weighted intensities, or the weighted profile *R*-factor, R_{wp} (Young, 1993):

$$R_{wp}^{2} = \frac{\sum_{i} w_{i} (y_{oi} - y_{ci})^{2}}{\sum_{i} w_{i} y_{oi}^{2}}$$
(8.3)

Another commonly calculated (but one which I do not find very useful) is the unweighted profile *R*-factor, R_p :

$$R_p = \frac{\sum_i |y_{oi} - y_{ci}|}{\sum_i y_{oi}}$$
(8.4)

Some programs calculate R_{wp} and R_p both for the full pattern and the backgroundsubtracted pattern. While the background-subtracted residuals can be useful for assessing the quality of the background fit, the most appropriate ones are the full pattern residuals. Other residuals (on *F* or F^2) sometimes calculated are those based on extracted structure factors. These are intended to be "comparable" to single-crystal *R* factors, but (since the structure factors are biased by the model) they do not really correspond to those measures.

It is worth considering what happens if we have an ideal model, that is, one which accurately predicts the value of each y_{oi} . The average value of $(y_{oi} - y_{ci})^2$ will then be $\sigma^2(y_{oi})$, and thus the expected value of $w_i(y_{oi} - y_{ci})^2$ equals one. The residual that one would obtain with this ideal model is the best possible value, if the $\sigma^2(y_{oi})$ are correct. This "best possible R_{wp} " is a very useful concept called the expected *R*-factor:

$$R_{\exp}^2 = \frac{N - P}{\sum_i w_i y_{oi}^2}$$
(8.5)

in which *N* is the number of data points and *P* is the number of least-squares variables (parameters). A related and very useful concept is that of χ^2 . If we have the ideal model, the expected value of $(y_{oi} - y_{ci})^2 / \sigma^2(y_{oi})$ is one, if the σ are correct. The χ^2 term is defined as the average of these values:

$$\chi^{2} = \frac{1}{N - P} \sum_{i} \frac{(y_{oi} - y_{ci})^{2}}{\sigma^{2}(y_{oi})}$$
(8.6)

Re-casting the mathematics into now more-familiar terms:

$$\chi^2 = \left(\frac{R_{wp}}{R_{exp}}\right) \tag{8.7}$$

The single-crystal community often uses the term *goodness of fit S*, for which $S^2 = \chi^2$.

During refinement, χ^2 starts out large, and decreases during the course of refinement. Ideally, χ^2 should equal one at convergence, but this is seldom the case. If $\chi^2 < 1$, it means that the $\sigma(y_{oi})$ are wrong, generally because of an error in data conversion or scaling. A χ^2 close to one is no guarantee that the model is correct; it merely means that the errors are dominated by statistical effects. In fact, some editors and reviewers do not understand that the easiest way to achieve a very low χ^2 is to collect poor (noisy) data, and have the statistical errors swamp out any errors in the model! If $\chi^2 > 1$ at the end of refinement, one (or more) of three things occur: (1) the model is reasonable but the σ are underestimated, (2) the model contains systematic errors, or (3) the model is wrong. High χ^2 can occur when the data are very good (high signal/noise, such as at a synchrotron or with a position-sensitive detector). Minor imperfections in the fit (such as peak shapes not modeled accurately by the profile functions available) become very large with respect to the experimental uncertainty. Many excellent papers with correct structures and high χ^2 are published, but the reasons for the poor fit are understood and described.

A useful way to test the quality of a Rietveld fit is to compare the χ^2 or R_{wp} to that obtained from a Pawley (Pawley, 1981) or Le Bail (Le Bail *et al.*, 1988) fit, which are ways of fitting the pattern without the structural model but using the global parameters. If the crystallographic fit is comparable to the Pawley/Le Bail fit, both the structural and experimental features (typically profile shapes and background) may be modeled well, but if the crystallographic fit is much poorer, there are likely to be problems with the structural model.

I tend to pay more attention than most people to the difference Fourier map. A difference Fourier calculation yields a map of the electron density which is "in" the data but not yet in the model. While such maps calculated from powder data are always flatter than those calculated using single-crystal data (because the model is used to partition the intensity among reflections), it is still a good thing if they contain no unexpected positive or negative features.

Because Rietveld refinement is a pattern fitting technique, graphical measures are important. We all expect to see an observed/calculated/difference plot (Figure 8.1) in a paper reporting the results of a Rietveld refinement, but displaying the whole pattern in one plot can often obscure small (and important) details. The ability to alter the vertical scale in different angular ranges of the plot is very helpful. I find that the weighted difference plot (Figure 8.2) is a useful way of renormalizing the full-scale plot, and making differences in the weaker portions of the pattern more prominent.

A particularly useful plot is the delta/sigma plot (Figure 8.3), in which $(y_{oi} - y_{ci})/\sigma(y_{oi})$ is plotted for each data point as a function of 2θ . We all know enough statistics to know that for a good fit, 99% of the points should fall within $\pm 3\sigma$. I find this plot to be very useful for detecting impurity phases.



Figure 8.1 A "Rietveld" plot for calcium tartrate tetrahydrate. The crosses represent the observed data points, and the continuous line through them is the calculated pattern. The difference pattern (observed – calculated) is plotted below the other patterns. The vertical scale of the $>50^{\circ}$ portion of the pattern is multiplied by a factor of 20. The row of tick marks indicates the calculated peak positions.


Figure 8.2 A weighted observed/calculated/difference plot for the same refinement of calcium tartrate tetrahydrate. This plot shows the actual function minimized in the Rietveld refinement, and shows how important the weak high-angle peaks are!



Figure 8.3 A "delta/sigma" plot for calcium tartrate tetrahydrate. This plot shows $(y_{oi} - y_{ci})/\sigma(y_{oi})$ as a function of diffraction angle 2θ .



Figure 8.4 A normal probability plot for calcium tartrate tetrahydrate. The slope of the central region $(\pm 2\sigma)$ is 1.580, showing that the standard uncertainties reported by the least-squares program are underestimated by a factor of 1.58. The *y*-intercept is 0.0342; this is close enough to zero to suggest that there are no significant systematic errors in the model.

An under-appreciated plot is the normal probability plot (Figure 8.4) (Prince, 1994). For a normal distribution of errors, we know how many points to expect in each interval of Δ/σ . If we sort the observed data points in order of Δ/σ , and plot them against the expected distribution of errors, we obtain the normal probability plot. For an ideal fit, the plot is a line through the origin with a slope of unity. If the slope is >1 (say 1.58), the standard uncertainties estimated by the least squares are underestimated by a factor of 1.58. A non-zero *y*-intercept indicates the presence of systematic errors.

Of course, we need to look at small regions of the pattern (Figures 8.5 and 8.6) in addition to the big picture. Such large-scale looks reveal deficiencies in profile functions and peaks not accounted for by the model. Trends in errors with diffraction angle can also indicate errors in the model. The ability to plot the background function separately from the overall pattern (Figure 8.7) is very useful in identifying regions in which the fit is poor, and make it easier to decide if more background parameters are needed or if too many have been used. Another useful plot is the cumulative χ^2 plot (Figure 8.8). This plots χ^2 as a function of diffraction angle. An ideal plot should rise smoothly, with no sharp jumps. Such sharp jumps indicate small regions (single peaks) for which the fit is not good, and indicate errors in the structural model and/or preferred orientation.

It is not possible to give definite rules of thumb for what are good values of R_{wp} and χ^2 . Using data from a normal laboratory diffractometer with a point counter, I generally



Figure 8.5 The 12–14° region of the pattern of calcium tartrate tetrahydrate. The major error is in the asymmetry of these low-angle peaks. The error in the integrated intensities is small, so the structural results are probably accurate.



Figure 8.6 The 40–50° portion of the calcium tartrate tetrahydrate pattern, illustrating the excellent fit of most of the peaks.



Figure 8.7 A Rietveld plot which shows the background function as a separate curve. The fact that the background function is above the observed data points $\sim 30^{\circ} 2\theta$ suggests that too many background terms (six) were used in this refinement.

feel good about $R_{wp} < 0.10$, but with synchrotron data or laboratory data collected with a position-sensitive detector, it is not unusual to achieve $R_{wp} < 0.01$. I almost always feel good about $1 < \chi^2 < 2$, but even in this range the structure can be wrong, and many chemically correct structures come from refinements with higher χ^2 .

8.3 Functions for describing peak shapes, backgrounds, and diffuse scattering

Because we must model all contributions to the intensity at a point y_{oi} , in carrying out a Rietveld refinement we often spend more time worrying about the global parameters than the structure. X-ray powder diffraction peak profiles arise from the convolution of a variety of instrumental and specimen-related effects (Ida *et al.*, 2001; Pecharsky and Zavalij, 2003). In the fundamental parameters approach (Cheary and Coelho, 1998) these effects are modeled explicitly, but a more-common approach is to use an empirical profile function. The most-effective function has been a pseudo-Voigt function, a linear combination of Gaussian and Lorentzian (more correctly known as Cauchy) components, modified for asymmetry and anisotropic broadening contributions. Different Rietveld programs parameterize this function in different (and sometimes unexpected) ways, so I will keep this discussion general.



Figure 8.8 A cumulative χ^2 plot for calcium tartrate tetrahydrate. The largest jumps in the plot occur at the strongest peaks, showing that the largest relative errors occur there. As we have seen, the asymmetry of these low-angle peaks is not modeled perfectly.

The Gaussian component of the profile is generally described using a Caglioti function (Caglioti *et al.*, 1958; Cheary and Cline, 1995), which was designed to describe broad peaks obtained using a monochromatic neutron source. Its use for X-ray peaks is completely empirical. This function contains a series of terms, which describe the Gaussian breadth (FWHM or a more fundamental quantity) of a diffraction peak. These terms generally include $U \tan^2 \theta$ (in which θ is one-half the Bragg angle 2θ), $V \tan \theta$, and a constant W. The coefficient U can include both instrumental and microstrain broadening. The coefficient V is intrinsically negative, and is generally zero for laboratory diffractometers. Sometimes include are $X \cot^2 \theta$ to describe wider peaks at low angles and $P/\cos^2 \theta$ to account for size broadening.

The Lorentzian (Cauchy) terms generally include a size broadening term $X/\cos\theta$ and a microstrain broadening term $Y \tan \theta$. Some programs include additional terms to permit description of anisotropic size and strain broadening, using a simple uniaxial model.

The detailed interpretation of the refined profile coefficients depends on the implementation in your particular Rietveld program. The size broadening coefficients can be converted into crystallite sizes using modifications of the Scherrer equation (Klug and Alexander, 1974). In my experience, size broadening is almost always Lorentzian rather than Gaussian. The strain coefficient(s) can be converted into average values of microstrain, which represent the average fractional variation in the lattice parameters, and represent the accumulation of the effects of various sorts of defects and imperfections in the crystallites. While it is possible to interpret them on an absolute basis, it is more generally useful to consider the relative degrees of microstrain in related specimens.

Peak asymmetry is generally described using either the "Rietveld" model (Rietveld, 1969; Cooper and Sayer, 1975; Thomas, 1977), which often works well for real samples, or the lessempirical "Finger" model (Finger *et al.*, 1994; Van Laar and Yelon, 1984). Generally, only one of the two coefficients in the Finger model can be refined successfully (stably), but since they can be calculated from the geometry of the instrument (a fundamental parameters approach), the best practice is to leave them fixed at their correct values.

Simple pseudo-Voigt functions often do not describe the profiles from real specimens well, especially in synchrotron data. Anisotropic peak broadening is very common, and led Stephens (1999) to derive a very useful and fundamentally correct model for anisotropic microstrain broadening (the most common kind). The number of coefficients depends on the crystal symmetry. Use of this model leads to much better fits in general, which then leads to better structures from the better intensities, and useful information from the anisotropy of the broadening.

Some programs include additional profile coefficients, which begin to attempt to describe additional contributions to the profiles from stacking faults and incommensurate/ modulated structures. Such materials are better modeled using special-purpose software (Treacy *et al.*, 1991; Dusek *et al.*, 2001) rather than conventional Rietveld packages.

Some programs, notably GSAS (Larson and Von Dreele, 2000), require an instrument parameters file, which along with other quantities contains instrumental values for the profile coefficients. Defining such a file is often a major hurdle for beginners at Rietveld refinement. The way to determine the instrumental profile coefficients is to collect data (of as wide an angular range as possible) from a specimen which exhibits neither size nor strain broadening. I recommend NIST SRM 660a, LaB₆ and its successors. Using the known structure and lattice parameters, the user can refine the various profile and instrument coefficients, and then enter these values into a new version of the default instrument parameter file supplied with GSAS.

Here is a sample GSAS instrument profile file:

```
123456789012345678901234567890123456789012345678901234567890
```

```
INS BANK 1
INS HTYPE PXCR
INS 1 IRAD 3
INS 1 ICONS 1.540629 1.544451 -0.990 0 0.5 0 0.5
INS 1I HEAD NIST SRM 660a LaB6 VANTEC-1 0.3 mm div slit
   29 Apr 2004
INS 11 ITYP 0 5.0000 150.0000 1
INS 1PRCF1 2 18 0.01
INS 1PRCF11 0.287900E+00 0.000000E+00 1.124000E+00 2.477000E+00
INS 1PRCF12 2.103000E+00 0.442000E+00 2.052000E+00 -4.818000E+00
INS 1PRCF13 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
INS 1PRCF14 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
INS 1PRCF15 0.000000E+00 0.000000E+00
INS 1PRCF2 3 13 0.01
INS 1PRCF21 0.336500E+00 0.000000E+00 1.032000E+00 0.000000E+00
INS 1PRCF22 2.526000E+00 2.051000E+00 0.269500E-01 0.005000E-01
```

INS 1PRCF23 0.444100E+00 -5.024000E+00 0.000000E+00 0.000000E+00
INS 1PRCF24 0.000000E+00
INS 1PRCF3 4 12 0.01
INS 1PRCF31 0.336500E+00 0.000000E+00 1.032000E+00 0.000000E+00
INS 1PRCF32 2.526000E+00 0.000000E+00 0.000000E+00 0.000000E+00
INS 1PRCF33 0.000000E+00 0.150000E-01 0.750000E+00

To extract useful information from the profile coefficients, we need to know the instrumental values, so determining them to create an instrument parameter file is not really a hardship. Because the peaks are narrow, we expect the values of the profile coefficients to be small numbers. It is not best practice to use a function with large coefficients (such as +200 and -199), because then the peak widths will be the small differences between large numbers. After the mechanical alignment, we can use the known lattice parameters of the SRM to determine any residual error in the diffractometer zero and any systematic errors in peak positions. Since we then know the diffractometer zero for the instrument, it is never reasonable to refine this term for a real specimen; the peak position errors are likely dominated by specimen displacement, rather than a constant. I find that most contemporary laboratory instruments have similar instrumental profile functions, and that the default INST_XRY.PRM is a good place to start.

In doing X-ray diffraction, we are naturally most interested in the crystalline components of the specimen. We tend to lump all sort of other effects (air scattering, scattering from components of the instrument, the tail of the small angle scattering, thermal diffuse scattering, . . .) into "background." In this discussion I specifically exclude scattering from amorphous component(s) of the specimen. Because in a Rietveld refinement we must model all points of the pattern, the background must be described. We specifically do not want to subtract it away, for two reasons: (1) we always get it wrong (because the peak tails extend much farther away from the peaks than we suspect), and (2) such subtraction would distort the standard uncertainties of the intensities, thus rendering all of the statistical measures meaningless. The description of the background almost always involves an empirical function. Three types of functions are commonly used.

The first type of background function is a Chebyshev polynomial of the first kind. The background intensity I_b is calculated:

$$I_b = \sum_{j=1}^{N} B_j T_{j-1}(x)$$
(8.8)

in which the *N* B_j are the refined coefficients and the T(x) are the Chebyshev polynomials of order j - 1 (Abramowitz and Stegun, 1970). The first polynomial $T_0(x) = 1$, $T_1(x) = x$, $T_2(x) = 2x^2 - 1$, and successive polynomials are generated by the recursion relation $T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x)$. To make the polynomials orthogonal (and thus enhance the convergence) x is generally not degrees 2θ but something like:

$$x = \frac{2(2\theta - 2\theta_{\min})}{2\theta_{\max} - 2\theta_{\min}} - 1$$
(8.9)

The second type of background function is a cosine Fourier series (in GSAS notation):

$$I_b = B_1 + \sum_{j=2}^{N} B_j \cos[x(j-1)]$$
(8.10)

In this function x is often 2θ degrees, but some programs convert it into radians or other units.

