Manual for Software Program

Contents

ASF88

Calculation of atomic scattering factor of elements

This is a program to calculate the X-ray atomic scattering factors of elements in the periodic table of elements. The neutral atom and ionic scattering factors can be generated using this program. For neutral atoms, give the atom name. For ionic element, give the atom name followed by oxidation state., e.g. Ga3+. Give the correct chemical symbols.

Chemical symbols that can be used in this software

H He Li Be B C N O F Ne Na

Mg Al Si P S Cl Ar K Ca Sc Ti

V Cr Mn Fe Co Ni Cu Zn Ga Ge As

Se Br Kr Rb Sr Y Zr Nb Mo Tc Ru

Rh Pd Ag Cd In Sn Sb Te I Xe Cs

Ba La Ce Pr Nd Pm Sm Eu Gd Tb Dy

Ho Er Tm Yb Lu Hf Ta W Re Os Ir

Pt Au Hg Tl Pb Bi Po At Rn Fr Ra

Ac Th Pa U Np Pu Am Cm Bk Cf

H1- Li1+ Be2+ Cval O1- O2- F1- Na1+ Mg2+ Al3+

Siva Si4+ Cl1- K1+ Ca2+ Sc3+ Ti2+ Ti3+ Ti4+ V2+

V3+ V5+ Cr2+ Cr3+ Mn2+ Mn3+ Mn4+ Fe2+ Fe3+ Co2+

Co3+ Ni2+ Ni3+ Cu1+ Cu2+ Zn2+ Ga3+ Ge4+ Br1- Rb1+

Sr2+ Y3+ Zr4+ Nb3+ Nb5+ Mo3+ Mo5+ Mo6+ Ru3+ Ru4+

Rh3+ Rh4+ Pd2+ Pd4+ Ag1+ Ag2+ Cd2+ In3+ Sn2+ Sn4+

Sb3+ Sb5+ I1- Cs1+ Ba2+ La3+ Ce3+ Ce4+ Pr3+ Pr4+

Nd3+ Pm3+ Sm3+ Eu2+ Eu3+ Gd3+ Tb3+ Dy3+ Ho3+ Er3+

Tm3+ Yb2+ Yb3+ Lu3+ Hf4+ Ta5+ W6+ Os4+ Ir3+ Ir4+

Pt2+ Pt4+ Au1+ Au3+ Hg1+ Hg2+ Tl1+ Tl3+ Pb2+ Pb4+

Bi3+ Bi5+ Ra2+ Ac3+ Th4+ U3+ U4+ U6+ Np3+ Np4+

Np6+ Pu3+ Pu4+ Pu6+

The maximum limit for sin (theta)/lambda is 6.0. Any floating point value within this limit is allowed. The minimum step size is 0.001. Step size values above this are allowed.

The output Scattering Factor can be visualized in atomic_s_fac.bmp graphic file. The output Scattering Factor can also be visualized in atomic_s_fac.pdf file. Also, an outfile will be created in the file with name given earlier through keyboard as the element name. Atomic scattering factors are listed out in this file.

The expression for the calculation atomic scattering factor is as follows;

$$f\left(\frac{sin\theta}{\lambda}\right) = \sum_{i=1}^{5} \mathrm{a_i}\ exp\left(-b_i\left(\frac{sin\theta}{\lambda}\right)^2\right) + c$$

Where a1, a2, a3, a4, a5, b1, b2, b3, b4, b5, c are the analytical coefficients to calculate the a.s.factors. θ is the Bragg angle and λ is the wavelength of the X-rays.

All the above coefficients for elements in the periodic table have been incorporated in the ASF88 program. The analytical coefficients specific for the selected element will be listed in the file 'analytical' at the end of successful run of ASF88 which can be of useful to be used with other programs.

A partial output file for aluminum (Al) has been given below.

0.00000	0.00000	12.99855
0.00100	0.00000	12.99831
0.00200	0.00000	12.99758
0.00300	0.00001	12.99636
0.00400	0.00002	12.99466
0.00500	0.00003	12.99247
0.00600	0.00004	12.98980
0.00700	0.00005	12.98664
0.00800	0.00006	12.98300

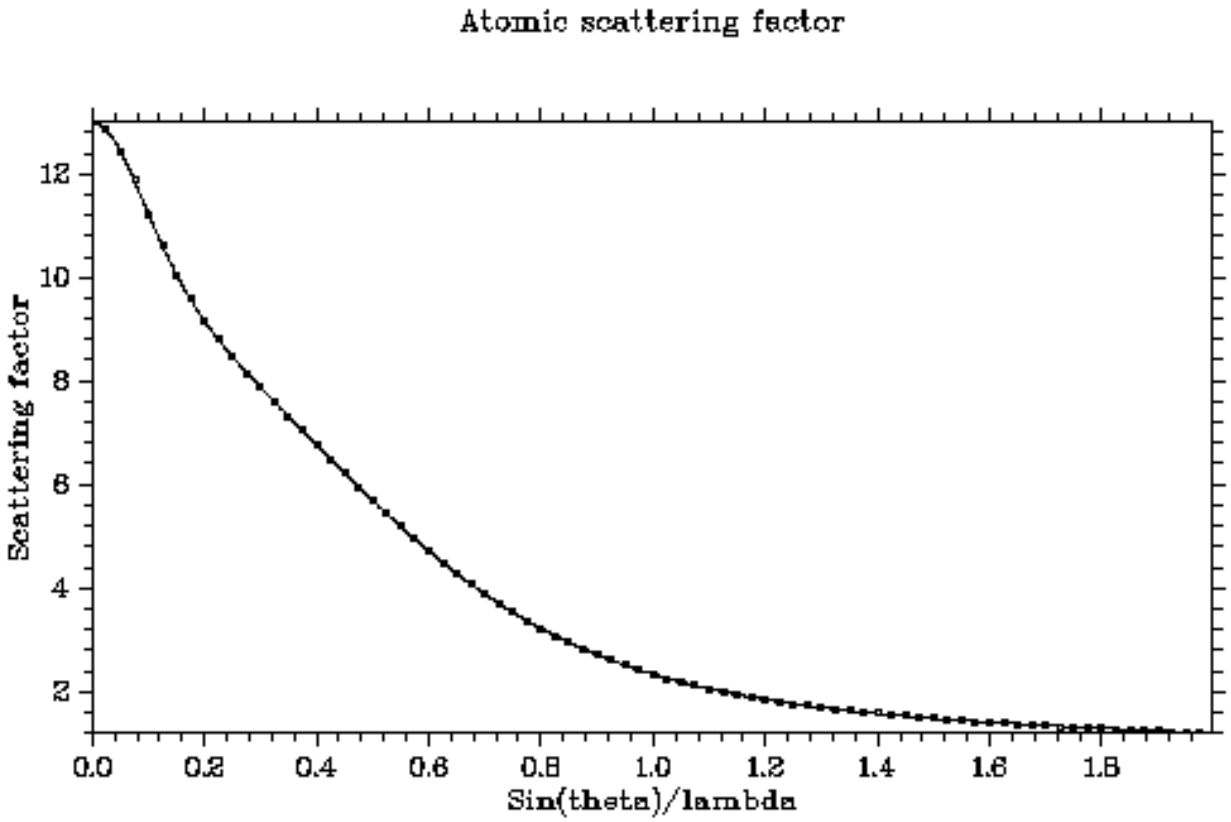
The first column represent the $\frac{sin\theta}{\lambda}$, the second column $\frac{sin\theta}{\lambda}$ **2 and the third column represents the atomic scattering factor of aluminum. For $\frac{sin\theta}{\lambda} = 0$, the value of the atomic scattering factor will be the atomic number of the element. In this example, it is 13, the atomic number of aluminum.

The file 'analytical' contains the following values.