A third common type of background function is a polynomial in 2θ or $Q = 2\pi/d$ (using FullProf notation):

$$I_b = \sum_{m=0}^{11} B_m \left(\frac{2\theta}{BKPOS} - 1\right)^m$$
(8.11)

Generally, the origin of the polynomial is not at $2\theta = 0$, but at some other angle *BKPOS* is chosen by the user.

All of these functions include a constant term. Because all Rietveld programs use the counts at each point (not counts/s or other units), one can generally make a good initial guess at the constant term in the background function. The backgrounds in contemporary instruments are gently varying functions, so only a few background coefficients should be necessary, whatever function is used. Even though the functions are constructed to be orthogonal, the correlation coefficients among the background terms are often very high. It is a general rule that fewer parameters are better, and that is certainly the case for background terms.

Because the background functions are empirical, the user needs to experiment with the available functions to see which one describes the background from the instrument using the fewest number of terms. A shifted Chebyshev polynomial works better for one of my laboratory instruments, and a cosine Fourier series for the other. Functions with 2–9 terms generally work well. Many real patterns contain scattering from an amorphous component. Such "bumps" cannot be described using the conventional background functions unless too many terms are used. The conventional model for this diffuse scattering is the Debye model (Bouman, 1951; Klug and Alexander, 1974) for glasses. The function consists of a series of terms:

$$I_{DS} = A \frac{\sin(RQ)}{RQ} \exp\left(-\frac{1}{2}UQ^2\right)$$
(8.12)

in which A is an intensity coefficient, R is a characteristic distance chosen by the user, U is a "temperature factor" or standard uncertainty on this distance, and $Q = 2\pi/d$. Each term in the Debye function thus requires three coefficients, and generates a large-magnitude gently decreasing function (Figure 8.9). The "bumps" in the diffraction pattern come from differences between such terms (Figure 8.10). The basic idea is that combining these terms generates a reduced intensity function for the amorphous phase (Figure 8.11). Some distances are more probable than in a random distribution of atoms, and some are less probable. Unlike the terms in the background functions, these Debye terms are not orthogonal, and the net diffuse scattering is a small difference between larger terms. Convergence of diffuse scattering functions is often difficult, and it is almost always necessary to include damping on the least-squares shifts. Very often it is only possible to refine the A terms; the R and U are fixed at reasonable values.



Figure 8.9 Debye diffuse scattering terms calculated for different values of the characteristic distance *R* and the "standard deviation" *U*, with an amplitude *A* of unity. The terms for R = 1.60(5) and 2.40(5) Å are virtually identical at this scale.



Figure 8.10 Differences between pairs of Debye terms from Figure 8.9. Note the much smaller vertical scale of this figure. The amorphous "bumps" result from small differences between very large terms in the diffuse scattering function.



Figure 8.11 The reduced intensity function for amorphous silica. The sums and differences of the Debye terms are used to generate this function.

8.4 Refinement strategies

New users of the Rietveld method often ask for a "recipe" for how to carry out a refinement. While in a production environment it is possible to set up macros to use the same strategy (parameter turn on sequence) for many similar samples, it is difficult to specify a general procedure. We must remember that the Rietveld method is a *refinement* technique and that if our initial or current model is "too far" away from the converged model, refinement will be difficult. How far is "too far"? I find that refinement generally converges smoothly if all atoms are within ~0.5 Å of their final positions, but have had many successful refinements in which some atoms moved more than that. You like to start from a good structural model. It is certainly good to include a large fraction of the total scattering power in the initial model; you do not want too many missing atoms.

To begin a refinement, I include the major phases with good structural models, and refine scale factors for each phase and a small number of background terms. A key to successful refinement is to have the peaks in the right places. In the setup of the leastsquares computation, all programs define which peaks from which phases contribute to which points of the pattern. In some programs (like GSAS) this is a separate "preparation" step, while in other programs it is transparent to the user. The peak positions are determined by the lattice parameters and position error corrections (normally specimen displacement), so often the next step is to include refinement of the lattice parameters of at least the major phases and a specimen displacement coefficient (constrained to be the same for all phases in a mixture).

To guide the next steps of refinement, I look at the Rietveld plot, and try to deal with the largest sources of error in succession. As an example of the process, let us consider a mixture of hematite and magnetite, which constituted the debris after a fire in a chemical plant (Figure 8.12). An initial refinement of 2 scale factors (phase fractions) and a 3-term cosine Fourier series background function led to $R_{wp} = 0.4816$ and $\chi^2 = 33.46$ (Figure 8.13).



Figure 8.12 A mixture of hematite and magnetite from the debris after a chemical plant fire.



Figure 8.13 A Rietveld plot after the refinement of two phase fractions and three background terms. The peaks are not calculated in the correct positions, so add lattice parameters for both hematite and magnetite and a specimen displacement coefficient to the refinement.



Figure 8.14 A Rietveld plot after refinement of phase fractions, three background terms, lattice parameters, and specimen displacement. The largest errors are in the hematite peak shapes and the peaks are Lorentzian, so add the hematite profile *X* and *Y* coefficients to the refinement.

The calculated peak positions are not the same as the observed ones, so add to the refinement the hematite and magnetite lattice parameters and a specimen displacement coefficient. Now $R_{wp} = 0.4613$ and $\chi^2 = 30.72$ for the nine variables. The largest errors are clearly in the peak shapes (Figure 8.14), and the peaks are Lorentzian in shape (almost always the case on this instrument), so include hematite size and strain broadening coefficients. After refinement $R_{wp} = 0.1676$ and $\chi^2 = 4.057$ (Figure 8.15). The hematite peaks include contributions from both size and strain broadening.

The largest errors seem to be anisotropic widths of the hematite peaks, the magnetite peak widths, and the background at low angles. The background below $17^{\circ} 2\theta$ contains no useful information, so rather than trying to fit it using more background terms, exclude that region. Include a size broadening coefficient for the minor magnetite phase, and switch to the Stephens anisotropic strain broadening model. Now $R_{wp} = 0.1165$ and $\chi^2 = 1.945$ for 13 variables. Looking at the delta/sigma plot (Figure 8.16) rather than the normal Rietveld plot indicates that the background model needs improvement, so add three more terms to the background function. Now $R_{wp} = 0.1040$ and $\chi^2 = 1.551$ for 16 variables. The delta/sigma plot is fairly flat (Figure 8.17); there seem to be some errors in the relative intensities of the hematite peaks, but refining the structure did not improve the fit. These errors seem to be the result of granularity, rather than an incorrect structure model.

I chose to stop the refinement at this point, having answered the questions I set out to answer. The deposit was 94 wt% hematite and 6 wt% magnetite. The hematite lattice



Figure 8.15 Rietveld plot after including hematite profile coefficients. The largest errors are in the lowangle background and hematite peak widths, which seem to be anisotropic. Exclude the region below $17^{\circ} 2\theta$, switch to the Stephens anisotropic strain broadening profile function, and add a magnetite size broadening profile coefficient.

parameters were different from those expected for pure Fe₂O₃, so I concluded that some of the other metals from the stainless-steel wall were incorporated into the hematite. From the profile coefficients I could calculate an average crystallite size for each phase, and the degree of microstrain (consistent with both phases being solid solutions).

8.5 Use of chemical knowledge in Rietveld refinement – organic examples

Although statistical and graphical measures of a Rietveld refinement are important, chemical reasonableness carries even more weight (McCusker *et al.*, 1999). What do we mean by "chemical reasonableness"? This is shorthand for saying that (with \sim 500 000 crystal structures reported) we have a pretty good idea of normal values for bond distances, angles, and other bits of molecular geometry. Structures refined by the Rietveld method ought to fall within these normal ranges. We can use our chemical knowledge in *ab initio* structure solution, and both during the Rietveld refinement and in the analysis of the results.

Our chemical knowledge is summarized in different ways for different classes of compounds. The repository of organic crystal structures is the Cambridge Structural Database (Allen, 2002). We apply this knowledge of molecular geometry by incorporating restraints



Figure 8.16 This delta/sigma plot suggests that the background function needs improvement, so add three more terms to the cosine Fourier series.



Figure 8.17 The Rietveld error plot at the end of the refinement. The errors in the intensities of the hematite peaks were not decreased by refining the structure or any other parameters (and are probably the result of granularity of the non-rotated specimen), so the refinement was stopped.

(soft constraints) and rigid bodies into Rietveld refinements, and by comparing our results to those of published structures. Analysis of intermolecular interactions often involves examining the hydrogen bonding patterns, ensuring that molecules/atoms do not overlap, and that there are no unexpected holes in the structure. Just as examining the graphical aspects of the refinement is useful, actually *looking at* the structure can pinpoint errors. Much chemical knowledge is incorporated into structure validation programs such as CHECKCIF (Helliwell *et al.*, 2006) and PLATON (Spek, 2003).

8.5.1 Calcium tartrate tetrahydrate

The solid isolated from the bottom of a glass of wine was highly crystalline calcium tartrate tetrahydrate. A tartrate is a common anion, and several hundred crystal structures containing it have been reported. The geometry of a tartrate is analyzed easily using Mogul (Bruno *et al.*, 2004). For bond distances and angles, histograms and statistics are output. The standard uncertainty on a bond is typically 0.02 Å, and that on a bond angle is 2°. The bonds and angles are quite well defined! For torsions, averages are not computed, since they can be less meaningful; many torsions have multimodal distributions.

The distances and angles with the standard uncertainties from Mogul were input as restraints (soft constraints) into GSAS (Kaduk, 2007). Angle restraints must be specified for atoms in the same asymmetric unit, so some care may be necessary in choosing the atoms in the asymmetric unit. Angles involving symmetry-related atoms can be restrained by combinations of bonded and non-bonded distance restraints.

The restraints are treated as additional observations in the least squares, which is why they are collected in "histograms"; they are additional data items. For each sort of restraint, a weighting factor can be defined. This is the value used in the w(observed-value)² terms which are calculated for each restraint, and incorporated into the calculation of the overall reduced χ^2 . Often a high (1000–10 000) weighting factor is used early in the refinement, and is gradually decreased (to 1–10) as refinement progresses. The best practice is for the restraint weights to be small in the final refinement; we want the results to be dominated by the data, and not by our prior knowledge! There is often not enough information in an X-ray powder pattern to refine individual atomic displacement coefficients (thermal parameters), and only rarely can anisotropic displacement coefficients be refined successfully. Atoms can often be grouped by similarity of environment or topology. A common isotropic displacement coefficient was refined for the tartrate carbon atoms, another for the tartrate oxygens, and another for the four water molecule oxygens. The U_{iso} of each hydrogen was set to be 1.3× that of the atom to which it is attached; this is essentially the riding model often used in single-crystal refinements.

The CSD (Crystal Structure Database) does not report displacement coefficients, so we are faced with the problem of defining the initial values for the U_{iso} . For a known structure like this one, we can consult the original papers for the values (if they are reported at all). It might be necessary to consult deposited supplementary material. With experience, one can generally make reasonable guesses for the initial U_{iso} . For this refinement, I used 0.02 Å² for Ca, 0.03 Å² for C and O, and 0.039 Å² for the hydrogens. In refinements using X-ray data (especially laboratory data), it may be necessary to fix the U_{iso} of at least some atoms (especially lighter atoms) at reasonable values. Sometimes the data do not support

refinement of displacement coefficients, especially if the angular range is limited. The U_{iso} are often highly correlated to other parameters; for example, those for heavy atoms are correlated to the scale factor of the phase. It is never good practice to report non-positive-definite (negative) displacement coefficients, as these are not physically meaningful.

A difference Fourier is an electron density map calculated using the difference between the observed and calculated structure factor amplitudes F_o and F_c and the phases calculated from the current structure model. Positive peaks in the difference Fourier indicate electron density which is "in" the data but not yet in the model. Negative peaks (holes) indicate places where the model includes too much electron density. Difference maps calculated from powder data are flatter than single-crystal difference maps, because the F_o for overlapping reflections are partitioned according to the F_c , and are thus biased by the model. Nevertheless, they are useful for locating missing atoms and assessing whether atom types have been assigned correctly. For such a "complete" organic structure, the difference map should be flat, say to $\pm 1.0 \ e \ A^{-3}$. Difference maps for inorganic structures may exhibit larger peaks and holes, especially at special positions.

An excellent refinement was obtained (Figure 8.1). The final residuals for the refinement of 66 variables using 17 563 observations were $wR_p = 0.0455$, $R_p = 0.0352$, R(F) = 0.0927, $R(F^2) = 0.0897$, and $\chi^2 = 3.328$. The restraints contributed 0.5% to the final reduced χ^2 . The largest peak and hole in the final difference Fourier map were 0.76 and $-0.74 e \text{ Å}^{-3}$. The slope and intercept of the normal probability plot were 1.580 and 0.0342.

This structure contains a normal tartrate anion; all bond distances, angles, and torsion angles fall within the normal ranges. The carbon backbone exhibits the expected *trans* planar geometry; the average deviation from the mean plane is 0.013 Å. One of the carboxyl groups (C2–O6–O7) is rotated 53° from the backbone plane, and the other (C5–O10–O11) is 30° from that plane. The tartrate chelates to two Ca, using a hydroxyl group and one of the carboxylate oxygens. The other carboxylate oxygens (O7 and O10) bind to two additional Ca.

The Ca is 8-coordinate, and the coordination is irregular. Besides the six bonds to tartrates, the Ca is coordinated by two different water molecules. Two of the water molecules are solvates. The Ca–O bond distances range from 2.35 to 2.53 Å. Analysis of CaO₈ coordination spheres in the CSD shows that the expected Ca–O distance is 2.48 Å. The Ca–O distance expected by the bond valence formalism is 2.48 Å. The sum of the Ca–O bond valences is 2.22, showing that the Ca is "crowded."

A prominent feature of the crystal structure is the hydrogen bonding. Both hydroxy groups act as donors in very strong hydrogen bonds, O8–H18 to a solvated water molecule and O9–H19 to coordinated carboxylate oxygen. O9 also acts as an acceptor from a coordinated water molecule O12, but O8 does not act as an acceptor. Additional strong hydrogen bonds occur between the water molecules. Several weak hydrogen bonds also seem to be present, including the two C–H groups. The large amount of energy gained by the formation of these hydrogen bonds helps explain the high Ca bond valence and the relatively high density of this compound $(1.844 \text{ g cm}^{-3})$. Were such hydrogen bonds not present, I would consider the refined structure chemically unreasonable.

The data and the quality of the Rietveld refinement were good enough that the accuracy and precision of the chemically interesting quantities were nearly as good as those of singlecrystal refinements (Kaduk, 2007). Deciding whether the displacement coefficients (thermal parameters) are reasonable can be a challenge, because the CSD does not include them (although they are archived for current structures). Sometimes the displacement coefficients are included in the original publication, but more and more often they are relegated to supplemental material, which may or may not be accessible. Even if you can find them, there may be unit conversions required, because there have been many different conventions for reporting displacement coefficients. With experience, one gets a feel for what is reasonable and what is not.

Displacement coefficients from Rietveld refinements have a bad reputation, because they are often "too low," or even negative (physically unreasonable). If the various systematic intensity errors at low angles (such as beam spillover and surface roughness) are modeled and/or dealt with, reasonable displacement coefficients can be obtained from Rietveld refinements. Because the slurry mounting used for this specimen results in significant surface roughness, reasonable coefficients (fixed based on experience) in the Suortti model (Suortti, 1972) were included in the refinement.

8.5.2 Guaifenesin

Considering what is chemically reasonable can be important in the structure solution process. It can make the problem smaller, and save the crystallographer from wrong structures. A good example is the solution and refinement (Kaduk, 2004) of the common expectorant guaifenesin, 3-(2-methoxyphenoxy)-1,2-propanediol

The initial attempt to solve the crystal structure by applying Monte Carlo simulated annealing techniques to synchrotron data used five torsion angles. A retrospective analysis of torsion angles in the CSD showed that the torsion angles involving the phenyl-oxygen bonds had very narrow distributions around 180°. These two torsions could have been fixed during the structure solution, making the problem smaller. In the CSD, the three torsion angles in the propyl side chain exhibited the normal trimodal *trans/±-gauche* trimodal distributions. It is always worth carrying out such an analysis before the structure solution, rather than after.

The initial model yielded a reasonable fit to the powder pattern, but the torsion angles in the propyl side chain were very far from the expected values. The isotropic displacement coefficient U of the benzene ring carbon atoms was smaller than expected, while those of the side chain atoms became unreasonably large. Clearly this model was incorrect.

These clues forced me to consider other structural models, including different conformations of the propyl side chain. The actual thought process was more convoluted (Kaduk, 2004), but eventually a successful model was derived. It led to a much better fit, lower (quantum mechanical) energy, and a more chemically reasonable result.

Many common organic fragments are essentially rigid, and so can be described as rigid bodies to decrease the number of variables in the Rietveld refinement. There is really no need to refine all of the structural parameters of a benzene ring! One needs to check whether one's preconceived notions are correct, because some fragments (such as aromatic carboxylic acids, Kaduk *et al.*, 1999a) are more flexible than we chemists believe. A rigid body was used to model the C_6H_4 benzene ring fragment of guaifenesin.

Rigid bodies in GSAS are described using a local Cartesian coordinate system. The basis vectors are defined using interatomic vectors. It sometimes is valuable to include zero-occupancy dummy atoms in the rigid body to make the vector definitions more



Figure 8.18 Atom names and sequence numbers for the C₆H₄ rigid body in guaifenesin.

Atom	X	У	Z	
C1	-1	0	0	
C2	-0.5000	-0.8660	0	
C3	0.5000	-0.8660	0	
C4	1	0	0	
C5	0.5000	0.8660	0	
C6	-0.5000	0.8660	0	
H7	-1.6895	0	0	
H8	-0.8448	-1.4632	0	
H9	0.8448	-1.4632	0	
H10 1.6895		0		

Table 8.1 Local Cartesian coordinates of the C_6H_4 rigid body in guaifenesin. C–C bond length = 1.392 Å. The local x-axis points from C1 to C4, and the local y-axis points from C2 to C6

straightforward. The magnitudes of the Cartesian basis vectors can be 1 Å, but I find it more useful to make the lengths of the basis vectors correspond to one of the bonds in the fragment (which can then be used as a least-squares variable).

I numbered the atoms of the C_6H_4 rigid body as shown in Figure 8.18. We define the positive *x*-direction as pointing from C1 to C4, and the positive *y*-direction as pointing from atom C2 to C6. The *z*-axis is computed as the cross product of *x* and *y*. The interatomic vectors define the directions of the axes, not the origin of the coordinate system. We choose the origin to make computing the Cartesian coordinates as simple as possible. I chose as the length of the basis vectors 1.392 Å, the length of the C–C bond in the benzene ring. With these definitions, I could derive the rigid-body coordinates in Table 8.1.

In addition to the rigid body, restraints were applied. The phenyl carbon–oxygen bonds C6–O11 and C5–O16 were restrained to 1.44(1) Å, the sp^3 carbon–oxygen bonds O11–C12 and O16–C17 were restrained to 1.42(1) Å, the sp^3 C–C bonds C17–C18 and C18–C19 to 1.52(1) Å, and the C-hydroxyl bonds C18–O21 and C19–O20 to 1.40(1) Å. The sp^2 C–O– sp^3 C angles were restrained to 115(3)°, and the angles around the sp^3 carbon atoms to 109(3)°. All of these values were derived from a fragment analysis in Mogul. The final hydrogen positions were determined by a quantum mechanical geometry optimization (Segall *et al.*, 2002). Several of the hydrogens could be located in a difference Fourier map.



Figure 8.19 A Rietveld plot for guaifenesin. The vertical scale of the $2\theta > 9^\circ$ portion of the pattern has been multiplied by a factor of 6.

The U_{iso} of the phenyl ring carbon atoms were constrained to the same value. Common U_{iso} were refined for the methoxy group O11/C12, O16/C17, C18/C19, and O20/O21. The U_{iso} of the hydrogens were constrained to be $1.3 \times$ of that of the heavy atom to which they are attached. Chemically similar atoms were assumed to have the same U_{iso} , and an effective riding model was used for the hydrogens.

The final refinement of 56 variables using 8213 observations yielded the excellent residuals $wR_p = 0.1092$, $R_p = 0.0856$, $\chi^2 = 1.643$, $R(F^2) = 0.1179$, and R(F) = 0.0931(Figure 8.19). The restraints contributed 1.5% to the final reduced χ^2 . The final torsion angles fell within the expected ranges. By all measures – statistical, graphical, and chemical reasonableness – this was an outstanding refinement, and could be used to assess the energetics of the conformation in the crystal and in the gas phase, as well as the hydrogen bonding.

8.6 Use of chemical knowledge in Rietveld refinement – inorganic examples

Inorganic crystal structures are archived in the Linus Pauling File/PDF-4+ (Villars *et al.*, 1998), the Inorganic Crystal Structure Database (Hellenbrandt, 2004), and CRYSTMET (White *et al.*, 2002). Our knowledge of inorganic bond distances is most conveniently

summarized in the bond valence formalism (Brown and Altermatt, 1985; Brown, 1996, 2002) and tables of ionic radii (Shannon and Prewitt, 1969, 1970). Typical interatomic distances in inorganic compounds are tabulated (Bergerhoff and Brandenburg, 1999).

Just as with organic compounds, we apply this knowledge of molecular geometry by incorporating restraints (soft constraints) and rigid bodies into Rietveld refinements, and by comparing our results to those of published structures. Analysis of the displacement coefficients can often give a clue that something is wrong with a structural model. The behavior of the refinement (particularly if it does not converge) can be a sign of an error in describing the symmetry. Just as examining the graphical aspects of the refinement is useful, actually *looking at* the structure can pinpoint errors.

8.6.1 Bond valence

As crystallographic techniques developed, it became clear that there was a relationship between the length of a bond and its strength [(Brown, 2002), and references therein]. We can consider the atomic valence V_i (the absolute value of the oxidation state) of atom *i* in a crystal structure to be the sum of the individual bond valences:

$$V_i = \sum_j S_{ij} \tag{8.13}$$

and that the bond valence between atoms i and j is approximated by the two-parameter expression:

$$S_{ij} = \exp\left(\frac{R_0 - R_{ij}}{B}\right) \tag{8.14}$$

in which R_{ij} is the distance between atoms *i* and *j* and R_0 and *B* are parameters chosen to ensure good agreement between the sums of bond valences and the atomic valences (formal charges or oxidation states) in a large number of well-determined crystal structures. For many bonds, *B* is close to 0.37 Å. Brese and O'Keeffe (1991) determined these parameters for a large number of cation–anion pairs, and I. D. Brown maintains a current set of bond valence parameters at http://www.ccp14.ac.uk/ccp/webmirrors/i_d_brown/bond_valence_param. Workers on a specific subset of compounds often determine more precise bond valence parameters for their particular system (e.g., Sidey, 2006). It is often useful to incorporate the expected values for the bond distances in a particular cation–anion coordination sphere into a Rietveld refinement as restraints (soft constraints).

8.6.2 Hexaaquairon(II) tetrafluoroborate, [Fe(H₂O)₆](BF₄)₂

A deposit isolated from a linear alpha-olefins plant (which used a BF₃ catalyst) turned out to be mainly boric acid, but the pattern contained a few weak peaks which did not match any entry in the Powder Diffraction File (PDF). Most of the boric acid could be washed away with methanol, leaving a nearly white highly crystalline powder (Figure 8.20).



Figure 8.20 The powder pattern of a methanol-washed linear alpha-olefins plant deposit, showing the trace of boric acid remaining. The vertical scale is logarithmic.

The pattern could be indexed (Visser, 1969) on a primitive orthorhombic unit cell having a = 7.686, b = 13.286, c = 5.376 Å, and V = 548.95 Å³. This cell accounted for 17 of the first 20 peaks, with a figure of merit of 34.4. This figure of merit is high enough that we can believe there is some truth to the cell, even though it does not account for a small number of impurity peaks. The ITO output suggested that "the cell is probably hexagonal, with a = 15.34 and c = 5.38 Å." ITO's suggestions of higher symmetry (based on the reduced form of the unit cell (Mighell and Rodgers, 1980; Stalick and Mighell, 1986)) are correct often enough that they need to be taken seriously – but in this case I believe the program was wrong.

Reduced cell searches of both the orthorhombic and hexagonal cells in the Inorganic Crystal Structure Database, using 0.2 Å tolerances (larger than the default of 0.1 Å) on the cell lengths and 1° on the angles, yielded no hits. Searches using even larger tolerances on the edges yielded what eventually turned out to be the correct structure model – but the actual thought process was more convoluted. Similar reduced cell searches in the NIST Crystal Data Identification File (Mighell and Karen, 1996) using 0.3 Å tolerances on the cell edges yielded a number of divalent metal perchlorate and tetrafluoroborate hexahydrates (ClO_4^- and BF_4^- are very similar in size, and identical in shape) – most of them from the same paper (Moss *et al.*, 1961). The lattice constants were determined using a 9 cm diameter Debye–Scherrer camera, so I could not be really sure that the cells were hexagonal or pseudo-hexagonal, but we can be reasonably sure that the compound I isolated is $Fe(BF_4)_2(H_2O)_6$.

Fe(BF₄)₂(H₂O)₆ is present in the PDF as entry 00-021-0427 (Ostrovskaya *et al.*, 1967), and is reported to crystallize in *Pmn2*₁ with a = 7.71, b = 13.54, and c = 5.42 Å. This is essentially the same cell determined by ITO. The pattern does not look particularly like the observed pattern (Figure 8.21), but it contains visual intensities, was measured using FeK α radiation, and has a Smith–Snyder figure of merit F(18) = 1(0.088, 185). This is



Figure 8.21 Comparison of the observed pattern and the PDF entry for $[Fe(H_2O)_6](BF_4)_2$.



Figure 8.22 The twinned crystal structure of $[Fe(H_2O_6)](ClO_4)_2$.

not a high-quality pattern, consistent with its "blank" quality mark. The PDF entry lists $Mg(ClO_4)_2(H_2O)_6$ as the prototype structure. This turns out to be correct.

The crystal structure of $Fe(ClO_4)_2(H_2O)_6$ (which should be isostructural to $Fe(BF_4)_2(H_2O)_6$) has been reported (Ghosh and Ray, 1981): space group $P6_3mc$, with a = 7.815 and c = 5.13 Å. The structure (Figure 8.22) looks unusual – and chemically unreasonable. There are columns of half-occupied face-sharing octahedral Fe sites, bridged by three water molecules. The nature of the problem is clear if we read the comments in the ICSD (Inorganic Crystal Structure Database) entry. The structure was determined in a subgroup using data collected from a 3-component twin. The true space group is reported

as *Pmn*2₁. The pictured structure thus represents a superposition of multiple images of the true structure. Since we do not have twins in a powder experiment, we may actually have an advantage attempting to solve and refine such a structure compared to a twinned single crystal!

The hexagonal cell suggested by ITO has a = 15.34 and c = 5.38 Å; *a* is twice that reported for Fe(ClO)₄(H₂O)₆. I thus built a 2 × 2 × 1 supercell in space group *P*1, deleted every other Fe (up/down and side/side), and searched for higher symmetry (Accelrys Software, 2005). The suggested space group was *Pmn*2₁ with a = 7.686, b = 13.286, and c = 5.376 Å – the original orthorhombic cell determined by ITO! A reduced cell search in the ICSD and PDF-4+ 2006 yielded the iron tetrafluoroborate we have already encountered, the deleted PDF entry 6-197 for zinc perchlorate hexahydrate (*Pmn*2₁), and Mg(ClO₄)₂(H₂O)₆ (01-085-0609/24250 (West, 1935)). This structure is stable from 272 to 324 K (important later), and is very strange. West describes the structure as a "hermaphrodite"; the perchlorate sublattice is orthorhombic and ordered, but the hexagonal metal/water sublattice is threefold twinned within the anion sublattice. The ordered Mg(ClO₄)₂(H₂O)₆ model proved to be an acceptable initial model for refining the structure of Fe(BF₄)₂(H₂O)₆.

A good refinement ($wR_p = 0.0142$, $R_p = 0.0111$, $\chi^2 = 1.490$ for 59 variables) was obtained (Figure 8.23). The compound is moisture-sensitive, and so was protected from the atmosphere by a Kapton window, which yielded the amorphous background.

In the early stages of refinement, the two crystallographically independent BF₄ anions were described as rigid bodies (Table 8.2). The GSAS definitions and conventions described



Figure 8.23 Rietveld plot for the refinement of $[Fe(H_2O)_6](BF_4)_2$.

Atom	X	У	Z
B1	0	0	0
F2	-0.8165	0	-0.5774
F3	0.8165	0	-0.5774
F4	0	-0.8165	0.5774
F5	0	0.8165	0.5774

Table 8.2 GSAS Cartesian coordinates of a tetrahedral AX₄ rigid body in terms of the A–X bond length (1.42 Å for BF₄). The *x*-axis of the coordinate system points from atom 2 to 3, the *y*-axis from atoms 4 to 5, and the *z*-axis is $x \times y$

previously (Kaduk, 2007) were followed. The central atom of the tetrahedral group is located at the center of a cube, and the outer atoms occupy alternate corners of the cube. The B–F bond length b is $\frac{1}{2}$ the body diagonal of the cube edge a, or $2b = 3^{1/2}a$. A little solid geometry shows that the $\pm x$, y coordinates of the F atoms are $(2^{1/2}/2)a = (2^{1/2}/3^{1/2})b$, and that the $\pm z$ coordinates are $\frac{1}{2}a = (1/3^{1/2})b$. The x-axis of the local Cartesian system points from atom 2 to 3, and the y-axis from atoms 4 to 5. A trick (or potential problem) in defining such a tetrahedral rigid body is ensuring that the atoms are listed in the same order as you have defined the body, and that the chirality of the group is not inverted. In all refinements, restraints of 2.14(2) Å were applied to the Fe–O bonds and $90(3)^{\circ}$ to the O-Fe-O cis angles. In the final refinement, the BF4 rigid bodies were removed, and replaced with restraints of 1.42(1) Å on the B-F bonds and 109.5(30)° on the F-B-F angles. Analysis of all 59 Fe²⁺O₆ coordination spheres in the Cambridge Structural Database (Allen, 2002) suggested a value of 2.10(6) Å, and bond valence parameters yield 2.16 Å. The standard uncertainties on the restraints were my own typical estimates. Analysis of 5546 hits in the CSD suggested a value of 1.36(6) Å for the B-F bond distance, bond valence parameters suggest 1.39 Å, the International Tables suggests 1.37(7) Å, and analysis of tetrafluoroborates in the ICSD suggested a value of 1.37(3) Å. Since BF₄ anions are often disordered and/or exhibit large thermal motion (both of which lengthen the apparent bond distance), I chose a larger value for the restraint.

In this refinement, I chose to restrain the tetrahedral F–B–F angles directly. Three of the four F atoms in each BF₄ were part of the asymmetric unit (one is a symmetry-generated atom). Angle restraints require all of the atoms to be within the asymmetric unit, so three F–B–F angles could be restrained. I felt that would be enough to restrain the tetrahedral geometry. Distance restraints can be defined between atoms of different asymmetric units, so an alternate way of defining angle restraints is to use a combination of bonded and non-bonded distance restraints. For the B–F distance of 1.42 Å, it is easy to use the law of cosines ($c^2 = a^2 + b^2 - 2ab \cos \gamma$) to calculate ideal the F ··· F distance as 2.32 Å.

The refinement yielded a reasonable structure (Figure 8.24). The Fe–O bonds range from 2.13 to 2.16 Å, the O–Fe–O *cis* angles from 65 to 100°, and the O–Fe–O *trans* angles from 165 to 175°. The B–F bonds are all between 1.41 and 1.42 Å, and the F–B–F angles vary from 83 to 114 and 104 to 112° in the two tetrafluoroborates. One of the BF₄ is slightly distorted. The U_{iso} of the Fe and O atoms are 0.037(2) and 0.056(3) Å²; higher than we



Figure 8.24 Crystal structure of $[Fe(H_2O)_6](BF_4)_2$.

might expect in an inorganic compound, but not unreasonable. The U_{iso} of the atoms in the two BF₄ were uncomfortably large at 0.158(6) and 0.092(5) Å².