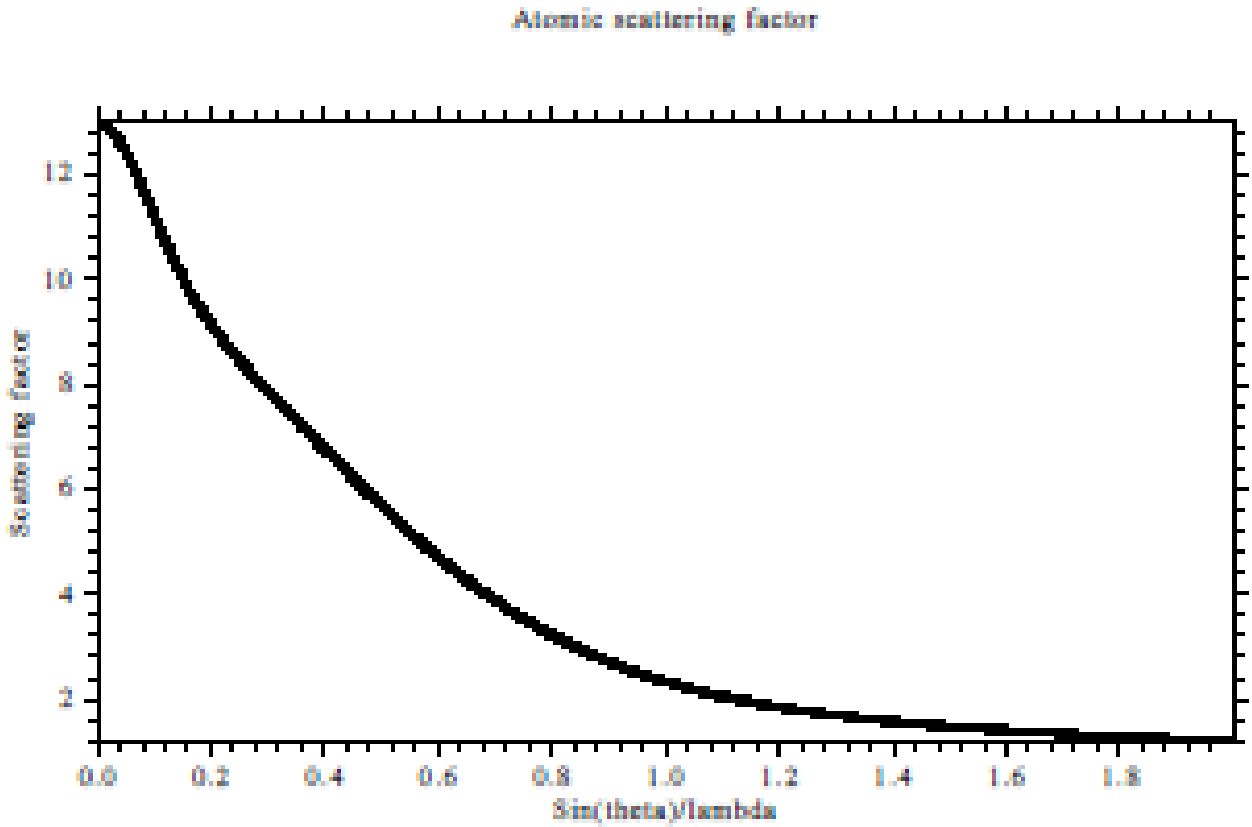
4.731 2.314 1.542 1.118 3.155 3.629 43.051 0.096108.932 1.556 0.140,

and they are the a1, a2, a3, a4, a5, b1, b2, b3, b4, b5, c values of aluminum (Al).

The a.s.factor curve of aluminum will be given in a graph as follows;



The pdf version of the above graph is as below.



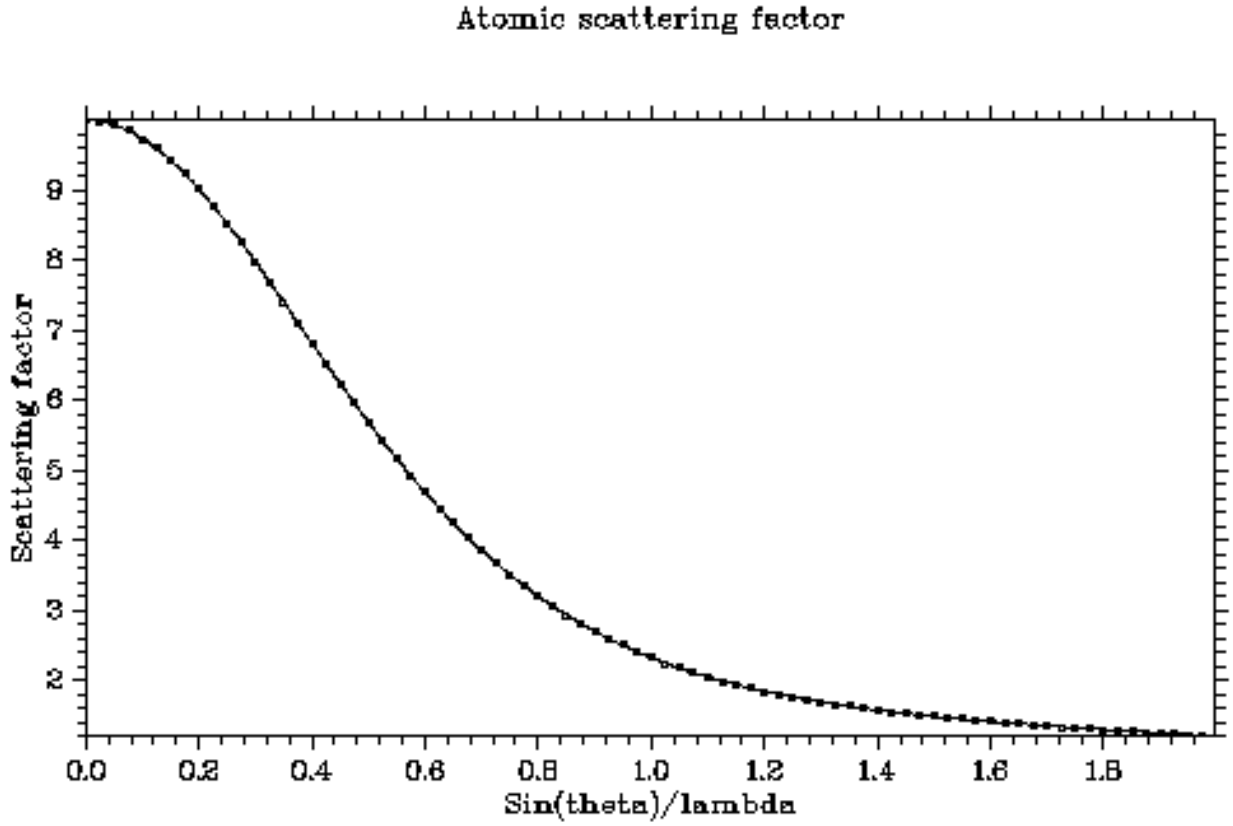
Analytical coefficients of the elements in the periodic table have been incorporated in the program ASF88 along with the real and imaginary parts of the (f' and f") dispersion correction of X-rays for all wavelengths and all elements.

Another case – Al^{3+} . The partial output file is as follows;

0.00000	0.00000	9.99990
0.00100	0.00000	9.99987
0.00200	0.00000	9.99979
0.00300	0.00001	9.99966
0.00400	0.00002	9.99947
0.00500	0.00003	9.99923
0.00600	0.00004	9.99893
0.00700	0.00005	9.99859
0.00800	0.00006	9.99818
0.00900	0.00008	9.99773
0.01000	0.00010	9.99722

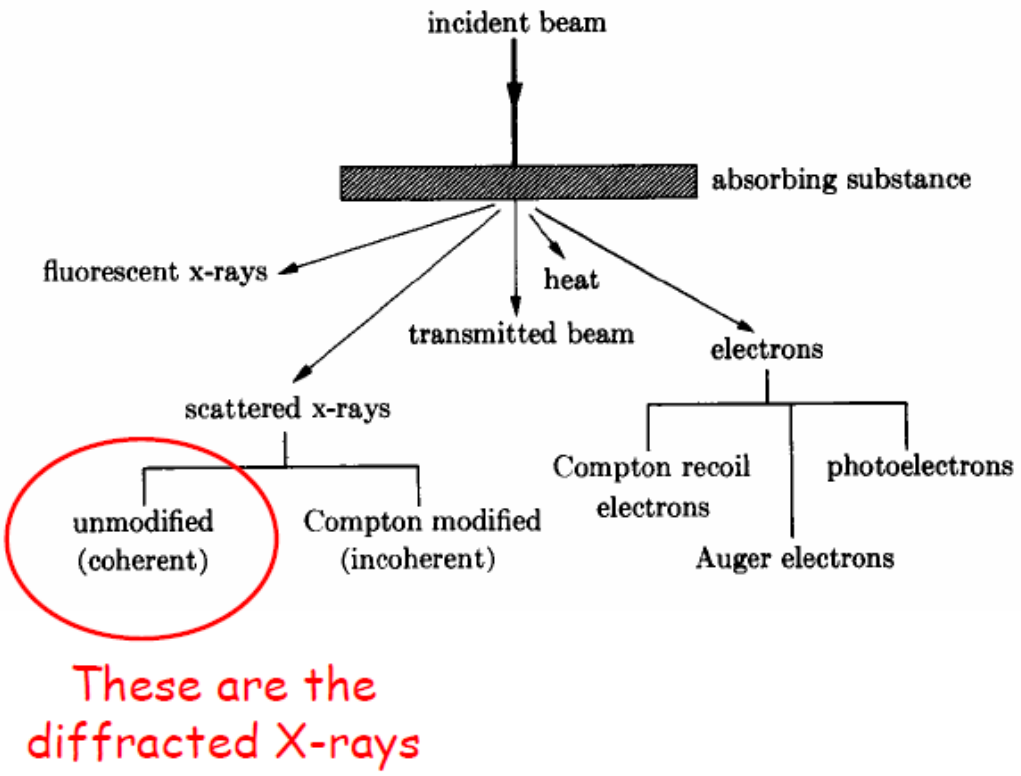
The value of a.s.factor at $\frac{sin\theta}{\lambda} = 0$ is 10, which means 3 electrons removed from aluminum (Al^{3+}).