Most chemists know that, as a tetrahedral group, the tetrafluoroborate is often disordered statically or dynamically in crystal structures. We might, then, expect the U_{iso} to be large, but how large is unreasonably large? Because the BF₄ is often the disordered counterion to a more chemically interesting cationic complex, there are fewer well-defined BF4 structures than one might expect. Of the 67 BF₄ structures in release 2006/2 of the ICSD, 28% of them have missing displacement coefficients or (almost as bad) coefficients reported as betas. For low-temperature (<200 K) structures the U_{iso} for BF₄ lie mainly in the range 0.02–0.06 Å², but some are in the range 0.12–0.16 Å². In room temperature structures, they are, of course, higher, generally ranging from 0.03 to 0.07 Å², but some range much higher. In the overall universe of BF₄ U_{iso} , the values observed here are not too unreasonable. The CCDC (Cambridge Crystallographic Data Centre) for a long time did not even archive displacement coefficients, and those for newer structures are not reported in the current releases of the CSD. Many of the tetrafluoroborate atom coordinates are not even reported, as the anions are badly disordered. Checking a few of the primary papers for CSD BF₄ structures suggests that the 0.16 and 0.09 Å² observed here are not exceptionally high, and so are chemically reasonable.

The final hydrogen positions were determined by a quantum chemical geometry optimization (Segall *et al.*, 2002). This DFT calculation permitted an analysis of the hydrogen bonding. Each of the water molecule hydrogens acts as a hydrogen bond donor, as expected; every hydrogen bond that *can* form *does* form. If the refined structure did not show such hydrogen bonds, I would consider it chemically unreasonable. The hydrogen bond geometries are reasonable, but the H-bonds are weaker than I might have expected. The hydrogen bond pattern provides more evidence for the chemical reasonableness of this structure. Measurements of the physical properties of this and other divalent metal tetrafluoroborate hexahydrates shows that they all melt close to room temperature. My deliberate and accidental examinations of compounds close to their melting points convinces me that values of U_{iso} of 0.16 and 0.09 Å² are not at all unreasonable for a structure determined within 5° of the melting point! Knowledge of chemical reasonableness played a role at almost every point in the solving and refining of the crystal structure of $[Fe(H_2O)_6](BF_4)_2$, and shows how important such knowledge can be to success in a Rietveld refinement.

8.6.3 Barium strontium titanium oxides, $(Ba_{2-x}Sr_x)TiO_4$

Since the discovery of the ferroelectric effect in Rochelle salt in 1920, extensive research in new ferroelectric materials has been conducted in the BaO–TiO₂ and SrO–TiO₂ systems (Line and Glass, 1997). Despite disagreements on the existence of a number of Ba–Ti–O phases in this system, the 2:1 phase (Ba₂TiO₄) has consistently been reported. Crystal structures of Ba₂TiO₄ in both the orthorhombic α' (Günter and Jameson, 1984) and monoclinic β (Wu and Brown, 1973; Bland, 1961) forms have been reported. Sr₂TiO₄ was the first member of the n = 1 Sr_{n+1}Ti_nO_{3n+1} series discovered by Ruddlesten and Popper (Ruddlesden and Popper, 1957). It adopts a tetragonal *I*4/*mmm* structure (Lukaszewicz, 1959) which is different from that of Ba₂TiO₄.

To explore the influence of cation substitution on crystallographic and other properties, characterization of solid solution compounds in the (SrO–TiO₂):(BaO–TiO₂) systems was undertaken (Wong-Ng *et al.*, 2007). In the $(Ba_{2-x}Sr_x)TiO_4$ series, it is important to understand the detailed crystallography and crystal chemistry of the intermediate members, since the structures of the two end members are not the same. No detailed structure of $(Ba_{2-x}Sr_x)TiO_4$ has been reported, although powder patterns of the orthorhombic phases $Ba_{0.56}Sr_{1.44}TiO_4$ (PDF 00-013-0269) and $Ba_{1.91}Sr_{0.09}TiO_4$ (PDF 00-013-0522) have been published (Kwestroo and Paping, 1959).

A preliminary pattern of $(Ba_{1.5}Sr_{0.5})TiO_4$ suggested that this compound was orthorhombic, "like Ba_2TiO_4 ," but the pattern showed evidence of granularity (Figure 8.25). Accordingly, it was ground in a McCrone micronizing mill using corundum media and ethanol as the milling liquid. The volume of sample was, however, too small for the micronizing mill, and the sample was diluted with amorphous silica for grinding. I judged it better to have a random powder with a high background (which could be modeled) than to have a granular specimen.

Orthorhombic β' -Ba₂TiO₄ crystallizes in $P2_1nb$, with a = 6.107(1), b = 22.952(4), and c = 10.540(2) Å. I used the coordinates and cell of ICSD entry 29389 as the initial model, but the refinements diverged. The refined lattice parameters of (Ba_{1.5}Sr_{0.5})TiO₄ turned out to be a = 6.0634(2), b = 22.6606(9), and c = 10.4040(4) Å. These are significantly different from the initial values! In this case, the initial values of the lattice parameters were far enough from the true values that many peak positions were calculated in regions where there was only background intensity, and the least squares had essentially no "signal" to work with when attempting to optimize the peak positions by refining the lattice parameters, and "got lost" (diverged). In this case, I made some manual adjustments to the lattice parameters to make them smaller, and eventually got the peaks in the right places. A more generally



Figure 8.25 Powder pattern of (Ba_{1.5}Sr_{0.5})TiO₄, showing evidence of granularity.



Figure 8.26 A Rietveld plot of the first wrong structure for (Ba_{1.5}Sr_{0.5})TiO₄.

useful and efficient strategy is to index the pattern and get more reasonable initial values for the lattice parameters.

Eventually I obtained an excellent refinement (Figure 8.26). All of the statistical measures were acceptable: $R_{wp} = 0.1090$, $R_p = 0.0838$, $\chi^2 = 1.345$, and $R(F^2) = 0.1199$ – but the structure was wrong! How did I know? The refinement of the atom coordinates never

converged, even with a coordinate damping factor of 9 (applying only 1/10 of the calculated shift to the coordinates in each least-squares cycle). A refinement that does not converge is a sure sign that something is wrong with the model or the data, or both. You never want to report the results from a non-converged refinement, because all variables affect each other; a good practice is to turn on the output of the correlation matrix in the print options. The stoichiometry derived from the fractional occupancies of the Ba/Sr sites was wrong. The difference between the 56 electrons of Ba and the 38 electrons of Sr is large enough that we should expect to get the fractional occupancies right, even using laboratory X-ray data. The standard uncertainties of the fractional coordinates were higher than I am used to seeing using data from this instrument. I would expect the standard uncertainties on the xyz fractional coordinates of the Ba/Sr sites to be in the 4th (or perhaps 5th decimal place for such a system, and here they were $\sim 0.006/0.001/0.002$. We expect the standard uncertainties on the Ti coordinates to be larger, but the 0.012/0.0028/0.0047 obtained here are much too high to be reasonable; I would expect them to be of the order of 0.0003. In the presence of such heavy atoms, we expect to determine the oxygen coordinates less precisely, but standard uncertainties $\sim 0.02/0.005/0.02$ are much too large; we could reasonably expect the standard uncertainties to creep into the third decimal place. The U_{iso} of the oxygen atoms did not refine to a reasonable value, but that is not unusual in the presence of heavy atoms using X-ray data.

This combination of problems is often associated with getting the symmetry wrong. I thus input the coordinates into the MISSYM program of the NRCVAX system (Gabe *et al.*, 1989). This functionality is now included in PLATON and *checkCIF*. It is always worth checking your refined structure using such programs, and if you submit to *Acta Crystallographica*, you will be forced to! The program suggested the presence of a center of symmetry at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ – and thus that the space groups was really *Pmnb*. As a consequence, the six Ba/Sr sites, the three Ti, and six of the oxygens are located on a mirror plane rather than a general position in *P*2₁*nb*. Attempting to refine a structure in a space group with symmetry too low can yield the symptoms observed here.

I therefore (manually) moved the appropriate atoms to the special positions and changed the space group. The resulting refinement (Figure 8.27) was just about as good as the first: $R_{wp} = 0.1101$, $R_p = 0.0851$, $\chi^2 = 1.370$, and $R(F^2) = 0.1424$, but this one used only 61 instead of 85 variables. This refinement still never converged (the shifts of the atom coordinates alternated between positive and negative, and never went to zero), but the Ba/Sr site occupancies were better. The composition was Ba_{1.3}Sr_{0.7}; closer to the known Ba_{1.5}Sr_{0.5} but still disappointing. The U_{iso} of the heavy atoms fell within normal ranges, but it still was not possible to refine the U_{iso} for the oxygen atoms. The standard uncertainties on the fractional coordinates were still too large: 0.001–0.004 for the heavy atoms, and 0.003–0.012 for the oxygen atoms. The most worrisome feature was that this (fairly large) unit cell required that many low-angle peaks be unobserved accidentally (not extinct by symmetry). It is always unsettling to have many very weak (unobserved) peaks, for it causes you to question whether you have the correct unit cell. This idea is built into the definition of the Smith–Snyder figure of merit for indexing; a smaller unit cell which accounts for all of the peaks is favored over a larger cell.

Another application of MISSYM (with larger than the default tolerances) suggested the presence of additional translational symmetry, with the translation vector 0,1/3,0. At this point, I finally *looked* at the structure (Figure 8.28) – and realized that $\beta'Ba_2TiO_4$ is clearly



Figure 8.27 A Rietveld plot of the second wrong structure for $(Ba_{1.5}Sr_{0.5})TiO_4$.



Figure 8.28 A view of the second wrong structure of $(Ba_{1,5}Sr_{0,5})TiO_4$.

a superstructure with its *b*-axis $3 \times$ that of a smaller unit cell! Searching the *a*, $\frac{1}{3}b$, *c* cell against the NIST Crystal Data Identification File, I discovered that $(Ba_{1.5}Sr_{0.5})TiO_4$ is actually isostructural to K₂SO₄, and that I had been using a unit cell three times too large.

Starting over with coordinates based on those of K₂SO₄, I obtained an excellent refinement (Figure 8.29). The residuals were $R_{wp} = 0.1115$, $R_p = 0.0864$, $\chi^2 = 1.396$, and $R(F^2) = 0.1565$, and the model was chemically reasonable! The refinement of only 32 variables yielded a composition Ba_{1.58}Sr_{0.42}, acceptably close to the expected Ba_{1.5}Sr_{0.5}. The



Figure 8.29 The final Rietveld plot for (Ba_{1.5}Sr_{0.5})TiO₄.

Ba/Sr U_{iso} was 0.017(1) Å²; reasonable for a disordered large cation site. The Ti U_{iso} was a reasonable 0.013(3) Å², and the O U_{iso} refined to 0.054(7) Å², perhaps a little high for a ceramic, but remember that the oxygen atoms are bonded to Ba/Sr which are disordered. The standard uncertainties on the Ba/Sr, Ti, and O fractional coordinates were ~0.0004, 0.0011, and 0.00*n* respectively, about what I would expect for such a system. The interatomic distances (subjected to restraints) and the O–Ti–O angles (free) were reasonable. Finally, a structure which all of the statistical, graphical, and chemical measures suggest is correct!

The next compound in the series was $(Ba_{1.25}Sr_{0.75})TiO_4$. Given the trouble I had with $(Ba_{1.5}Sr_{0.5})TiO_4$, I collected synchrotron data (at the MR-CAT ID10 beam line at APS) on this compound from a rotated capillary specimen using a wavelength of 0.4959 Å (25 KeV). Starting from the final $(Ba_{1.5}Sr_{0.5})TiO_4$ model yielded a reasonable refinement (49 variables): *Pnma*, a = 7.48904(3), b = 6.03638(3), c = 10.32873(5) Å, V = 466.928(4) Å³, $wR_p = 0.0847$, $R_p = 0.0621$, $\chi^2 = 2.625$. The refined stoichiometry was $(Ba_{1.13}Sr_{0.87})TiO_4$. The U_{iso} for Ba/Sr, Ti, and O were 0.0245(5), 0.0240(16), and 0.066(3) Å², respectively. The Ti and (notably) the O U_{iso} seemed a little high, especially since I had very good synchrotron data.

A full-scale Rietveld difference plot (Figure 8.30) looked good, but a blow-up of the pattern (Figure 8.31) revealed the presence of a number of weak peaks not accounted for by the model. Searches of these peaks (manually picked off from the difference plot) against the PDF showed that they did not correspond to any known phase, or to a new composition isostructural to a known phase.



Figure 8.30 A full-scale Rietveld plot of (Ba_{1.25}Sr_{0.75})TiO₄.



Figure 8.31 A Rietveld plot of $(Ba_{1.25}Sr_{0.75})TiO_4$, with an expanded vertical scale, to show the extra peaks not accounted for by the model.

To test the hypothesis that these peaks were part of the pattern of the major phase, I added them one at a time to the 43 strongest low-angle peaks (this is really too many for indexing, but that's another story), and tried to index the pattern using DICVOL91 (Boultif and Louër, 1991). An often-annoying feature of DICVOL91 (and one overcome in later versions) was that it allowed no un-indexed lines; this proved to be a useful feature in this problem. No matter which line I added, the program kept coming up with the same primitive orthorhombic unit cell: a = 14.9760, b = 10.3177, c = 6.0366 Å, and V = 932.77 Å³. The *a*-axis was twice that I had been using; apparently this compound crystallized in a 2× supercell of the original cell. A reduced cell search in the ICSD (with expanded tolerances of 0.2 Å and 1°) yielded (NH₄)₂BeF₄, which crystallizes in space group *Pna2*₁ (Srivastava *et al.*, 1999).

In addition to the distance (Ti–O = 1.82(1) Å) and angle (O–Ti–O = 109.5(10)°) restraints, a restraint was placed on the composition of the major phase. Each Ba/Sr site was modeled as a mixture of Ba and Sr. The Ba were atoms 1, 3, 5, and 7, and the Sr were atoms 2, 4, 6, and 8. The fractional coordinates of the Ba1/Sr2, Ba3/Sr4, Ba5/Sr6, and Ba7/Sr8 atom pairs were *constrained* to be the same. The initial *x*-coordinates of Ba1 and Sr2 were the same (I entered them that way), and by the constraint, the same shift is applied to each of them in each least-squares cycle, so they remain the same. If we had wanted to constrain the total occupancy of the Ba1/Sr2 site to be unity, we could start with the Ba1/Sr2 *frac* each = 0.5, and enter the constraint: 1 frac 1 1/1 frac 2 – 1. The sum of the site occupancies, but the Ba/Sr fraction would vary. In this case I chose not to constrain the Ba/Sr sites to full occupancy (sometimes you do not know if vacancies are present), but place a *restraint* on the site occupancies.

In this structure, each of the four Ba/Sr sites occupies a 4-fold general position, so there are 16 cation sites in the unit cell. The nominal composition $Ba_{1.25}Sr_{0.75}$ corresponds to 10 Ba and 6 Sr in the unit cell. I specified that there were a total of 10.0(3) Ba atoms distributed among sites 1, 3, 5, and 7, and 6.0(3) Sr atoms among sites 2, 4, 6, and 8. I guessed a standard uncertainty of 0.3 atoms for the sums. For each atom, a coefficient is also entered. These come into play when the multiplicities of the various sites are not equal. The refined site occupancies were $Ba_1/Sr_2 = 0.90/0.10(3)$, $Ba_3/Sr_4 = 0.39/0.61(3)$, $Ba_5/Sr_6 = 0.93/0.07(3)$, and $Ba_7/Sr_8 = 0.37/0.63(3)$. Two of the sites are occupied many by Ba, and the other two by Sr, but the cation ordering is not complete. A major objective of the study (Wong-Ng *et al.*, 2007) was to determine how the Ba/Sr site occupancies changed as the overall composition varied.

A refinement of this model (90 variables) using combined synchrotron and laboratory patterns yielded an excellent refinement (Figure 8.32): $R_{wp} = 0.0621$, $R_p = 0.0477$, $\chi^2 = 1.561$, R(F) = 0.0726. The largest peak and hole in the difference Fourier map were +1.75 and -2.15 e Å⁻³. The refined lattice parameters were a = 14.97814(5), b = 6.03634(2), and c = 10.32873(4) Å; the space group was $Pna2_1$. MISSYM suggested that an additional center of symmetry was present, but refinements in *Pnam* yielded poorer residuals, and chemically less-reasonable geometry; in this case, the suggested extra symmetry was only approximate.

The refined composition of the major phase was $(Ba_{1.30}Sr_{0.70})TiO_4$, in good agreement with the expected $(Ba_{1.25}Sr_{0.75})TiO_4$. A cubic $(Ba_{\sim 0.9}Sr_{\sim 0.1})TiO_3$ (5 wt%), Sr₂TiO₄ (0.3 wt%), and corundum from the micronizing mill were also present. The U_{iso} for Ba/Sr,



Figure 8.32 Final Rietveld plot for (Ba_{1.25}Sr_{0.75})TiO₄.

Ti, and O were 0.0141(3), 0.0166(11), and 0.0267(20) Å² – much more reasonable for a hard ceramic such as this. In these two refinements, chemical reasonableness was important at almost every step in obtaining correct structures.

8.7 X-ray/neutron combined refinement – inorganic examples

8.7.1 $K_2AI_2B_2O_7$

It is fairly often the case that not all of the chemical questions of interest can be answered using a single X-ray powder pattern. The structure (Figure 8.33) of the potassium aluminum borate, $K_2Al_2B_2O_7$ (Kaduk *et al.*, 1999b) provides an example. The structure of this compound was investigated to gain insight into the nature of a black semiconducting amorphous phase formed near it in the $K_2O-Al_2O_3-B_2O_3$ phase diagram.

Although a high-quality laboratory pattern was available (Figure 8.34), the precision of the bond distances and angles from the Rietveld refinement was relatively poor (Table 8.3). Because X-rays scatter off the electrons in atoms and the overlap of reflections in the atomic-resolution portion of the powder pattern limits the accuracy of the integrated intensities, the positions of light atoms derived from an X-ray Rietveld refinement are often a little "fuzzy." Light atoms can be located more precisely by using neutron diffraction data. Neutrons scatter off of the atomic nuclei, and the scattering power of light (to X-rays) atoms is often comparable or larger than metal atoms (Table 8.4).



Figure 8.33 Crystal structure of K₂Al₂B₂O₇, viewed approximately down the trigonal *c*-axis.



Figure 8.34 Laboratory powder pattern of K₂Al₂B₂O₇.

The B and O atoms are the strongest scatterers of neutrons, so the combination of X-ray and neutron powder data can lead to improved structural accuracy and precision. Since ¹⁰B is a strong neutron absorber, ideally ¹¹B-enriched samples should be used, but for this work only natural abundance B was available. The neutron powder data were obtained on the Special Environment Powder Diffractometer at the Intense Pulsed Neutron

Refinement	Laboratory	Combined	
d _{min} , Å	1.005	1.005, 0.747, 0.600, 0.717	
a, Å	8.55884(14)	8.55816(1)	
c, Å	8.45645(19)	8.45599(2)	
V, Å ³	536.474(21)	536.359(1)	
U _{iso} , К, Å ²	0.0190(14)	0.0244(3)	
Al	0.0174(21)	0.0180(4)	
В	0.0293(77)	0.0047(5)	
0	0.0107(19)	0.0149(3)	
K1-O7 × 2	3.282(16)	3.219(5)	
K1-O8 × 2	2.740(15)	2.777(5)	
K1-O8 × 2	3.654(18)	3.651(5)	
K1-O9 × 2	2.663(11)	2.713(4)	
K1-O9 × 2	3.234(11)	3.232(5)	
K1-O11 × 2	2.902(17)	2.925(5)	
K1-O11	3.507(33)	3.413(11)	
K2-O7 × 2	2.759(16)	2.695(5)	
K2-O7 × 2	3.283(17)	3.348(5)	
K2-O8 × 2	3.031(19)	3.024(5)	
K2-O8 × 2	3.658(15)	3.628(5)	
K2-O9 × 2	3.207(11)	3.200(4)	
K2-O10 × 2	2.952(6)	2.954(2)	
Al3-O8 \times 3	1.742(6)	1.728(5)	
Al3-O10	1.739(10)	1.712(7)	
08-Al3-08	112.3(8)	111.0(2)	
O8-Al3-O10	106.4(10)	107.9(2)	
Al4-O9 × 3	1.737(10)	1.736(5)	
Al4-O10	1.751(10)	1.723(7)	
O9-Al4-O9	106.5(5)	108.2(2)	
O9-Al4-O10	112.3(5)	110.7(2)	
Al5-O7 × 3	1.738(6)	1.749(5)	
Al5-011	1.742(10)	1.712(5)	
07-Al5-07	108.1(6)	107.7(2)	
B6-O7	1.373(9)	1.376(8)	
B6-O8	1.385(9)	1.373(8)	
B6-O9	1.368(9)	1.385(8)	
O7-B6-O8	120.1(10)	120.3(7)	
O7-B6-O9	119.4(12)	121.5(6)	
O8-B6-O9	120.3(8)	118.3(6)	
Sum O-B-O	359.8	360.1	

Table 8.3 Selected structural parameters from refinements of the $K_2Al_2B_2O_7$ structure using laboratory data only, and from a combined refinement using two X-ray and two neutron patterns. Space group P321

Table 8.4 X-ray and neutron scattering amplitudes for the atoms in $K_2Al_2B_2O_7$

Atom	К	Al	В	Ο
# electrons	19	13	5	8
$b, \times 10^{-12} \text{ cm}$	0.37	0.35	0.54	0.58



Figure 8.35 Crystal structure of hydrated sodium aluminate, NaAlO₂ · 5/4H₂O.

Source at Argonne National Laboratory. A synchrotron pattern, measured at beam line X3B1 at the National Synchrotron Light Source at Brookhaven National Laboratory using a wavelength of 0.89978 Å, was also available.

Combining four powder patterns (laboratory, synchrotron, and 150 and 90° detector banks of neutron data) with two histograms of distance and angle restraints led to improved precision (and, I believe, accuracy) of chemically relevant quantities (Table 8.3). Part of the improvement comes from the complimentariness of the X-ray and neutron data, and another part comes from the increased sampling of reciprocal space obtained when using short X-ray wavelengths and neutrons.

8.7.2 NaAlO₂ · $5/4H_2O$

The structure of commercial hydrated sodium aluminate, $NaAlO_2 \cdot 5/4H_2O$, was solved by applying conventional direct methods and difference Fourier techniques to synchrotron powder data (Kaduk and Pei, 1995). The structure (Figure 8.35) consists of layers of cornersharing tetrahedral Al, with sodium ions and water molecules located in pockets between the layers. Although the hydrogen atoms could not be located in a difference Fourier map,
approximate positions for the hydrogens of the two water molecules could be determined by an analysis of potential hydrogen bonding patterns. (The positions of many missing hydrogens in published structures can be established in this way.) The O···O distances involving the Al–OH group were long enough that it was not obvious where the hydroxyl proton was.

A common past and current use of neutron diffraction is the accurate characterization of hydrogen bonding patterns. Because H has a high incoherent neutron scattering cross section (leading to very high backgrounds in the powder patterns), it is preferable to use D-containing compounds for neutron diffraction studies. Deuterium has a large neutron scattering cross section of 0.667×10^{-12} cm, so it is often the "heaviest" atom in the compound, making it easy to determine the positions accurately and precisely.

Hydrated sodium aluminate was dehydrated to NaAlO₂ thermally, reconstituted by allowing the solid to equilibrate with D_2O vapor. The powder patterns were measured on the General Purpose Powder Diffractometer at the Intense Pulsed Neutron Source at Argonne National Laboratory at ambient conditions and 150 and 20 K. The X-ray positions of the non-hydrogen atoms were used as the initial structural model (which could not be refined successfully because the heaviest atoms were missing!) in a joint refinement to establish the global parameters, and a neutron difference Fourier map was calculated. The positions of the D atoms were obvious, and they could then be included in the model, and their positions and displacement coefficients refined. The refinement (Figure 8.36) led to a complete understanding of the hydrogen bonding pattern between the layers. The low-temperature



Figure 8.36 Crystal structure of $NaAlO_2 \cdot 5/4D_2O$ at 20 K, illustrating the details of the hydrogen bonding and the Na–O coordination.

structures were not significantly different, but these refinements provided useful reference points for quantum calculations (which are generally done at 0 K).

8.7.3 ZnNa-FAU

Fourier maps derived using X-ray diffraction data yield the electron density in the crystal. Crystallographers associate these "blobs" of electron density with atoms, and use the size of the blobs, their density relative to each other, and trends in occupation and position with changes in composition to identify the atom types. When the blob can represent one of more of several atom types (perhaps also including vacancies), its identification can be difficult. For example, a sodium cation, a water molecule, and an ammonium cation all contain 10 electrons. Distinguishing them in a partially exchanged zeolite can be a real challenge. The availability of synchrotron radiation makes possible resonant scattering experiments (Finkelstein, 2003), in which data can be collected near an absorption edge of an element of interest. The effect is to vary the scattering power of this element compared to that obtained far from the edge. By refining a single structural model using data collected at several wavelengths, mixed site occupancies can be determined unambiguously.

The ZnNa-FAU Na₁₃Zn₁₉Al₅₂Si₁₄₀O₃₈₄(H₂O)_{~220} was examined (Kaduk, 2005) as a diamagnetic model for more catalytically interesting transition metal exchanged zeolite Y. Powder patterns were collected in the laboratory using CuK α radiation and at X3B1 at NSLS using wavelengths of 1.14982 and 1.28520 Å; this last wavelength is just below the Zn K edge, and resulted in a variation of ~20% in the Zn scattering power. By trying several different combinations of cation site occupancies, the combined refinements were very clear about telling which was the correct model.

In hydrated ZnNa-FAU, the Zn occupy sites II' and II, with the Na at site I' (Table 8.5 and Figure 8.37). There is significant electron density at the center of the sodalite cage (site U). While it is possible that this density represents extra-framework Al (dealumination of the

Site	l'	U	11′	Ш
27°C, xxx	0.0738(3)	1/8	0.1681(2)	0.2683(2)
Occupation	11 Na	7.5 O	6 Zn	5 Zn
Cation-O2, Å	3.18 × 3		3.05×3	3.16 × 3
Cation-O3, Å	2.68×3			
Cation-O4, Å				3.47×3
Cation-OU, Å	2.19		1.84	
300°C, xxx	0.0539(1)	1/8	0.2088(5)	0.2385(4)
Occupation	15 Zn	6.5 O	4 Zn	13 Na
Cation-O2, Å	2.93×3		2.18 × 3	2.37×3
Cation-O3, Å	2.04×3			
Cation-O4, Å			3.03×3	3.03×3
Cation-OU, Å	3.57		3.57	

Table 8.5 Extra-framework sites in ZnNa-FAU



Figure 8.37 Crystal structure of ZnNa-FAU at ambient conditions and at 300°C, determined using secondary scattering techniques. The views are of a slice of the structure containing the cubic 3-fold axis (vertical).

framework), the Zn–U distances are about right for Zn–O bonds. I believe that this density represents an O coordinated to the hydrated Zn ions at site II'. The Zn occupying site II are also hydrated; the metal-framework oxygen distances are too long for direct bonding, but are consistent with hydrogen bonding of hydrated cations to the framework. At 300°C, the Zn atoms move to site I', and site II' moves closer to the framework, indicating direct coordination. The Na⁺ ions are displaced to site II in the supercage. The central oxygen density is still present. This resonant study determined the occupancies unambiguously. These cation occupancies in the dehydrated material correspond to those reported by Wilkinson *et al.* (1992).

8.8 Quantitative analysis by Rietveld refinement

In what we might call classical quantitative analysis, the ratio of the weight fractions *X* of two phases α and β (β is often an internal standard) is given by

$$\frac{X_{\alpha}}{X_{\beta}} = \left(\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}}\right) \left(\frac{I_{(hkl)'\beta}^{rel}}{I_{(hkl)\alpha}^{rel}}\right) \left(\frac{RIR_{\beta,c}}{RIR_{\alpha,c}}\right)$$
(8.15)

in which the *I* are the measured integrated intensities of two peaks of phases α and β , the *I*^{*rel*} are the relative intensities of these peaks in the pattern (we do not have to use the strongest peaks of each phase), and the *RIR* are the intensity ratios of the strongest peaks of phases α and β with respect to a third phase *c*. This phase *c* is often corundum, and the relative

intensity ratios are designated I/I_c and are tabulated in the PDF. If the relative intensities and I/I_c are taken from the literature of the PDF, the results should be considered only in a semiquantitative manner.

The structure models used in a Rietveld refinement include all of the information necessary to calculate the I^{rel} and I/I_c , so the method should be useful for quantitative phase analysis. Because the Rietveld method fits the whole diffraction pattern, we might expect higher accuracy and precision than single-peak-based methods.

The use of the Rietveld method for quantitative phase analysis if often called the "*SMZ*" method (Hill, 1991; Kaduk, 2000). *S* is a refinable parameter which is proportional to the number of unit cells of a phase present in the specimen volume, *M* is the molecular weight of the phase, and *Z* is the number of formula weights per unit cell. The product *SMZ* is thus proportional to the mass of the unit cells of the phase, and thus a quantitative analysis can be derived. The definition of *S* (a scale factor or phase fraction) has varied through the years and from program to program; the principal variation has been whether the unit cell volume is incorporated into *S* or not. Most contemporary Rietveld programs incorporate the volume into *S*, so the algebra described here can be used.

The concentration of phase α is calculated by

$$X_{\alpha} = \frac{S_{\alpha} M_{\alpha} Z_{\alpha}}{\sum SMZ}$$
(8.16)

in which the sum is carried out over all crystalline phases. If no amorphous material is present (or assumed), the method is essentially equivalent to Chung's matrix flushing method (Chung, 1974a,b), but using a single scale factor for each phase rather than for individual peaks.

As an example, let us consider a partially crystalline vanadium phosphate butane oxidation catalyst precursor (Figure 8.38), to which a known concentration of NIST SRM 640b



Figure 8.38 Powder pattern of a vanadium phosphate catalyst precursor, to which a known concentration of NIST 640b Si had been added as an internal standard.

VO(HPO ₄)(H ₂ O) _{0.5} 5.82(3) 171.91 4 4002 66.0 30.3 35.9(2) Si 9.17(7) 28.086 8 2060 33.9 15.58 -	Phase	S	М	Ζ	SMZ	wt%	True wt%	Si-free wt%
Amorphous 0 54.1 64.1(2) Sum 6062 99.9 100 100	VO(HPO ₄)(H ₂ O) _{0.5} Si Amorphous Sum	5.82(3) 9.17(7)	171.91 28.086	4 8	4002 2060 6062	66.0 33.9 0 99.9	30.3 15.58 54.1 100	35.9(2) - 64.1(2) 100

Si was added as an internal standard. The question to be answered was the concentration of crystalline phase(s) in the sample. I used SRM 640b because its linear absorption coefficient μ is similar to that of the vanadium phosphate. This material was perhaps not the best one to use, because it was known to contain occasional large grains (and thus suffer from granularity), but it was handy. SRM 640c and successors do not suffer from large grains.

The crystalline phase was $VO(HPO_4)(H_2O)_{0.5}$. I used a locally derived structure model, which is close to the published crystal structure. After obtaining an acceptable Rietveld refinement, the refined phase fractions can be used to derive the quantitative analysis (see Table 8.6).

The refined phase fractions of the two phases were 5.82 and 9.17, respectively, with standard uncertainties of 0.03 and 0.07. The molecular weights were calculated from the formulas, and the Z are known from the crystal structures. The two *SMZ* are calculated and summed, and divided by the sum to yield the apparent concentrations. Most Rietveld programs today include this calculation in the default output. This calculation strictly speaking yields the ratio of the concentrations of the crystalline phases. If there is no amorphous material present, then these concentrations are accurate. If amorphous material is present, and we know one of the concentrations (the 15.58 wt% Si internal standard), the relative concentrations can be re-normalized to yield absolute concentrations of the crystalline phases, and the amorphous concentration by difference.

My customer did not care about the concentrations in the specimen after I added the internal standard, but in the sample he gave to me. To obtain the concentration of interest, the intermediate concentrations were again re-normalized (by dividing by 0.8442 = 1 - 0.1558) to account for the Si in the actual specimen. The standard uncertainties in the final concentrations were calculated from the relative standard uncertainties in the phase fractions (assuming that all of the other quantities are exact). The raw pattern did not look like that of a sample which is only 36% crystalline, but this analysis was confirmed by other techniques. Quite large concentrations of amorphous material can be present without affecting the background very much. One quickly learns not to integrate by eye!