The a.s.factor curve is as follows;



Theory of atomic scattering factor

Interaction of X-rays with Matter



Elastic Scattering by an Electron

Charged particles (electron) scatter electromagnetic radiation (x-rays)

- The varying electric field of the X-ray induces an oscillation of the electron
- The oscillating electron then acts as a source of electromagnetic radiation
- In this way the x-rays are scattered in all directions

JJ Thompson analyzed the scattering and found that:

$$I = I_0[(\mu_0/4p)^2(e^4/m^2r^2)\sin^2\alpha]$$

$$I = I_0(K/r^2)\sin^2\alpha$$

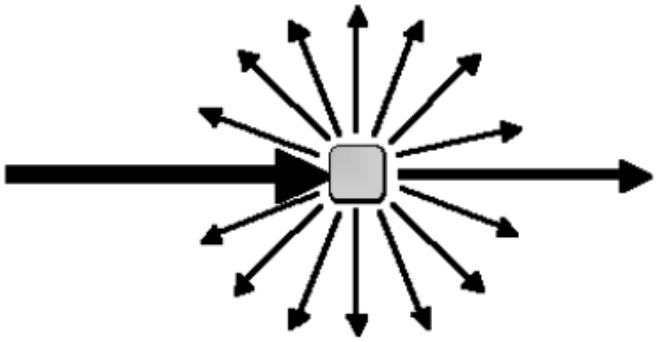
α is the angle between the scattering direction and the direction in which the electron is accelerated

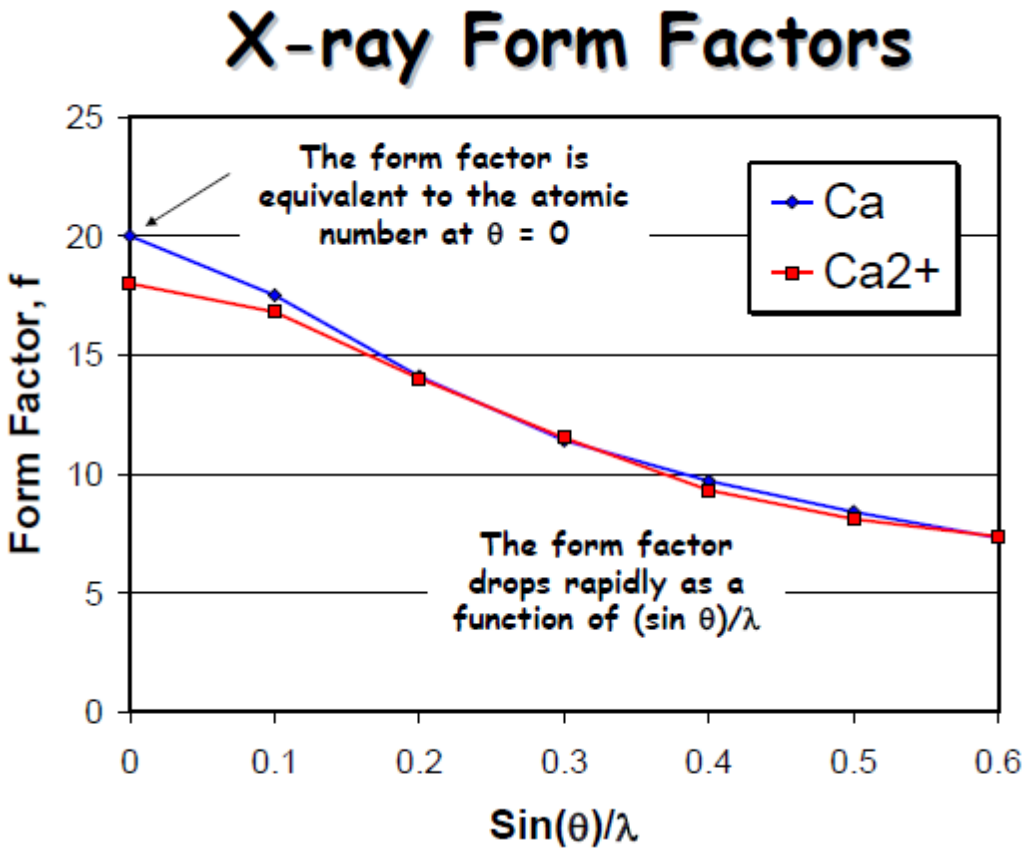
r is the distance from the scattering electron

K is a constant

Scattering by an Atom

We can consider an atom to be a collection of electrons. The electrons around an atom scatter radiation in the manner described by Thompson. However, due to the coherence of the radiation we need to consider interference effects from different electrons within an atom. **This leads to a strong anglular dependence of the scattering**. We express the scattering power of an atom by its form factor (f).




X-ray Form Factors
25
20
15
10
5
0
Form Factor, f
The form factor is equivalent to the atomic number at θ = 0
Ca
Ca2+
The form factor drops rapidly as a function of (sin θ)/λ
0
0.1
0.2
0.3
0.4
0.5
0.6
Sin(θ)/λ

BCC

About the program

This is a refinement program (to refine the single crystal/powder XRD experimental data to (i) match the observed and calculated structure factors (ii) to refine the Debye-Waller factor (iii) hence to find experimental mean square amplitudes. Applicable to BCC (single element) type systems.

This program can process the observed X-ray structure factors or the observed intensities converted into X-ray structure factors of BCC structure. BCC structure factors will be CALCULATED in the program BCC and the observed and calculated structure factors will be matched using least-squares refinement method. The (i) Debye-Waller factor and (ii) the scale factor are the prime parameters refined in this program. The output file will contain the results of refinement in each least-squares refinement.

Also, the listing will have the h k l values of the reflections, FOBS (observed) structure factor, FCAL (calculated) structure factor, the difference DELF (between Fobs and Fcal) , error as the % (ERR), atomic scattering factor of the atom involved SF(I,1), the Bragg angle THETA, and sin(theta)/Lambda (SINT).

The observed powder XRD intensities from a powder data set can be utilized. First, the observed X-ray intensities should be converted into observed X-ray structure factors. The supplied SCAT771 program can be used for this purpose. Or any other method can be used to get the observed structure factors of each reflection from the observed intensities. The prime corrections to be applied to convert the X-ray intensities into X-ray structure factors are (i) multiplicity and (ii) Lorentz-polarization corrections. SCAT771 program can do this.

After, converting the X-ray intensities into structure factors using SCAT771, the input file for running BCC should be prepared.

Input

Prepare an input file for running BCC. The input is FORMAT sensitive. Hence adhere to the spacings and other syntaxes. The name should be in_bcc. (without full-stop)

A typical input will be as follows;

```
Refinement of BCC parameters (eg. BCC-Fe)
 1 20  1  0
1.540560 2.86600009.500000 1.200000
12.311  1.877  3.066  2.070  6.975  5.009  0.014 18.743 82.768  0.347 -0.305
-1.133  3.197
 1  1  0   0.8600
 2  0  0   0.8302
 2  1  1   0.6330
 2  2  0   0.5527
 3  1  0   0.5637
 2  2  2   0.3828
99
```

First line is the title line

Second line, I parameter 1 indicates the number of species of atoms (allowed value is 1, since the program is for BCC monoatomic system)

Second line, II parameter 20 indicates user inputted number of cycles of least-squares refinement, typically 10 to 20 enough for convergence.