The Rietveld program knows only what it has been told by the user. If the structure models are incomplete, we can expect systematic errors in the quantitative analysis. A common problem with literature structure models (especially older ones) is that not all of the atoms, such as hydrogens, were located. It is not uncommon for the hydrogens to account for 5% of the molecular weight. The approximate positions for many such atoms can be deduced

from chemical knowledge, and so they can be included in the model. Alternatively, the molecular weight from the Rietveld model can be corrected in the manual calculation of *SMZ*.

Zeolites and other materials of variable composition can pose a particular challenge to quantitative analysis by the Rietveld method. As an example, consider a hydrated sodium-exchanged faujasite, Na-FAU. The faujasite structure is commonly encountered in two varieties, Zeolite X and Zeolite Y, which differ in their framework compositions. The framework Al content can be determined from the cubic lattice parameter by one of a number of established correlations. It is uncommon for all of the Na cations to be located using data collected at ambient conditions, so they are not all included in the structural model. The actual number of Na in the unit cell may need to be determined by bulk chemical analysis or more sophisticated analytical techniques. Most zeolites at ambient conditions contain extra-framework water molecules, which are so disordered that they cannot be located and included in the model. The water content can often be determined by thermogravimetric analysis. A typical hydrated Na Zeolite Y has a unit cell formula Na₅₆Al₅₆Si₁₃₆O₃₈₄(H₂O)₂₂₀. Not including the water molecules in the molecular weight can thus lead to concentration errors of 24%! Manual intervention and other analytical information are often required to obtain accurate quantitative analyses by the Rietveld method.

A "work around" to such difficulties is to report results in atom% rather than weight%, and use what might be called the "*SZ*" method. From the Rietveld refinement we know how many unit cells are present in the specimen, but (especially using only laboratory X-ray data) we may be uncertain about the weight of the contents of those unit cells. Consider an improperly calcined propane ammoxidation catalyst (Figure 8.39), which contains a phase commonly known as M_2 , a rutile-structure phase, MoO₃, and "Mo₅O₁₄."



Figure 8.39 Powder pattern of an improperly calcined propane ammoxidation catalyst, showing the four crystalline phases present.

Each of these phases have a variable composition, and determining the composition of each phase may present a significant challenge. The M2 phase has the ideal unit cell composition (Z = 1) SbMo₃O₁₀, but may contain other metal cations and/or vacancies at both the large cation (Sb) and the octahedral cation (Mo) sites. The rutile-structure phases has the ideal composition VSbO₄ (Z = 1), but may contain other cations and/or vacancies at both the cation and oxygen positions. The MoO₃ (Z = 4) may indeed be stoichiometric, but it is prone to stacking faults and other imperfections which make it difficult to describe by the Rietveld method. Mo₅O₁₄ (Z = 16!) requires the presence of other metal cations to form (typically ~7% of the Mo), so its composition is inherently variable. This phase also illustrates another interesting feature of choosing the structural model.

Rietveld programs typically know about only some of the many possibilities for describing space groups. In particular, they assume that the origin is at a center of symmetry (Origin Choice 2 in the *International Tables*), so if the structure has been reported in Origin Choice 1, a coordinate transformation is required before using the structure. The Mo_5O_{14} (or A5X14) (Yamazoe and Kihlborg, 1975) structure illustrates more subtle problems which can be encountered. The experimental powder pattern 31-1437 reproduces real materials well, but patterns calculated from the crystal structures in the ICSD do not. Most of these structures are reported in tetragonal sub-cells of a true orthorhombic cell, but even the orthorhombic model requires extra attention. The authors used not only a non-conventional setting of the space group but a non-standard choice of origin. A coordinate transformation had to be carried out before the literature model could be used in a Rietveld refinement.

Because the compositions of these phases were only known approximately, for comparing catalysts it is useful (at least until the compositions are established) to calculate the concentrations in mole%, since these values are closer to the experimental data and probably more accurate (see Table 8.7).

The structure model is more important to accurate quantitative analysis than is commonly realized. This point can be illustrated by considering the I/I_c for the anatase and rutile polymorphs of TiO₂ contained in the PDF-4+ 2006 database. Even ignoring the nonstoichiometric and hypothetical structures, the I/I_c for rutile exhibit a surprisingly large range (Figure 8.40). The average is 3.47(20), the median is 3.50, and the value obtained by fitting a Gaussian peak to the distribution is 3.53(4). Most of the variation in the structures lies in the displacement coefficients (thermal parameters). Some of the structure reports did not contain displacement coefficients, so for the calculations ICDD used default values. The experimental value in PDF entry 00-021-1276 is 3.4. The situation is even worse for anatase (Figure 8.41). The average I/I_c is 5.03(41), the median is 4.96, and an attempt to

Phase	М2	Rutile	MoO ₃	Mo ₅ O ₁₄
mole%	5.0(5)	54.8(5)	26.1(3)	14.1(1)
"wt %"	9.9(9)	35.2(2)	15.1(2)	39.8(1)

 Table 8.7
 Comparison of concentrations in a multiphase mixture expressed both in w% and mole%



Figure 8.40 Rutile I/I_c from PDF-4+ 2006.



Figure 8.41 Anatase I/I_c from PDF-4+ 2006.

fit a Gaussian peak to the distribution yielded 5.38(10) (but did not converge). The experimental value in PDF entry 00-021-1272 is 3.3. The question "Which value do I use?" is equivalent to the question "Which structure model do I use?"

As can be seen from the variations in I/I_c as a result of variations in the structure model, such differences can have practical consequences. A catalyst supports vendor and my lab disagreed on the anatase and rutile concentrations in a series of supports. The vendor used a traditional I/I_c method and I used the Rietveld method. The vendor used I/I_c of 5.0 and

3.4 for anatase and rutile. The structure models I used corresponded to I/I_c of 5.04 and 3.65, so we could explain a systematic difference in anatase and rutile concentrations. The anatase concentrations I obtained were 8% relatively higher than expected. When I allowed the anatase and rutile U_{iso} to refine, the concentrations became too low. Manual adjustment of the U_{iso} led to acceptable agreement in a series of anatase and rutile mixtures. The new structural models corresponded to I/I_c of 5.04 and 3.58. Use of these models and relative intensity ratios led to good agreement between the two analysis methods. The structural models used in a Rietveld refinement may need to be modified to obtain the most accurate results.

Because the whole pattern is utilized, systematic errors from preferred orientation, extinction, and instrument/specimen configuration are minimized. The crystal structures can be refined or not as appropriate, providing quantitative analysis on a microscopic as well as a macroscopic scale simultaneously, and eliminating the effects of structural changes on the relative intensities. The background is fitted over the whole pattern leading to better definition of individual integrated intensities. I particularly appreciate the correct propagation of error estimates through the least-squares analysis. With the use of an internal standard, both crystalline and amorphous phases can be quantified. All of these advantages might make the Rietveld method the *preferred* method for quantitative phase analysis. I do virtually all of my routine and non-routine quantitative analysis by the Rietveld method, and only rarely use a peak-based method such as specified in various ASTM methods.

In classical treatments of quantitative analysis, errors from such factors as beam spillover at low angles, surface roughness, granularity, and microabsorption are discussed. The signal/noise ratio of the pattern can be important (noisy data can obscure surprisingly high concentrations of minor components), and the possibility that the specimen changes during preparation may need to be considered. These errors do not go away when the Rietveld method is used, because they are specimen effects. They can sometimes be surprisingly important.

As an example, the anatase concentrations in a series of anatase/rutile mixtures were \sim 20% relatively too high, even using the optimized structure models described above. The phase-pure rutile was prepared from the anatase by calcining at 1180°C. The source of the systematic error turned out to be microabsorption (Brindley, 1945). When particle (not crystallite, so this is not a measurement than can be done using X-ray methods alone) size is large enough and absorption contrast large enough, the ideal intensity ratio $I_{(hkl)\alpha}/I_{hkl}$ ' β is multiplied by a factor:

$$K = \frac{\tau_{\alpha}}{\tau_{\beta}} = \frac{V_{\beta} \int_{0}^{V_{\alpha}} e^{-(\mu_{\alpha} - \overline{\mu})x} \mathrm{d}x}{V_{\alpha} \int_{0}^{V_{\beta}} e^{-(\mu_{\beta} - \overline{\mu})x} \mathrm{d}x}$$
(8.17)

K is the factor mentioned in the text. It is often written as the quotient of two terms τ_{α} and τ_{β} , which correspond to the two phases α and β . V_{α} and V_{β} are the volumes of particles of phases α and β . μ_{α} and μ_{β} are the linear absorption coefficients of the two phases. $\overline{\mu}$ is the linear absorption coefficient of the mixture, and *x* is the path of the radiation in a particle. The anatase reagent has an average particle size (measured by laser light scattering) of 3 μ m. Only $\frac{1}{3}$ of the rutile had this particle size; $\frac{2}{3}$ had sintered into particles with an average diameter of 150 μ m! Even though anatase and rutile have the same mass absorption coefficients, their different densities and particle diameters led to a

Phase	Anatase	Rutile
μ/ρ , cm ² g ⁻¹	125.7	125.7
ρ , g cm ⁻³	3.893	4.250
μ , cm ⁻¹	489.4	534.2
$\mu - \mu_{avg}$, cm ⁻¹	-31.2	+13.6
<i>D</i> , μm	3	150
μD	0.147	8.01
Brindley size	Coarse powder	Very coarse powder

 Table 8.8
 Calculation of potential microabsorption effects in a 30/70 wt% anatase/rutile mixture.

significant microabsorption effect (calculated for a 30/70 wt% anatase/rutile mixture) (see Table 8.8).

Both the anatase and rutile particles are large enough that we might expect significant systematic concentration errors from microabsorption. The correction factor is

$$\frac{\tau_A}{\tau_R} = \frac{1.014}{0.75} = 1.35\tag{8.18}$$

so the anatase concentrations should be 35% too high. Only $\frac{2}{3}$ of the rutile was "large," so we would expect the anatase concentrations to be "only" 23% too high in this system, compared to the 20% too high actually observed. The problem was corrected by micronizing the mixtures. The average concentration error was then reduced to 0.2 wt% absolute. Generally I encounter microabsorption effects only when I make mixtures of Standard Reference Materials for calibration and example purposes, but they can pop up in unexpected systems.

An important part of developing any analytical method is quantifying its accuracy and precision. Unlike many of our analytical colleagues, in X-ray powder diffraction we very rarely measure on an absolute scale, so rely primarily on internal standards to ensure accuracy. The precision of a Rietveld analysis can be assessed readily by replicating the whole analysis, including the specimen preparation (which often dominates the accuracy and precision). For a routine Rietveld analysis, it is worthwhile to optimize all steps in the process, as in the anatase/rutile analysis described above. A beauty of the Rietveld method is that it can be applied to all of the one-of-a-kind analyses faced in many laboratories. We are then faced with assessing the accuracy of the method itself.

The best way to assess an analytical method are to reproduce the compositions of known mixtures and to participate in Round Robins. The IUCr Commission on Powder Diffraction organized two Round Robins on quantitative phase analysis (Madsen *et al.*, 2001; Scarlett *et al.*, 2002). A good summary of the application of the Rietveld method to analysis of Portland cements is given in De la Torre and Aranda (2003). The first IUCr Round Robin involved analysis of several mixtures of corundum, fluorite, and zincite. In all cases I could reproduce the known concentrations to within 2 wt% absolute, and most results were within 1 wt% absolute of the true values. Such errors naturally translate into larger relative errors for minor components.

The second Round Robin involved more challenging samples, and introduced the idea of an absolute Kullback–Liebler distance (Kullback, 1968) as a measure of the overall quality of an analysis to a wider audience. For a single phase, the *KLD* is defined as

$$KLD = 0.01 \times wt\%_{true} \times \ln\left(\frac{wt\%_{true}}{wt\%_{measured}}\right)$$
(8.19)

The underlying premise is that errors in the concentrations of major components are more important than errors in minor constituents. As an overall measure of the quality of the analysis the absolute Kullback–Liebler distance is computed:

$$AKLD = \sum_{i=1}^{n} |KLD_i|$$
(8.20)

by summing over all of the *n* phases. In the Round Robin, many analyses we would normally consider good had $AKLD \leq 0.1$. My experience, and that of others, is that we can reasonably expect accuracies of $\pm 2-3$ wt% absolute without taking special care. The specimen issues that plague classical quantitative phase analysis do not go away when the Rietveld method is used, although I find it easier to achieve high accuracy and precision by using the whole diffraction pattern.

8.9 Limitations of Rietveld refinement

It is tempting to give the answer "not many," but of course there are limitations. With reasonable care, we can expect the accuracy of structural parameters to be equivalent to single-crystal refinements, but the precision of bond distances and angles will be a factor of 2–3 less (Kaduk and Partenheimer, 1997; Kaduk, 1998). If you have or can get a single crystal, you should use it to obtain the most precise structural information!

The basic limitations come from the fact that we are fitting a model to data, and the results will only be as good as the model is appropriate and the data are of high quality. In the Rietveld method, we assume a crystalline model, so we obtain the long-range average ordered electron density. If reality is more complex, then results will be approximate. Some systems scatter coherently but are not crystalline in the normal sense; they contain many stacking faults or defects, or are incommensurate/modulated. Phases with a bimodal size or strain distribution can have hyper-Lorentzian peaks, which are not possible to model using the normal pseudo-Voigt profile model. If several closely related phases are present in a single specimen (say, 3 or 4 rutile-structure phases of slightly different compositions), it will probably not be possible to obtain structure or profile information on the individual phases, because the extensive peak overlap leads to high correlation of variables.

Less information can be obtained from poor (noisy) data than from a high-quality pattern. The availability of synchrotron radiation makes much more sophisticated refinements possible. For best results, it is wise to collect as wide an angular range as possible. It then becomes easier to separate various angle-dependent effects. Because so much information is contained in the profile parameters, it is wise to collect data using fine enough steps to define the peaks well. A good rule of thumb is to have 4–5 points across the FWHM of the sharpest peaks. I find that the data are pretty good at telling you when you ask too much; the refinements diverge, forcing you to use fewer parameters. The folding of three dimensions of reciprocal space into a one-dimensional powder pattern ultimately limits the information we can extract by the Rietveld method. The positions of light atoms may be defined less-precisely than we would like. It is often necessary to group the U_{iso} by atom type and/or environment. It is not common to obtain reliable individual atom displacement coefficients from laboratory X-ray data, and it is almost never possible to refine anisotropic displacement coefficients. Neutron and synchrotron data help here. It is often necessary to use chemical knowledge in the form of restraints and rigid bodies, but used carefully, such extra information will not bias the results. We can reasonably expect accuracy in quantitative analysis of $\pm 2-3$ wt% absolute; to obtain more accurate results requires extra care. Because the Rietveld method permits extraction of the maximum amount of information from powder diffraction in a chemically and physically meaningful way, it is a vital part of the arsenal of every practicing diffractionist.

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Chapter 9 Other Topics

E. Andrew Payzant

9.1 Size/strain determination

9.1.1 Background

There are many contributions to peak broadening in powder diffraction, as already covered in this book. In order to obtain suitable peak shapes and reproducible intensities, it has always been important to ensure that there are a sufficiently large number of grains randomly oriented in the diffracting volume. It is important to keep in mind for Bragg–Brentano powder diffraction each specific *hkl* is characterized by a diffraction peak derived from a unique subset of grains. Consequently, it is essential that the grain size be small so that a statistically large number of grains are present in the diffracting volume. It has been common practice to use finely sieved (typically 325 mesh or higher) powders to avoid sampling large grains, but of course this method cannot be applied to solid polycrystals (e.g., rolled metals). Users of highly parallel X-ray sources are well aware of the fact that particle statistics become even more restrictive as the X-ray source is less divergent and more highly monochromatic, so that fewer grains meet the tighter Bragg conditions for diffraction. Sample spinners and oscillators can help with this problem by bringing additional grains temporarily into the Bragg condition.

A "perfect" powder sample has a small particle size (of <50 μ m), no shape anisotropy, no compositional inhomogeneity, or any other defects. In practice, of course, this is not so easy to achieve. Metal powders and filings are often highly defective, with dislocations, shear bands, and so on and this may be true also for many non-metals. Thermal annealing can sometimes be used to remove these defects and improve the powder pattern. Conversely, careful examination of the peak broadening introduced by smaller particle sizes, microstrain, defects, and so on, may be used to quantitatively analyze these phenomena, which is variously termed "line profile" or "peak shape" analysis. Peak shapes may be analyzed either by "integral breath" approaches, or by "Fourier methods" fitting the peak with an appropriate Fourier series.