Second line, III parameter 1 indicates Wilson plot analysis is done for finding Debye-Waller factor using Fobs and Fcal. 0 will not do Wilson plot analysis.

Second line, IV parameter 0 indicates the no. of observed reflections to be omitted from refinement process (in this case 0). This can be decided after initial refinements and checking the results for reflections with large differences in Fobs and Fcal.

Third line, I parameter (1.54056) indicates the wavelength of X-rays used for XRD powder data recording.

Third line, II parameter (2.866) indicates the cell constant of the BCC system (in this case Fe with cell constant 2.866 angstrom).

Third line, III parameter (9.5) indicates the initial scale factor to be used in the refinement to match Fobs and Fcal. Any random value is OK so that refinement converges.

Third line, IV parameter (1.2) indicates the initial B value (Debye-Waller factor of Fe atom) to be used in the refinement to match Fobs and Fcal. A small value is enough.

Fourth line indicates the analytical co-efficients (5 parameter model) to calculate the atomic scattering factors of the (here, Fe atom) atom. A1, A2, A3, A4, A5, B1, B2, B3, B4, B5, and C. A total of 11 coefficients are to be used. These values are listed in international tables for X-ray crystallography. But, if you use SCAT771 program you can find these values in one of the output files (PAR1) and use them in the input for BCC.

Fifth line indicates (-1.133 3.197) two values, the anomalous dispersion corrections terms of the atom (here, Fe) for the X-ray wavelength used. These values are listed in international tables for X-ray crystallography. But, if you use SCAT771 program you can find these values in one of the output files (DIS1) and use them in the input for BCC.

In this input examples, **the next 6 lines indicate the h k l values and the observed structure factors (FOBS)** derived from SCAT771 program.

In the **last line 99 indicates** the parameter to terminate the reading of the input.

Output

The output file name is out_bcc. All the inputted values are listed first. Then, a typical output cycle shows as follows.

```
---------------
CYCLE NUMBER= 1
---------------
 SCALE FACTOR = 0.25580E-01     +/-     0.88180E+01
 B OF ANION     = 0.11963E+01     +/-     0.54364E+01
 CORRELATION BETWEEN  1 AND  2 IS  =  0.84362686
 RMINIMUM =  0.195561
```

These results are self-explanatory. RMINIMUM will show the Reliability index at each cycle. At the end of 20th cycle (here, the no. of cycles is 20 in this example), you can see the following.

```
************************
  ************************
  ** 5R  MINIMUM=0.0756***
  ************************
  ************************
```

5R MINIMUM=0.0756, indicates that the minimum R factor occurs at 5th cycle and the R value is 7.56 %.

The parameter listed in the 5th cycle are the refined parameter as follows.

```
---------------
CYCLE NUMBER= 5
---------------
 SCALE FACTOR = 0.26253E-01     +/-     0.22074E-02
 B OF ANION   = 0.14873E+00     +/-     0.44008E+00
 CORRELATION BETWEEN  1 AND  2 IS  =  0.85451484
 RMINIMUM=  0.075567
```

Note, the most successful results can be obtained through a large no. observations. That is - good statistics only will lead to convincing results.

A typical output for BCC iron (Fe) is as follows;

```
                Refinement of BCC parameters (eg. BCC-Fe)
 1 20  1  0
1.540560 2.866000 9.500000 1.200000
12.311  1.877  3.066  2.070  6.975  5.009  0.014 18.743 82.768  0.347 -0.305
-1.133  3.197
 1  1  0   0.86
 2  0  0   0.83
 2  1  1   0.63
 2  2  0   0.55
 3  1  0   0.56
 2  2  2   0.38
99  0  0   0.00
--------------------------------------------------------------------------------
OUTPUT DATA FOR  Refinement of BCC parameters (eg. BCC-Fe)
--------------------

       TOTAL NO OF REFLECTIONS=    6

       TOTAL OMITTED REFLECTIONS=  0
   RMINIMUM=297.553955

   ---------------
   CYCLE NUMBER= 1
   ---------------
    SCALE FACTOR = 0.25580E-01    +/-    0.88180E+01
    B OF ANION   = 0.11963E+01    +/-    0.54364E+01
    CORRELATION BETWEEN  1 AND  2 IS  =  0.84362686
    RMINIMUM=  0.195561
   ---------------
   CYCLE NUMBER= 2
   ---------------
    SCALE FACTOR = 0.25586E-01    +/-    0.61146E-02
    B OF ANION   =-0.18242E+00    +/-    0.13994E+01
    CORRELATION BETWEEN  1 AND  2 IS  =  0.84365475
    RMINIMUM=  0.087202
   ---------------
   CYCLE NUMBER= 3
   ---------------
    SCALE FACTOR = 0.26280E-01    +/-    0.23919E-02
    B OF ANION   = 0.15117E+00    +/-    0.47264E+00
    CORRELATION BETWEEN  1 AND  2 IS  =  0.85910058
    RMINIMUM=  0.075776
     ---------------
   CYCLE NUMBER= 4
   ---------------
    SCALE FACTOR = 0.26252E-01    +/-    0.22081E-02
    B OF ANION   = 0.14860E+00    +/-    0.43989E+00
    CORRELATION BETWEEN  1 AND  2 IS  =  0.85448134
    RMINIMUM=  0.075567
```

```
---------------
CYCLE NUMBER= 5
---------------
 SCALE FACTOR = 0.26253E-01    +/-    0.22074E-02
 B OF ANION   = 0.14873E+00    +/-    0.44008E+00
 CORRELATION BETWEEN  1 AND  2 IS  =  0.85451484
 RMINIMUM=  0.075567
 ---------------
CYCLE NUMBER= 6
---------------
 SCALE FACTOR = 0.26253E-01    +/-    0.22074E-02
 B OF ANION   = 0.14872E+00    +/-    0.44008E+00
 CORRELATION BETWEEN  1 AND  2 IS  =  0.85451323
 RMINIMUM=  0.075567
 ---------------
CYCLE NUMBER= 7
---------------
 SCALE FACTOR = 0.26253E-01    +/-    0.22074E-02
 B OF ANION   = 0.14872E+00    +/-    0.44008E+00
 CORRELATION BETWEEN  1 AND  2 IS  =  0.85451341
 RMINIMUM=  0.075567
 ---------------
CYCLE NUMBER= 8
---------------
 SCALE FACTOR = 0.26253E-01    +/-    0.22074E-02
 B OF ANION   = 0.14872E+00    +/-    0.44008E+00
 CORRELATION BETWEEN  1 AND  2 IS  =  0.85451347
 RMINIMUM=  0.075567
 ---------------
CYCLE NUMBER= 9
---------------
 SCALE FACTOR = 0.26253E-01    +/-    0.22074E-02
 B OF ANION   = 0.14872E+00    +/-    0.44008E+00
 CORRELATION BETWEEN  1 AND  2 IS  =  0.85451323
 RMINIMUM=  0.075567
 ---------------
CYCLE NUMBER=10
---------------
 SCALE FACTOR = 0.26253E-01    +/-    0.22074E-02
 B OF ANION   = 0.14872E+00    +/-    0.44008E+00
 CORRELATION BETWEEN  1 AND  2 IS  =  0.85451341
 RMINIMUM=  0.075567
 ---------------
CYCLE NUMBER=11
---------------
 SCALE FACTOR = 0.26253E-01    +/-    0.22074E-02
 B OF ANION   = 0.14872E+00    +/-    0.44008E+00
 CORRELATION BETWEEN  1 AND  2 IS  =  0.85451335
 RMINIMUM=  0.075567
```

CYCLE NUMBER=12

SCALE FACTOR = 0.26253E-01 +/- 0.22074E-02
B OF ANION = 0.14872E+00 +/- 0.44008E+00
CORRELATION BETWEEN 1 AND 2 IS = 0.85451323
RMINIMUM= 0.075567

CYCLE NUMBER=13

SCALE FACTOR = 0.26253E-01 +/- 0.22074E-02
B OF ANION = 0.14872E+00 +/- 0.44008E+00
CORRELATION BETWEEN 1 AND 2 IS = 0.85451341
RMINIMUM= 0.075567

CYCLE NUMBER=14

SCALE FACTOR = 0.26253E-01 +/- 0.22074E-02
B OF ANION = 0.14872E+00 +/- 0.44008E+00
CORRELATION BETWEEN 1 AND 2 IS = 0.85451323
RMINIMUM= 0.075567

CYCLE NUMBER=15

SCALE FACTOR = 0.26253E-01 +/- 0.22074E-02
B OF ANION = 0.14872E+00 +/- 0.44008E+00
CORRELATION BETWEEN 1 AND 2 IS = 0.85451347
RMINIMUM= 0.075567

CYCLE NUMBER=16

SCALE FACTOR = 0.26253E-01 +/- 0.22074E-02
B OF ANION = 0.14872E+00 +/- 0.44008E+00
CORRELATION BETWEEN 1 AND 2 IS = 0.85451323
RMINIMUM= 0.075567

CYCLE NUMBER=17

SCALE FACTOR = 0.26253E-01 +/- 0.22074E-02
B OF ANION = 0.14872E+00 +/- 0.44008E+00
CORRELATION BETWEEN 1 AND 2 IS = 0.85451341
RMINIMUM= 0.075567

CYCLE NUMBER=18

SCALE FACTOR = 0.26253E-01 +/- 0.22074E-02
B OF ANION = 0.14872E+00 +/- 0.44008E+00
CORRELATION BETWEEN 1 AND 2 IS = 0.85451335
RMINIMUM= 0.075567

CYCLE NUMBER=19

SCALE FACTOR = 0.26253E-01 +/- 0.22074E-02
B OF ANION = 0.14872E+00 +/- 0.44008E+00
CORRELATION BETWEEN 1 AND 2 IS = 0.85451323
RMINIMUM= 0.075567

```
 ---------------
 CYCLE NUMBER=20
 ---------------
  SCALE FACTOR = 0.26253E-01     +/-     0.22074E-02
  B OF ANION   = 0.14872E+00     +/-     0.44008E+00
  CORRELATION BETWEEN  1 AND  2 IS  =  0.85451341

                                 ************************
                                 ****************************
                                 ** 5R  MINIMUM=0.0756***
                                 ************************
-------  ----     ----       ----    --- ------- ------  -----     ----    -    ---
H  K  L  FOBS      FCAL       DELF    ERR SF(I,1) SF(I,2) THETA     SINT    Y    TDS
-------  ----     ----       ----    --- ------- ------  -----     ----    -    ---
1  1  0   32.758   34.937    -2.2  -6.7 17.6276  0.0000 22.3393 0.060870.000000.00000
2  0  0   31.615   28.446     3.2  10.0 14.4831  0.0000 32.5156 0.121740.000000.00000
2  1  1   23.997   24.196    -0.2  -0.8 12.4312  0.0000 41.1731 0.182620.000000.00000
2  2  0   20.950   21.190    -0.2  -1.1 10.9858  0.0000 49.4802 0.243490.000000.00000
3  1  0   21.331   18.974     2.4  11.0  9.9264  0.0000 58.2018 0.304360.000000.00000
2  2  2   14.475   17.297    -2.8 -19.5  9.1313  0.0000 68.5957 0.365230.000000.00000

      --------------------------------
      WILSON PLOT FOR  Refinement of BCC parameters (eg. BCC-Fe)
      --------------------------------
 -------    ----       -----       ----       ---          ----       ---------
 H  K  L    FOBS       FCALC       DELF       ERR          SINT       LN(FO/FC)
 -------    ----       -----       ----       ---          ----       ---------
   THERMAL PARAMETERS FROM WILSON PLOT =   -0.401009       +OR-       0.314966
   Y AXIS INTERCEPT FROM WILSON PLOT =    0.047164     +OR-         0.074667
```

Y and TDS will be having values if single crystal XRD data sets are used for the refinement.

Here, Y = Secondary extinction correction for X-ray intensities (the value in excess of 1.0 is the extinction correction applied.

TDS = Thermal Diffuse Scattering correction.

Theory of least-squares refinement

Least Squares method - General

Given data $\{(x_1, y_1), \ldots, (x_N, y_N)\}$, we may define the error associated to saying $y = ax + b$ by

$$E(a, b) = \sum_{n=1}^{N} (y_n - (ax_n + b))^2 . \tag{3.10}$$

This is just N times the variance of the data set $\{y_1 - (ax_1 + b), \ldots, y_n - (ax_N + b)\}$. It makes no difference whether or not we study the variance or N times the variance as our error, and note that the error is a function of two variables.

The goal is to find values of a and b that minimize the error. In multivariable calculus we learn that this requires us to find the values of (a, b) such that

$$\frac{\partial E}{\partial a} = 0, \quad \frac{\partial E}{\partial b} = 0. \tag{3.11}$$

Note we do not have to worry about boundary points: as $|a|$ and $|b|$ become large, the fit will clearly get worse and worse. Thus we do not need to check on the boundary.

Differentiating $E(a, b)$ yields

$$\begin{aligned} \frac{\partial E}{\partial a} &= \sum_{n=1}^{N} 2 (y_n - (ax_n + b)) \cdot (-x_n) \\ \frac{\partial E}{\partial b} &= \sum_{n=1}^{N} 2 (y_n - (ax_n + b)) \cdot 1. \end{aligned} \tag{3.12}$$

Setting $\partial E/\partial a = \partial E/\partial b = 0$ (and dividing by 2) yields

$$\begin{aligned} \sum_{n=1}^{N} (y_n - (ax_n + b)) \cdot x_n &= 0 \\ \sum_{n=1}^{N} (y_n - (ax_n + b)) &= 0. \end{aligned} \tag{3.13}$$

We may rewrite these equations as

$$\begin{aligned} \left(\sum_{n=1}^{N} x_n^2\right) a + \left(\sum_{n=1}^{N} x_n\right) b &= \sum_{n=1}^{N} x_n y_n \\ \left(\sum_{n=1}^{N} x_n\right) a + \left(\sum_{n=1}^{N} 1\right) b &= \sum_{n=1}^{N} y_n. \end{aligned} \tag{3.14}$$

We have obtained that the values of a and b which minimize the error (defined in (3.10)) satisfy the following matrix equation:

$$\begin{pmatrix} \sum_{n=1}^{N} x_n^2 & \sum_{n=1}^{N} x_n \\ \sum_{n=1}^{N} x_n & \sum_{n=1}^{N} 1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \sum_{n=1}^{N} x_n y_n \\ \sum_{n=1}^{N} y_n \end{pmatrix}. \tag{3.15}$$

We will show the matrix is invertible, which implies

$$\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \sum_{n=1}^{N} x_n^2 & \sum_{n=1}^{N} x_n \\ \sum_{n=1}^{N} x_n & \sum_{n=1}^{N} 1 \end{pmatrix}^{-1} \begin{pmatrix} \sum_{n=1}^{N} x_n y_n \\ \sum_{n=1}^{N} y_n \end{pmatrix}. \tag{3.16}$$

Denote the matrix by M. The determinant of M is

$$\det M = \sum_{n=1}^{N} x_n^2 \cdot \sum_{n=1}^{N} 1 - \sum_{n=1}^{N} x_n \cdot \sum_{n=1}^{N} x_n. \tag{3.17}$$

As

$$\overline{x} = \frac{1}{N} \sum_{n=1}^{N} x_n, \tag{3.18}$$

we find that

$$\begin{aligned} \det M &= N \sum_{n=1}^{N} x_n^2 - (N\overline{x})^2 \\ &= N^2 \left(\frac{1}{N} \sum_{n=1}^{N} x_n^2 - \overline{x}^2 \right) \\ &= N^2 \cdot \frac{1}{N} \sum_{n=1}^{N} (x_n - \overline{x})^2, \end{aligned} \tag{3.19}$$

where the last equality follows from simple algebra. Thus, as long as all the x_n are not equal, $\det M$ will be non-zero and M will be invertible.