One of the simplest and most frequently used method to analyze crystallite size is the Scherrer method, which was first described by Paul Scherrer in 1918 (Scherrer, 1918) to determine the size of colloidal gold particles in solution. This method can be extended to the analysis of powders and polycrystalline solids, and even to crystallites with significant shape anisotropy, yet the Scherrer equation is very simple, and is consequently very popular. For a typical laboratory X-ray diffraction (XRD) instrument it provides sensitivity to

crystallite size in the 10–1000 Å range. The upper limit is set by the instrumental broadening, and so can be somewhat extended by altering the instrument optics.

As is often the case with simple models, the Scherrer equation does not consider all the contributions to peak shape and peak broadening, and so can yield results that are far from accurate *if these other effects contribute significantly to peak shape or broadening*. These effects include lattice strains (microstrains), dislocations, stacking faults, chemical inhomogeneities, and so forth. While these effects impact the crystallite size measurement, they open the possibility to estimate strains from X-ray diffraction data as well, provided that the peak broadening effects can be adequately separated, as will be discussed in the following sections.

9.1.2 Integral breadth analysis of size and strain

The Scherrer equation provides a simple estimate of crystallite size based upon the breadth of any diffraction peak:

Size
$$(A) = k\lambda/(\Delta\theta * \cos\theta)$$
 (9.1)

In this equation the crystallite size is directly related to the breadth ($\Delta\theta$) of a particular diffraction peak, λ is the wavelength of the X-ray radiation employed and k is a constant whose value is normally between 0.5 and 1.0. One must first consider the instrumental broadening, usually done by running an instrumental calibration scan, using standard materials such as silicon or lanthanum hexaboride to determine the strain-free line width. This instrumental peak width provides the lower limit on measurable peak breadth, and hence the upper limit on crystallite size estimation. It is important to select a standard with peaks in a similar 2θ range as the sample. Then the sample (powder or polycrystalline material) is scanned with the identical combination of slits and collimators, and the increase in the breadth (typically full-width at half-maximum or FWHM) of the line compared to the standard is determined and converted into crystallite size by the Scherrer equation.

In principle, a Scherrer analysis can be applied to any diffraction peak, and determines the volume-averaged size of the crystallites oriented with a specific *hkl* direction parallel to the diffraction vector Q ($2\sin\theta/\lambda$). There is an (usually un-stated) assumption that the crystallites have a narrow Gaussian distribution of sizes, and that no other effects significantly contribute to the broadening. These conditions are rarely met in real samples and yet the Scherrer method is very popular in practice, primarily because of its simplicity.

It is essential to understand that a Scherrer analysis will be completely invalid if there is a broad (or worse, non-uniform) distribution of crystallite sizes, as the peak shape may be dominated by presence of the larger crystallites. This important fact has been well known for many years, though it is frequently ignored: "*Without information concerning the distribution function, the average particle size cannot be determined*" (Clark, 1940).

The next logical extension to integral breadth analysis assumes the total breadth $\Delta\theta$ of a peak to be the simple sum of the previously discussed size term $(k\lambda/\Delta\theta\cos\theta)$ and a new microstrain term $(4\varepsilon \tan\theta)$. A Williamson–Hall plot (Hall, 1949; Williamson and Hall, 1954) can be used to separate the effect of crystallite size from microstrain. In this method the inverse breadth is plotted as a function of inverse *d*-spacing, with the data points

labeled by their respective *hkl* indices. While this method ignores the actual peak shape and only utilizes the integral breadth, the method can prove extremely useful for separating size from strain effects. To a good approximation, the slope of the line indicates the amount of microstrain, whereas the intercept indicates the crystallite size. If all the points lie on a straight line then the crystallite size is the same in all directions (the particles are roughly spherical), and if this line is horizontal, then microstrain effects are negligible. If higher order reflections of a given *hkl* (e.g., *001, 002, 003, 004*, etc.) are on one line, but on another parallel line for different *hkl* directions (e.g., *h00* reflections lie on a line with the same slope, but different intercepts than *hh0*, etc.) this indicates shape anisotropy – the crystallites are not spherical, but may be plates or needles or some other shape. Finally if the families of higher order *hkls* lie on lines with different slopes, then the microstrain is anisotropic.

9.1.2.1 The Warren–Averbach method

A more mathematically rigorous approach to size-strain analysis is the Warren-Averbach method (Warren, 1969; Warren and Averbach, 1950), which is based on fitting a Fourier series to the peak, thereby fully describing the peak profile. Details of the derivation of the method are presented in all the standard textbooks on X-ray diffraction analysis (Klug and Alexander, 1974; Warren, 1969), but briefly the method is based on the fact that in reciprocal (Fourier) space, that is, when the intensities are considered with respect to $Q = 1/d = 2 \sin \theta / \lambda$, in Å⁻¹), the size effects are independent of the diffraction order, whereas the strain effects are not, so comparison of two (or more) peaks of different order (e.g., 111 and 222) allows the constant size and varying strain effects to be separated. From a practical standpoint this requires first removing the instrumental contribution from the measured profile to obtain the "real" diffraction profile, whose shape is due to a combination of size- and strain-induced broadening. For laboratory diffractometers, a line shape standard such as LaB₆ may be used to determine the instrumental broadening, whereas for synchrotron beamlines, the instrumental contribution may be so small that it can be neglected. The "real" profile is then modeled by a Fourier series, the sine coefficients of which are zero, or nearly so. The cosine coefficients are non-zero, and each may be considered to consist of a size component and a distortion (strain) component, which can be separated by considering two peaks of different order (e.g., 100 and 200). In the absence of significant microstrain it may be possible to even determine a size distribution, rather than simply the volume average size from a Warren-Averbach analysis, though this is non-trivial and the errors may be significant.

The Warren–Averbach method is more difficult to apply to low symmetry samples, because it requires at least two non-overlapped X-ray peaks (of lower and higher order *hkl*) collected over a considerable range of 2θ space, which may not be easy (or even possible) to collect in some cases. For cubic materials (including many common metal alloys), the third-order powder diffraction reflections are always overlapped with another reflection (e.g., 300/221, 330/411, and 333/511), and so they cannot generally be used.

9.1.2.2 Rietveld methods

Most modern Rietveld analysis software includes size and "strain" analysis capabilities that may be selected by the user. In the most popular Rietveld packages, the diffraction peak profiles are fit to an empirical peak shape function, the most common of which is the pseudo-Voigt (a linear combination of Gaussian and Lorentzian peak shape functions) for which the angle-dependent peak width is modeled by three coefficients U, V, and W in the Cagliotti equation (Cagliotti *et al.*, 1958):

$$H = (U\tan^2\theta + V\tan\theta + W)^{1/2}$$
(9.2)

The first popular approach as used in GSAS (Larson and Von Dreele, 2000) is to empirically determine the "instrumental" peak broadening from a standard pattern (run separately) on a powder standard certified free from size and strain broadening effects. The refined parameters U, V, W, and P [$P/\sin 2\theta$ is introduced when the modified pseudo-Voigt profile (Thompson *et al.*, 1987) is selected in GSAS], which all relate to the Gaussian fraction of the pseudo-Voigt profile, are then fixed as the "instrumental parameters," and not refined in subsequently collected data. This leaves only the Lorentzian peak width to be varied to account for sample broadening as follows:

$$H_{\rm L} = X/\cos\theta + Y\tan\theta \tag{9.3}$$

where the refined value *X* relates to the crystallite size broadening and *Y* to the microstrain broadening as follows:

Size
$$[\text{Å}] = (180/\pi)k\lambda/X$$
 (9.4)

$$Strain = (\pi/180)Y \tag{9.5}$$

Equation (9.4) is essentially equation (9.1), that is, the Scherrer equation. Anisotropic size and strain may be modeled, as needed by adding additional terms to the preceding three equations. Peak asymmetry due to axial divergence (Finger *et al.*, 1994) and anisotropic microstrain broadening (Stephens, 1999) can also be modeled by selecting more complex profile functions in GSAS.

An alternative approach (Coelho *et al.*, 2004), termed "fundamental parameters," models the instrumental peak shape parameters based on the actual diffractometer configuration, rather than based on an "instrument parameters" refinement of a standard. This is an innovative technique that can be applied to any diffractometer, and the parameters have physical meaning, rather than simply empirically fitting an arbitrary shape function. In the codes that use this approach, computation of size and strain is still very similar to the previous description.

It should be noted that Rietveld programs are capable of generating a "correlation matrix," describing the degree of correlation between the refined variables. It is recommended that one always checks this for significant correlation of size and strain to other refined variable, as the accuracy of highly correlated results, no matter how precisely refined, must be considered doubtful.

9.1.3 Summary

All of the X-ray diffraction methods for determining crystallite size have a large number of inherent assumptions that restrict their general application. The reader is strongly encouraged whenever possible to obtain complementary data to support the X-ray diffraction determined values, whether by optical or electron microscopy, by laser interference spectroscopy, or other means. Additionally, one should be wary of quoting too many significant figures in the determined values of size and strain – always be cognizant of the estimated errors in precision and accuracy.

9.2 Non-ambient diffraction methods (temperature, pressure, humidity)

9.2.1 Background

The vast majority of X-ray diffraction studies are conducted on samples at ambient temperature. Most materials change dimension with temperature – typical engineering metals have thermal expansion coefficients on the order of $10^{-5\circ}C^{-1}$. This means that in order to specify an accurate lattice parameter to 1 part in 30 000 for such a material, you need to specify the temperature to within 1°C. It is therefore good practice to monitor the temperature in your laboratory, even for ambient studies. Non-ambient experiments add temperature measurement errors and more complexity to sample mounting, and therefore add additional systematic errors to the data. Consequently, ambient temperature experiments are recommended for accurate quantitative analysis, whenever it is possible to do so. Nevertheless, non-ambient studies are required to investigate many problems.

High-temperature experiments were reported as early as the 1920s, and by the 1930s, high-temperature Debye–Scherrer cameras were being manufactured for sale. Today there are several suppliers of non-ambient attachments for commercial X-ray diffraction systems. Furnace designs based on metal heater strips are sold by Johanna Otto GmbH and Anton Paar KG, while capillary heater stages are sold by Huber Diffraktionstechnick GmbH, Stoe & CIE GmbH, and Bruker AXS, among others. Similarly, low-temperature stages have been available for over a half-century, with several different designs commercially available today from all the major manufacturers.

9.2.2 Experimental considerations

Until the development of vertical $\theta - \theta$ goniometers, securing powder or polycrystalline samples on a high-temperature holder that would become tilted as θ increased was a major challenge. With vertical $\theta - \theta$ instruments, the heating stage lies horizontal at all times, greatly simplifying the sample mounting.

Most commercial systems use water-cooled chambers, which may result in condensation of vaporized sample on the cooler inner walls (and windows) of the chamber. This raises additional issues of cross-contamination between successive experiments, and (sometimes) severe attenuation of the incident and diffracted X-rays through the coated windows.

Depending on the furnace design, temperature and temperature gradients may be a major issue for accurate high-temperature X-ray diffraction. It is essential that the sample be at a uniform temperature, and that temperature is both accurate and precisely measured. What we want to know is the temperature of the sample, but usually what we are measuring is the temperature of something else located near the sample, which is more convenient to measure. This is important to consider, as the temperature sensor may not be registering the temperature of the portion of the sample contributing to the diffraction pattern (as little as a few microns near the sample surface for laboratory X-ray diffraction).

Optical pyrometers allow non-contact temperature measurement, and so can be useful for high-temperature X-ray diffraction. You do need an optical line of sight to the sample, though this can be accomplished with combinations of transparent windows, lenses, optical fibers, or mirrors and you have to deal with the fact that the geometry is such that the sample is not a black body. Highly reflective samples may in fact act as mirrors, and a pyrometer will record the temperature of the heat source instead of the cooler sample.

Thermocouples and resistance temperature detectors may provide a conductive heat leakage path, so that the temperature is locally lower at the measurement point. Unless they are thermally well-coupled to the sample, it is likely that the precise measurement will be somewhat inaccurate. Users of thermocouples need to be cognizant of electrical consideration, since a thermocouple works by converting a measured electromagnetic field into a calibrated temperature. Consequently, any pick up of stray electrical currents will produce an offset in this temperature. One way to test for this problem is to reverse the leads in the heater and see whether the apparent temperature changes for a fixed input current/voltage. Thermocouples are extremely accurate, but you need to watch for problems. As stated already, thermocouples are sensitive to DC electric fields, and current loops or electromagnetic field pickup can be interpreted as a temperature offset. They are sensitive to chemical attack, check the literature (the free Omega Temperature Handbook is recommended) and avoid contact with problem materials or atmospheres at high temperatures. Some thermocouples cold-work, and cannot be easily bent without breaking. Thicker thermocouples conduct heat away from the specimen. You need to have good thermal and mechanical contact with the specimen, which may be difficult (or impossible) to achieve with many real samples.

When accuracy matters (and it nearly always matters) the use of temperature calibration standards is strongly recommended. As with X-ray powder standards for peak position and shape, temperature standards may be run as external or internal standards. The high-temperature chamber may be calibrated by running one or more external standards separately from the sample. One can select from melting point standards, solid-state phase transformation standards, and/or thermal expansion standards. The sample stage or heater strip may provide a useful temperature reference. Just as with " 2θ " standards, external temperature standards provide a useful calibration/correction for systematic errors in the physical setup. External standards cannot correct for temperature errors unique to your sample setup, and you risk adding errors unique to your standard setup. On the other hand, internal standards reduce the sample intensity, may overlap with some of your sample peaks, and may interact with the sample itself, though there are methods to minimize this issue (Mantler and Hammersschmid, 2000).

High-temperature attachments often fail to keep the sample at a fixed height as the temperature changes, due to thermal expansion of the furnace internals, and even the sample itself. This is specially a problem in metal heater-strip-based furnaces, but occurs to some extent in all designs. Consequently, in addition to incorporating a temperature standard, it is often desirable to have an internal 2θ standard. Ideally such a standard would have accurately known peak positions with a low thermal expansion coefficient, so that inaccuracies in temperature measurement would not create additional errors in the

 2θ calibration. Alternatively, the sample height could be adjusted before each high-temperature scan, based on bisecting the direct beam, but this is a tedious process and will not be feasible for most studies.

A common high-temperature X-ray diffraction design mounts the sample on a metal strip/foil that acts both as a sample holder and resistive heater under either AC or DC current. Such designs offer fast heating and cooling, and high maximum temperatures – in excess of 2000°C for refractory metal strips such as Mo or Ta. Often a thermocouple is secured directly to the strip itself, so that the strip temperature at that location is known very accurately. However, one must be careful that the sample does not react with the strip – platinum alloys are a common refractory metal for such applications, but even platinum is very reactive with Si, Fe, C, and many other elements at elevated temperatures, especially in reducing environments. Another issue is that if the sample is electrically conducting, it may provide a short circuit for the heater current, resulting in unexpected thermal behavior. Both sample-strip reactions and electrical isolation can be solved by inserting a thin barrier layer between the sample and strip – common methods include use of thin quartz crystal plates, powdered glass, or sprayed coatings of boron nitride, but all of these have the potential to decrease the thermal coupling to the substrate and generate new complexity in the phase equilibrium diagram, so they need to be used with caution.

Should a liquid phase form, it will often wick away from the hot center of the strip toward the cooler ends, where it solidifies. Vapour phases are even more problematic, as they will tend to condense on the cold walls and/or windows of the chamber, slightly attenuating the incident and diffracted X-ray beams, and complicating the cleaning of the chamber, which is essential between experiments to avoid cross-contamination of experiments. Possible solutions include encapsulating the sample with an X-ray transparent cover (e.g., Kapton[®] or beryllium), or minimizing the time for data collection through use of high flux or high-speed detector.

Designs featuring separate heating elements arranged around a sample holder are generally more thermally stable, and with proper design can yield highly uniform temperatures, but generally such systems are unable to heat or cool as quickly as the strip/foil heaters.

Another critical issue for high-temperature X-ray diffraction experiments is interaction between the sample, the holder, the temperature sensor, and the atmosphere. Such interactions can alter the equilibrium phases and yield invalid results, and will be discussed in detail in the next section.