Thus we find that, so long as the x's are not all equal, the best fit values of a and b are obtained by solving a linear system of equations; the solution is given in (3.16)**.**

Least Squares method - Crystallography

- The refinement process is really a minimization process
  - minimize difference between observed and calculated structure factors
- It can be shown that the 'best' model can be obtained by minimizing

$$D = \sum_{h,k,l} w_{hkl} \left(|F_o| - k|F_c| \right)^2$$

  - this is a least squares minimization
  - uses many more observations than parameters
    - » W_{hkl} are weights related to the quality of the observation
    - » $|F_o|$ are the observed structure factor magnitudes
    - » $|F_c|$ are the structure factor magnitudes calculated from your model

- In the case where a function is linearly dependent upon a set of parameters
  - $F(x_1,x_2,..) = p_1x_1 + p_2x_2 + ...p_nx_n$
- m independent measurements of F for different values of x_i is enough to determine the n parameters p_i
  - if m = n just solve a set of simultaneous equations

- Unfortunately, the structure factors F(hkl) are not linear functions of the model parameters (coordinates, thermal parameters etc.)
- Can not solve for the correct parameters in one go

- Use least squares to give you a set of parameter shifts that improve the agreement between F_{obs} and F_{calc}
- Repeat the least squares process until the suggested shifts are insignificantly small
  - until parameter shift << esd on parameter

$$D = \sum_{h,k,l} w_{hkl} \left(|F_o| - k|F_c| \right)^2$$

- We want a set of parameters that minimizes D. At this minimum the derivative of D with respect to each parameter should be zero

$$\frac{1}{2}\frac{\partial D}{\partial x_m} = \sum_{h,k,l} w_{hkl} \left[|F_o(hkl)| - |F_c(hkl)| \right] \frac{\partial F_c}{\partial x_m} = 0$$

- Have set of n simultaneous equations with n unknown parameters x_m
  - However, they are nonlinear in x_m as F_c is a nonlinear function of x_m

Least squares refinement: $$Q = \sum_{hkl} w(hkl) \cdot \left(|F_{obs}(hkl)| - |F_{calc}(hkl)| \right)^2$$

Crystallographic R-Factor: $$R = \frac{\sum_{hkl} \left| F_{obs}(hkl) - k \cdot F_{calc}(hkl) \right|}{\sum_{hkl} \left| F_{obs}(hkl) \right|}$$

CUBINDEX

About the program

This program CUBINDEX performs the indexing procedure for cubic systems as well, in addition to many other tasks as follows;

1. Using inputted 2theta, d (inter planar spacing) and Iobs (observed intensities), it assigns h k l values to each observed reflection in a raw powder diffraction pattern.

2. It evaluates the cell constants (cubic system) from each observed 2theta.

3. It calculates Nelson-Riley function for each observed h k l and 2theta and subsequently the cell constant for each reflection.

4. It finds the most optimum cell constant from the least-squares method using the NR function and the observed cell constant.

5. It also processes the inputted observed intensities. It calculates the multiplicity and Lorent-Polarization factors and applies these factors to the Iobs values to convert them into observed structure factors (Fobs).

6. It also calculates the atomic scattering factors of the atoms involved.

7. It calculates the structure factors (Fcal) and fits the Wilson plot data using least squares method to find the Debye-Waller factors.

8. It calculates the real and imaginary parts of the structure factors.

Input

The input file name is icube.

A typical input will be as follows;

Give the No. of reflections available (You should give the no. of available sets of 2theta, d and Iobs)
9 (in this case its 9)
Give the 2theta, d and Iobs(Observed intensity) (Give below the numerical values of 2theta d and Iobs)
38.472 2.338 100.0
44.738 2.024 47.0
65.133 1.431 22.0
78.227 1.221 24.0
82.435 1.169 7.0
99.078 1.012 2.0
112.04 0.929 8.0
116.56 0.9055 8.0
137.45 0.827 8.0
Give the theta of Max intensity reflection (give below the 2theta value of most intense Bragg reflection and a squared addition of possible h k l value for the most intense reflection)
38.472 3
Give no. of elements,WAVElength, ISYS, ISTRUC (Give the no. of chemical species in the system, wavelength (alphabet), 8, 1)
1 Cu 8 1 (keep 8, 1 - they are parameters to extend the program to other systems - not yet completed)
Give the atom names in the system
Al (atom name)
Give the no. of atoms
4 (no. of Al atoms in the unit cell)
Give atomic coordinates of atoms (the x y z values of those 4 atoms)
0.0 0.0 0.0
0.5 0.5 0.0
0.0 0.5 0.5
0.5 0.0 0.5
4.731 2.314 1.542 1.118 3.155 3.629 43.051 0.096 108.932 1.556 0.140 (Analytical coefficients A1...A5, B1...B5, C) (See info for BCC)
-0.002600 0.003700 (dispersion corrections for X-rays for Al atom (here the atom invloved is Al)

Output

1. It creates 4 major output files.

2. Ocube - contains the following;
h k l d(A) Cell(A) Theta m Lp Fobs Fcal (S/L)**2 ln(Fo/Fc)
m = multiplicity; Lp = Lorentz-polarization factor; (S/L)**2 = (sin(theta)/Lambda)**2; ln(Fo/Fc) = Ln(Fobs/Fcal) for Wilson plot

3. Onr - contains the following;
h k l d(A) Theta NR_FUNCTION CELL
In addition, the least-squares fitted results of the cell constant and NR are given in this file, as follows;

```
    TOTAL NUMBER OF X VALUES =    9
    TOTAL NUMBER OF Y VALUES =    9
---------------------------------------------------------------
SUMX       =    9.217
SUMY       =   36.443
SLOPE      =        -0.001(0.000)
Y-INTERCEPT =          4.050(0.000)
(Y-INTERCEPT IS THE CELL CONSTANT)
---------------------------------------------------------------
THE CUBIC CELL CONSTSNT OF THE SYSTEM IS =     4.049694(0.000420)
```

4. The file PHASE contains the rela and imaginary parts of the structure factors.

5. The file OASF contains the calculated atomic scattering factors of the atoms involved.

6. The file PAR1 contains the analytical coefficients A1...A5, B1...B5, C of the atom to calculate the atomic scattering factors.

7. The file DIS1 contains the anomalous dispersion correction terms f' and f" of the atoms involved.

Typical outputs for Al are as follows;

Output file name **ocube**

```
ATOM(S) INVOVLED IN THE SYSTEM ARE THE FOLLOWING
 Al

THE FOLLOWINIG SYMBOLS FOR WAVELENGTHS ARE ALLOWED

CASE INSENSITIVE !!

TI (= 2.7485)
CR (= 2.2896)
FE (= 1.9360)
CO (= 1.7890)
CU (= 1.5405)
MO (= 0.7093)
AG (= 0.5594)
TA (= 0.2159)
AU (= 0.2090)
TI (= 0.1802)

THE WAVELENGTH USED IS = 1.540520

THE FOLLOWING ATOMS/IONS ARE ALLOWED
```

H He Li Be B C N O F Ne Na Mg
Al Si P S Cl Ar K Ca Sc Ti V Cr
Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
In Sn Sb Te I Xe Cs Ba La Ce Pr Nd
Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf
Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po
At Rn Fr Ra Ac Th Pa U Np Pu Am Cm
Bk Cf H1- Li1+ Be2+ Cval O1- O2- F1- Na1+ Mg2+ Al3+
Siva Si4+ Cl1- K1+ Ca2+ Sc3+ Ti2+ Ti3+ Ti4+ V2+ V3+ V5+
Cr2+ Cr3+ Mn2+ Mn3+ Mn4+ Fe2 Fe3+ Co2+ Co3+ Ni2+ Ni3+ Cu1+
Cu2+ Zn2+ Ga3+ Ge4+ Br1- Rb1+ Sr2+ Y3+ Zr4+ Nb3+ Nb5+ Mo3+
Mo5+ Mo6+ Ru3+ Ru4+ Rh3+ Rh4+ Pd2+ Pd4+ Ag1+ Ag2+ Cd2+ In3+
Sn2+ Sn4+ Sb3+ Sb5+ I1- Cs1+ Ba2+ La3+ Ce3+ Ce4+ Pr3+ Pr4+
Nd3+ Pm3+ Sm3+ Eu2+ Eu3+ Gd3+ Tb3+ Dy3+ Ho3+ Er3+ Tm3+ Yb2+
Yb3+ Lu3 Hf4+ Ta5+ W6+ Os4+ Ir3+ Ir4+ Pt2+ Pt4+ Au3+
Hg1+ Hg2+ Tl1+ Tl3+ Pb2+ Pb4+ Bi3+ Bi5+ Ra2+ Ac3+ Th4+ U3+
U4+ U6+ Np3+ Np4+ Np6+ Pu3+ Pu4+ Pu6+

Al Al

THE ANALYTICAL COEFFICIENTS (11 PARAMETER MODEL) ARE THE FOLLOWING FOR ATOM Al

A11 = 4.7308
A12 = 2.3140
A13 = 1.5420
A14 = 1.1176
A15 = 3.1548
B11 = 3.6289
B12 = 43.0512
B13 = 0.0960
B14 = 108.9324
B15 = 1.5559
C1 = 0.1395

Al Al

ATOMIC WEIGHT OF THE ATOM Al IS 26.98000
THE DISPERSION CORRECTION TERMS fp AND fpp ARE THE FOLLOWING FOR THE ATOM Al
DIS1= 0.2130
DIS2= 0.2455

h	k	l	d(A)	Cell(A)	Theta	m	Lp	Fobs	Fcal	(S/L)**2	ln(Fo/Fc)
1	1	1	2.3380	4.0495	19.2360	8	15.7386	0.8912	36.6709	0.0457	-3.7172
2	0	0	2.0240	4.0480	22.3690	6	11.2336	0.8351	34.8776	0.0610	-3.7321
2	2	0	1.4310	4.0475	32.5665	12	4.8194	0.6168	30.1661	0.1221	-3.8900
1	1	3	1.2210	4.0496	39.1135	24	3.3732	0.5445	27.5229	0.1677	-3.9230
2	2	2	1.1690	4.0495	41.2175	8	3.1150	0.5300	26.7291	0.1829	-3.9206
4	0	0	1.0120	4.0480	49.5390	6	2.7283	0.3495	23.8988	0.2441	-4.2250
3	3	1	0.9290	4.0494	56.0200	24	2.9684	0.3351	22.0865	0.2897	-4.1883
4	2	0	0.9055	4.0495	58.2800	24	3.1541	0.3251	21.5338	0.3049	-4.1933
2	2	4	0.8270	4.0515	68.7250	24	4.8963	0.2609	19.5478	0.3655	-4.3164

TOTAL NUMBER OF X VALUES = 9
TOTAL NUMBER OF Y VALUES = 9

SUMX = 1.784
SUMY = -36.106
SLOPE = -1.951(0.120)
Y-INTERCEPT = -3.625(0.027)
(SLOPE IS THE DEBYE-WALLER FACTOR)

m= multiplicity factor; Lp = Lorentz-polarization factor for X-rays;

Output file name **onr**

CALCULATION OF THE NELSON-RILEY FUNCTION

h	k	l	d(A)	Theta	NR FUNCTION	CELL
1	1	1	2.3380	19.2360	2.6805	4.0495
2	0	0	2.0240	22.3690	2.2187	4.0480
2	2	0	1.4310	32.5665	1.2845	4.0475
1	1	3	1.2210	39.1135	0.9181	4.0496
2	2	2	1.1690	41.2175	0.8226	4.0495
4	0	0	1.0120	49.5390	0.5203	4.0480
3	3	1	0.9290	56.0200	0.3481	4.0494
4	2	0	0.9055	58.2800	0.2984	4.0495
2	2	4	0.8270	68.7250	0.1255	4.0515

TOTAL NUMBER OF X VALUES = 9
TOTAL NUMBER OF Y VALUES = 9

SUMX = 9.217
SUMY = 36.443
SLOPE = -0.001(0.000)
Y-INTERCEPT = 4.050(0.000)
(Y-INTERCEPT IS THE CELL CONSTANT)

THE CUBIC CELL CONSTSNT OF THE SYSTEM IS = 4.049694(0.000420)

Output file name **oasf**

THE ATOMIC SCATTERING FACTORS OF THE ELEMENTS OF THE SYSTEM

(S/L)	(S/L)**2	f1	f2	f3	f4	f5	f6
0.214	0.046	9.168					
0.247	0.061	8.719					
0.349	0.122	7.542					
0.410	0.168	6.881					
0.428	0.183	6.682					
0.494	0.244	5.975					
0.538	0.290	5.522					
0.552	0.305	5.383					
0.605	0.366	4.887					

First column = sinθ/λ; Second column = (sinθ/λ)**2; f1=atomic scattering factor of first atom (Al here).

Output file name **PHASE**

1	1	1	36.6709	-0.0001	36.6709
2	0	0	34.8776	-0.0001	34.8776
2	2	0	30.1661	-0.0002	30.1661
1	1	3	27.5229	-0.0002	27.5229
2	2	2	26.7291	-0.0002	26.7291
4	0	0	23.8988	-0.0001	23.8988
3	3	1	22.0865	-0.0002	22.0865
4	2	0	21.5338	-0.0002	21.5338
2	2	4	19.5478	-0.0002	19.5478

The first three columns are h k l values. Next column (4^{th}) is the real part of structure factor F_A. The 5^{th} column is the imaginary part. The 6^{th} column is the calculated structure factor.

(The expression for structure factor is as follows;

$$F_{hkl} = \sum_{j=1}^{n} f_j \exp(2\pi i\ ((hx_j + k\,y_j + lz_j))$$

$F_A = \sum_{j=1}^{n} f_j \cos(2\pi\ ((hx_j + k\,y_j + lz_j))$ is the real part of structure factor.

$F_B = \sum_{j=1}^{n} i\,f_j \sin(2\pi\ ((hx_j + k\,y_j + lz_j))$ is the imaginary part of structure factor.

$F_B/F_A = \tan(\emptyset)$ is the phase of the structure factor.

f_j = atomic scattering factor of jth atom; h k l are Miller indices; $x_j,\ y_j, z_j$ are the fractional atomic coordinates of the jth atom.

Output File name **DIS1**

0.213000 0.245500

(Displays the real and imaginary parts of the anomalous dispersion correction terms for X-rays).

Output File name **PAR1**

4.731 2.314 1.542 1.118 3.155 3.629 43.051 0.096108.932 1.556 0.140

(Displays the a1,….a5, b1….b5, c values – analytical coefficients to calculate the atomic scattering factor of the atom).

OCUBE output file for **KBr** is given below

ATOM(S) INVOVLED IN THE SYSTEM ARE THE FOLLOWING
K Br

THE FOLLOWINIG SYMBOLS FOR WAVELENGTHS ARE ALLOWED

CASE INSENSITIVE !!

TI (= 2.7485)
CR (= 2.2896)
FE (= 1.9360)
CO (= 1.7890)
CU (= 1.5405)
MO (= 0.7093)
AG (= 0.5594)
TA (= 0.2159)
AU (= 0.2090)
TI (= 0.1802)

THE WAVELENGTH USED IS = 1.540520

THE FOLLOWING ATOMS/IONS ARE ALLOWED

H He Li Be B C N O F Ne Na Mg
Al Si P S Cl Ar K Ca Sc Ti V Cr
Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
In Sn Sb Te I Xe Cs Ba La Ce Pr Nd
Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf
Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po
At Rn Fr Ra Ac Th Pa U Np Pu Am Cm
Bk Cf H1- Li1+ Be2+ Cval O1- O2- F1- Na1+ Mg2+ Al3+
Siva Si4+ Cl1- K1+ Ca2+ Sc3+ Ti2+ Ti3+ Ti4+ V2+ V3+ V5+
Cr2+ Cr3+ Mn2+ Mn3+ Mn4+ Fe2 Fe3+ Co2+ Co3+ Ni2+ Ni3+ Cu1+
Cu2+ Zn2+ Ga3+ Ge4+ Br1- Rb1+ Sr2+ Y3+ Zr4+ Nb3+ Nb5+ Mo3+
Mo5+ Mo6+ Ru3+ Ru4+ Rh3+ Rh4+ Pd2+ Pd4+ Ag1+ Ag2+ Cd2+ In3+
Sn2+ Sn4+ Sb3+ Sb5+ I1- Cs1+ Ba2+ La3+ Ce3+ Ce4+ Pr3+ Pr4+
Nd3+ Pm3+ Sm3+ Eu2+ Eu3+ Gd3+ Tb3+ Dy3+ Ho3+ Er3+ Tm3+ Yb2+
Yb3+ Lu3 Hf4+ Ta5+ W6+ Os4+ Ir3+ Ir4+ Pt2+ Pt4+ Au3+
Hg1+ Hg2+ Tl1+ Tl3+ Pb2+ Pb4+ Bi3+ Bi5+ Ra2+ Ac3+ Th4+ U3+
U4+ U6+ Np3+ Np4+ Np6+ Pu3+ Pu4+ Pu6+

K K

THE ANALYTICAL COEFFICIENTS (11 PARAMETER MODEL) ARE THE FOLLOWING FOR ATOM K
A11 = 8.1640
A12 = 7.1469
A13 = 1.0701
A14 = 0.8773
A15 = 1.4864
B11 = 12.8163
B12 = 0.8089
B13 = 210.3270