Several low-temperature X-ray diffraction systems are commercially available, and depending on the temperature range may be based on thermoelectric or Peltier-effect coolers, open or closed-cycle Joule–Thompson coolers, or flow cryostats based on liquefied N₂ or He gas. For Bragg–Brentano diffractometers vertical θ – θ geometries are sometimes preferred, as they simplify sample mounting, though flow cryostats may be more easily mounted vertically on a horizontal goniometer. Debye–Scherer geometries, with the sample in a thin gas-cooled capillary are also frequently used, particularly at synchrotron sources. Accuracy and precision of the sample temperature are a primary concern, but reactions with the sample holder are not the serious problem as in high-temperature X-ray diffraction. Generally the problematic samples are those that decompose at ambient temperature, as care must be taken to avoid warming while loading them on the pre-cooled sample stage. Low-temperature X-ray diffraction is generally used for studying the structure of low-temperature phases, thermal expansion, and phase transformations.

High-pressure experiments can be realized using gas-pressure cells or mechanical loading. In the extreme limits of pressure, diamond-anvil cells have been used with great success over the past 50 years. Modern diamond-anvil systems are capable of applying pressures of several giga Pascals to millimeters size samples. As an extreme example, the Paris–Edinburgh cell design used at spallation neutron sources utilizes either tungsten carbide or industrial diamond anvils to apply up to 200 tons of pressure directly to the sample, achieving pressures up to 9 or 10 GPa. Such apparatus often restrict the access of X-ray beams to and from the sample, and so high-pressure systems often resort to using polychromatic incident X-rays and energy-dispersive detectors (Giessen and Ordon, 1968) so that minimal space is needed for X-ray transparent windows.

9.3 In situ diffraction experiments

9.3.1 Background

The motivation behind an *in situ* X-ray diffraction experiment may be to study phases that are not stable at ambient pressure, to perturbations of a phase with a non-ambient environment, or to study the interaction of phases in a non-ambient environment. A common application of this technique is to simulate a "real world" processing environment. In addition to temperature and pressure, one can examine other perturbations including changes in gas partial pressure (Specht *et al.*, 1988), relative humidity (Oetzel *et al.*, 2000), chemical, electromagnetic, and elastic loading on the structure. Modern high-flux sources and fast detector systems facilitate real-time monitoring (Cook *et al.*, 2007) of crystallographic responses to environmental changes.

9.3.2 Experimental considerations

Some of the fundamental concerns for an *in situ* experiment are exactly the same as for conventional data collection – the beam has to reach the sample and detector, the sample surface must be kept on the focusing circle, enough grains must be probed to allow for reasonable counting statistics. Meeting these criteria for an "*in situ*" study is usually complicated by the "*in situ*" chamber enclosing the sample.

Examining structure evolution while the atmosphere changes from oxidizing to reducing, or under a reactive gas, or controlled pO_2 , or under changing partial (or absolute) pressure may be of interest. Several commercial chambers are available, and there are many unique systems as well, that allow multiple gas inlets and outlets, vacuum, and so on gas flow should not blow the sample off the holder, so the rate of flow may be constrained. Changing gases may take some time, so ability to control and/or monitor gas composition at various points in the system would be advantageous. From a practical standpoint, the biggest issue may be simply not blowing away your powder partway through such an experiment.

Gas hazards must be identified and proper safety procedures put in place. Gas cabinets suitable for flammable or toxic gases should be installed. As an example, hydrogen gas is frequently used in studies of fuel cell or energy storage materials. It is colorless, odorless, and highly flammable. It is essential to restrict the ability of hydrogen to leak into oxygen (air) and for oxygen to leak into hydrogen. Because the hydrogen gas molecule is small, leak detection is very important. If dilute ($<6\%H_2$) gas can be used N₂–4%H₂ is recommended because it is not considered a flammable gas, and many of the safety issues relax. Ar–4%H₂ can be used but argon is highly attenuating, so you will get lower intensities and higher background. He–4%H₂ is more expensive, but the helium balance dramatically reduces air scatter losses making it ideal for many X-ray diffraction applications. Drawbacks include a much higher thermal conductivity (so more power is needed for high-temperature furnaces, and more heat is transferred to the outer walls and windows). Helium readily leaks through thin vacuum windows, so it should not be used where the He gas could leak onto the X-ray tube or detector windows. Helium leakage into the vacuum chamber is a sure way to ruin a tube or detector. Nevertheless, with proper controls, even high-pressure hydrogen gas experiments can be safely conducted.

If the project is of sufficient scope to merit the investment, electronic gas flow controllers can be installed operated under computer control to allow long-time experiments under changing gas conditions. Such experiments can be extremely useful to simulate process conditions.

Lithium ion battery materials are an excellent example of a research problem for which *in situ* X-ray diffraction can provide valuable information, but for which the experiment itself is complicated by safety and/or sample volatility issues. The reader is referred to innovative solutions published in the literature (Li *et al.*, 1993; Nagasubramanian and Rodriguez, 2007; Reimers and Dahn, 1992) as examples of how such problems have been solved in the past. Radioactive powders also pose hazards and need to be contained in order to prevent contamination of the diffractometer and exposure of the operator.

For mechanical properties, a useful *in situ* attachment is a stress jig, either using a 3-point or 4-point bending apparatus, or a tensile load frame. Such attachments need to allow for adjustment of the specimen displacement in order to keep the sample exactly on the focusing circle, though use of parallel-beam optics relaxes some of the dependence of peak shift on height.

9.3.3 Lattice expansion

A common application of *in situ* analysis is to determine the thermal expansion of crystalline materials. One of the key advantages of X-ray diffraction for this application is that the crystallographic, rather than bulk, coefficients are determined, and this can be important for highly anisotropic materials. In principle, the method is simple – the high precision of X-ray diffraction should yield high precision in the coefficients of thermal expansion – but once again care must be taken not to confuse precision with accuracy. In powder diffraction analysis, the lattice parameters are usually highly correlated with two systematic errors – the sample surface displacement and the 2θ zero error. The latter can be minimized by careful alignment, and quantified through use of a NIST-certified standard. Having done so, a modern diffractometer should remain in alignment for a reasonable period of time, and so the 2θ zero error can be set and not refined further in the analysis. This is not generally the case for sample displacement, which likely will vary with temperature, so this error should be refined along with the lattice parameters – this requires that data be collected over as wide a range of 2θ as possible to improve the accuracy of the refinement. The resulting

values of displacement should be plotted against temperature and fit to a smooth curve. This displacement calibration curve should then be used to determine the displacement for each data set, which value should be fixed and not refined. This practice ensures that you are minimizing the random correlation between lattice parameter and displacement, and should improve the accuracy of both.

In the compendium of thermal expansion data compiled by Touloukian (Touloukian *et al.*, 1977) it should be noted that the thermal expansion coefficients are referenced to 20° C. It is helpful to note your selection of baseline temperature if different data sources are to be comparable.

Validation of X-ray diffraction results by dilatometry is recommended where feasible, but this may not always give the required answer, as dilatometry on polycrystalline materials will give a bulk average thermal expansion, which may be a poor representative of the crystallographic lattice expansion in highly anisotropic materials. An example is orthorhombic cordierite, where the *c*-axis exhibits low, and even negative, thermal expansion, compared to positive values for the *a*- and *b*-axes (Figure 9.1). For such anisotropic materials it is essential to minimize the grain size to the extent that virtually every grain is a single crystal, otherwise the expansion of each crystallite will be modified by its randomly oriented neighbors within each grain, and this may greatly distort the result.

9.3.4 Reaction kinetics

Another application of *in situ* analysis is to examine time-resolved structural changes in materials (Anwar, 1993). Reduction of such data can determine reaction kinetics – reaction rates, a typical approach is to first determine the temperature of a time-dependent phase



Figure 9.1 The thermal expansion coefficients for cordierite, as determined by A. Payzant and B. Wheaton using high-temperature X-ray diffraction.

transformation, then collect time-resolved data at various isothermal temperatures around the transformation temperature. The reaction rates may be fit with a suitable model representing the rate of growth of phases, and the reaction rate parameters at different temperatures can be fit to an Arrhenius equation to determine the activation energy for the process.

Although a detailed review of kinetic models for phase transformations is beyond the scope of this chapter, some further discussion may be worthwhile, as this subject is not particularly well covered in standard X-ray diffraction texts.

For solid–solid phase transformations, diffusion-limited growth applies when a new phase forms at the interface between two existing phases, and the new phase then acts as a barrier for diffusion of the original species to continue the reaction. For the simple case of random nucleation events followed by normal growth ceasing when it meets another nucleus the Avrami model, or the Kolmogorov–Johnson–Mehl–Avrami model (Avrami, 1939, 1940, 1941; Johnson and Mehl, 1939; Kolmogorov, 1937), has been widely used to describe solid–solid phase transformations. The model assumes that the nucleation of the new phase is a uniform and random process wherein the particles grow continuously until the growth is terminated by impingement onto other growing nuclei. This is a good "general purpose" model for determining the kinetics of formation of a crystalline phase, whether from an amorphous precursor (Choi *et al.*, 2005), a solid-state phase transformation (Lind *et al.*, 2002), or from a solid–liquid or solid–vapour reaction (Kim *et al.*, 2005), particularly when a more exact description of the process is not known.

For a solid-state transformation, the Avrami behavior can be described by

$$\alpha = 1 - e^{-(k_a t)^n} \tag{9.6}$$

or equivalently in linearized form, by

$$\ln[-\ln(1-\alpha)] = n\ln k_a + n\ln t$$
(9.7)

where α is the fraction transformed to the product phase, k_a is the reaction rate constant, and n is the Avrami exponent. The k_a value depends on the nucleation and growth rates and is very sensitive to temperature due to the strong dependence of nucleation density on temperature. The Avrami exponent n in equation (9.3) is usually related to the geometry of the transformation. The original derivation of the general relation in equation (9.3) by Avrami (1941) included three limiting cases where $3 \le n \le 4$ for three-dimensional growth, $2 \le n \le 3$ for two-dimensional growth and $1 \le n \le 2$ for linear or one-dimensional growth. A low value of Avrami exponent (n < 1) may indicate rapid completion of the reactant species. If a phase transformation follows the Avrami behavior, a plot of $\ln[-\ln(1-\alpha)]$ vs $\ln t$ should yield a straight line with a slope that is equal to n and an intercept equal to $n \ln k_a$ (Hancock and Sharp, 1972).

For one-dimensional diffusion-controlled growth processes, a parabolic rate law is a more appropriate model, whereby the transformation kinetics is described by

$$\alpha = (k_p t)^{m=0.5} \tag{9.8}$$

For the diffusion-controlled growth phase, the parabolic rate law assumes a constant interface area and/or planar surfaces between the reactants and is valid when the proportionality between the fraction transformed and the square root of time is linear. If a parabolic rate law analysis results in a noticeable deviation from the linear square root proportionality (m = 0.5), this indicates that the constant interface area assumption is not satisfied.

In collecting "isothermal" time-resolved spectra, it is obviously not possible to instantaneously achieve the isothermal temperature, so it may be necessary to substitute a time offset in equations (9.6), (9.7), or (9.8), to properly model the experimental data, particularly for very fast reactions. Irrespective of the model selected, the temperature dependence of the derived rate constants may be used to obtain the activation energy for the phase transformation using the Arrhenius relationship:

$$k = A \exp(-E_a/RT) \tag{9.9}$$

where k is the kinetic rate constant $(k_a \text{ or } k_p) \text{ in } \text{s}^{-1}$, A is the pre-exponential or frequency factor, E_a is the activation energy in Jmol^{-1} , R is the universal gas constant and T is the temperature in Kelvin. A plot of ln k vs 1/T should yield a straight line with a slope equal to E_a/R . From a practical standpoint, obtaining the activation energy for a particular phase transformation using *in situ* X-ray diffraction data is a time-consuming process, both experimentally and analytically, requiring collection of large sets of time-resolved spectra under several different isothermal conditions. Only with the availability of high flux sources, high-speed detectors, and automated data processing have resulted in such experiments becoming a routine.

9.4 An introduction to PDF analysis

9.4.1 Background

Radial distribution studies to examine local structure in glasses and amorphous materials, where there is considerable short-range order, but no long-range order, have a long history going back to Debye, and an excellent description can be found in several older texts (Klug and Alexander, 1974; Warren, 1969). X-ray diffraction on such materials yields no sharp Bragg peaks, but instead there are broad peaks corresponding to the average short-range atomic distances between pairs, or small clusters, of atoms. In the other extreme, it has been recognized that materials with long-range order may show subtle peak splitting or broadening and diffuse scatter due to short-range defects and ordering. In these cases, a conventional Rietveld solution, based on fitting a long-range ordered crystal structure model to the experimental data will not be able to resolve all the available structure information, as much information is lost in fitting the "background." As detailed in a recent book (Egami and Billinge, 2003), the radial distribution analysis method has in recent decades been greatly extended to allow refinement of a local structure model to the real-space "pair distribution function" or PDF, to investigate disorder in crystalline materials and nanomaterials.

To summarize the principles behind the method, it is noted that from a diffraction experiment, the measured X-ray intensity, *I*, can be equally well described in terms of its dependence on 2θ (in degrees, common in the powder diffraction community), $d (=\lambda/2\sin\theta, \sin \text{ Å})$, or $Q (=1/d = 2\sin\theta/\lambda, \sin \text{ Å}^{-1})$. The latter convention emphasizes the reciprocal space relationship. For PDF analysis, the measured intensity must be corrected for air scatter, sample absorption, and polarization, and then scaled to determine the total scattering structure function, S(Q). The Fourier transform of a correctly scaled S(Q)



Figure 9.2 Calculated and experimental PDFs of La₂Zr₂O₇ from neutron powder diffraction data collected by A. Payzant, S. Speakman and T. Proffen.

yields the real-space atomic pair distribution function (PDF), G(r), for which the peaks correspond to atomic pairs separated by a distance r, with an intensity related to the scattering power of the atom pair. An example of a PDF generated by a well-ordered material is shown in Figure 9.2. A nanocrystalline G(r) would show a sharp drop in peak intensities at a distance, r, corresponding to the average radius of the nanoparticles. An amorphous G(r) would only show a few short-range ordered peaks (a few nearest neighbors) and no long-range peaks. Local ordering on some atom sites would show up as peak splitting on certain peaks at short distances, with no effect at longer ranges. Considerable effort has been made to develop new refinement strategies to fit short-range ordered structure models to an experimentally determined G(r). This has been particularly successful in extracting meaningful information from bulk metallic glasses (Fang *et al.*, 2006) and locally ordered structures. The reader interested in more detail is directed to a recent volume describing the basis and application of the method (Farrow *et al.*, 2007).

9.4.2 Experimental considerations

Laboratory X-ray sources are limited by low Q range, low flux, and complex radiation spectra (bremmstrahlung, multiple characteristic lines). Nevertheless, Petkov's group at Michigan State University have demonstrated that useful data can be collected on a laboratory-based diffractometer using a sufficiently high-energy source such as Mo $K\alpha$ or Ag $L\alpha$. Synchrotron sources provide a solution to these limitations, and can generate extraordinary data, particularly on modern beamlines that have been specifically designed with collection of PDF data as the major motivation, providing high flux, high energy, and fast data collection. As with all areas of diffraction, neutron diffraction may similarly be used to determine a PDF, particularly at pulsed sources where the available *Q*-range is large.

9.4.3 Data analysis

Unlike conventional powder diffraction, where there is a mix of commercial and opensource software, PDF and RDF software is primarily non-commercial open source. The CCP14 website [http://www.ccp14.ac.uk] provides a good starting point to find such programs. Some recent examples include the programs PDFgetX2 (for X-rays) and PDFgetN (for neutrons), which process the total scattering spectra, correct for background scattering, and normalize with respect to the scattering coefficients of the powder to obtain the G(r). Programs PDFfit and PDFgui, from the recent DiffPy package (Farrow *et al.*, 2007), allow refinement of a short-range ordered crystal structure model to the G(r).

9.5 Summary

While the topic areas covered in this chapter are each important in their own right, increasingly the modern practise is to combine two or more of these techniques in solving complex material problems. Increasingly, "*in situ*" studies examine the effects of changing sample environment on the rate of change of crystallite size and strain, phase transformations, and short- and long-range order. The potential of such integrated approaches is significant, as illustrated by the recent work of Kramer *et al.* (Kramer, 2007), who use PDF analysis of *in situ* high-temperature X-ray diffraction data to identify short-range structural changes. This work notes that in a series of scans, the errors and many of the uncertainties in the models will be closely similar if not identical, and so it is just the changes in G(r) that can quantitatively reveal the structural changes in the sample. This greatly simplifies the data reduction and analysis, which is very important given the considerable quantity of data collected.

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