B14 = 39.5977
B15 = 0.0528
C1 = 0.2536
K K
ATOMIC WEIGHT OF THE ATOM K IS 39.10000
THE DISPERSION CORRECTION TERMS fp AND fpp ARE THE FOLLOWING FOR THE ATOM K
DIS1= 0.3868
DIS2= 1.0657
Br Br
THE ANALYTICAL COEFFICIENTS (11 PARAMETER MODEL) ARE THE FOLLOWING FOR ATOM Br
A11 = 17.5506
A12 = 5.4119
A13 = 3.9372
A14 = 3.8806
A15 = 6.7078
B11 = 2.1192
B12 = 16.5572
B13 = 0.0025
B14 = 42.1640
B15 = 0.1621
C1 = -2.4921
Br Br
ATOMIC WEIGHT OF THE ATOM Br IS 79.90000
THE DISPERSION CORRECTION TERMS fp AND fpp ARE THE FOLLOWING FOR THE ATOM Br
DIS1= -0.6763
DIS2= 1.2805

h	k	l	d(A)	Cell(A)	Theta	m	Lp	Fobs	Fcal	(S/L)**2	ln(Fo/Fc)
1	1	1	3.8090	6.5974	11.6655	8	46.0335	0.1879	56.5061	0.0172	-5.7063
2	0	0	3.3020	6.6040	13.4920	6	33.8954	0.7012	179.9787	0.0229	-5.5478
2	2	0	2.3350	6.6044	19.2640	12	15.6881	0.5645	160.7958	0.0459	-5.6519
1	1	3	1.9910	6.6034	22.7615	24	10.8010	0.1757	49.2125	0.0631	-5.6353
2	2	2	1.9060	6.6026	23.8415	8	9.7245	0.5196	147.6349	0.0688	-5.6495
4	0	0	1.6490	6.5960	27.8320	6	6.8382	0.4937	137.8784	0.0919	-5.6322
3	3	1	1.5150	6.6037	30.5685	24	5.5368	0.1227	46.0385	0.1089	-5.9276
4	2	0	1.4760	6.6009	31.4615	24	5.1954	0.4005	130.2443	0.1148	-5.7845
2	2	4	1.3470	6.5989	34.8685	24	4.1765	0.3460	124.0320	0.1378	-5.8818
5	1	1	1.2710	6.6043	37.3190	24	3.6613	0.1509	43.2343	0.1548	-5.6580
4	4	0	1.1670	6.6015	41.3115	12	3.1053	0.2317	114.3459	0.1836	-6.2017
5	3	1	1.1160	6.6023	43.6695	48	2.9058	0.0847	40.3737	0.2007	-6.1671
6	0	0	1.0990	6.5940	44.4540	6	2.8573	0.5400	110.4203	0.2070	-5.3204
6	2	0	1.0440	6.6028	47.5735	24	2.7424	0.2465	106.9182	0.2294	-6.0724
5	3	3	1.0060	6.5968	49.9370	24	2.7305	0.1235	37.5154	0.2470	-5.7160
6	2	2	0.9950	6.6001	50.7150	24	2.7398	0.2136	103.7483	0.2525	-6.1856
4	4	4	0.9530	6.6026	53.9500	8	2.8451	0.2096	100.8441	0.2753	-6.1761
7	1	1	0.9240	6.5987	56.4500	24	2.9996	0.1179	34.7528	0.2928	-5.6865
6	4	0	0.9150	6.5982	57.2950	24	3.0665	0.1649	98.1571	0.2986	-6.3893
6	4	2	0.8820	6.6003	60.8450	48	3.4342	0.1349	95.6509	0.3214	-6.5639
7	3	1	0.8590	6.5981	63.6900	48	3.8426	0.0736	32.1498	0.3388	-6.0791
8	0	0	0.8250	6.6000	69.0150	6	4.9738	0.1831	91.0784	0.3673	-6.2097
8	2	0	0.8000	6.5970	74.2300	24	6.8588	0.1102	88.9754	0.3906	-6.6936

TOTAL NUMBER OF X VALUES = 23

```
    TOTAL NUMBER OF Y VALUES =   23
-------------------------------------------------------------------------------------------------------------
SUMX       =    4.431
SUMY       =  -136.536
SLOPE      =         -2.176(0.317)
Y-INTERCEPT =        -5.517(0.071)
( SLOPE IS THE DEBYE-WALLER FACTOR)
```

onr out put file for **KBr** is as follows;

```
CALCULATION OF THE NELSON-RILEY FUNCTION
-----------------------------------------------------------------
  h  k  l     d(A)       Theta      NR FUNCTION  CELL
-----------------------------------------------------------------
  1  1  1     3.8090     11.6655      4.7271     6.5974
  2  0  0     3.3020     13.4920      4.0342     6.6040
  2  2  0     2.3350     19.2640      2.6758     6.6044
  1  1  3     1.9910     22.7615      2.1691     6.6034
  2  2  2     1.9060     23.8415      2.0402     6.6026
  4  0  0     1.6490     27.8320      1.6424     6.5960
  3  3  1     1.5150     30.5685      1.4236     6.6037
  4  2  0     1.4760     31.4615      1.3596     6.6009
  2  2  4     1.3470     34.8685      1.1418     6.5989
  5  1  1     1.2710     37.3190      1.0071     6.6043
  4  4  0     1.1670     41.3115      0.8186     6.6015
  5  3  1     1.1160     43.6695      0.7221     6.6023
  6  0  0     1.0990     44.4540      0.6921     6.5940
  6  2  0     1.0440     47.5735      0.5824     6.6028
  5  3  3     1.0060     49.9370      0.5083     6.5968
  6  2  2     0.9950     50.7150      0.4855     6.6001
  4  4  4     0.9530     53.9500      0.3981     6.6026
  7  1  1     0.9240     56.4500      0.3383     6.5987
  6  4  0     0.9150     57.2950      0.3194     6.5982
  6  4  2     0.8820     60.8450      0.2476     6.6003
  7  3  1     0.8590     63.6900      0.1979     6.5981
  8  0  0     0.8250     69.0150      0.1219     6.6000
  8  2  0     0.8000     74.2300      0.0669     6.5970
-----------------------------------------------------------------
    TOTAL NUMBER OF X VALUES =   23
    TOTAL NUMBER OF Y VALUES =   23
-----------------------------------------------------------------
SUMX       =   27.720
SUMY       =  151.808
SLOPE      =        0.001(0.000)
Y-INTERCEPT =        6.600(0.001)
(Y-INTERCEPT IS THE CELL CONSTANT)
-------------------------------------------------------------------
THE CUBIC CELL CONSTSNT OF THE SYSTEM IS =     6.599621(0.000588)
-------------------------------------------------------------------
```

6.599621(0.000588) is the least-squares fitted cell parameter of KBr.

Diffraction Intensities

The integrated intensity (peak area) of each powder diffraction peak is given by the following expression:

$$I(hkl) = |S(hkl)|^2 \times M_{hkl} \times LP(\theta) \times TF(\theta)$$

- $S(hkl)$ = Structure Factor
- M_{hkl} = Multiplicity
- $LP(\theta)$ = Lorentz & Polarization Factors
- $TF(\theta)$ = Temperature factor (more correctly referred to as the displacement parameter)

This does not include effects that can sometimes by problematic such as absorption, preferred orientation and extinction.

Structure Factor

The structure factor reflects the interference between atoms in the basis (within the unit cell). All of the information regarding where the atoms are located in the unit cell is contained in the structure factor. The structure factor is given by the following summation over all atoms (from 1 to j) in the unit cell:

$$S(hkl) = \Sigma_j \, f_j \, \exp\{-i2\pi(hx_j+ky_j+lz_j)\}$$

- f_j = form factor for the j^{th} atom
- h, k & l = Miller indices of the hkl reflection
- x_j, y_j & z_j = The fractional coordinates of the j^{th} atom

To evaluate the value of the imaginary term in the exponential function, remember Euler's equation:

$$\exp(-ix) = \cos(x) - i\sin(x)$$

The value of this function is a real number when x is a multiple of 2π. It is equal to 1 for even multiples of 2π and -1 for odd multiples of 2π.

Multiplicity Factor

In a powder diffraction experiment the d-spacings for related reflections are often equivalent. Consider the examples below:

Cubic

- (100), (010), (001), (-100), (0-10), (00-1) → Equivalent

Multiplicity Factor = 6

- (110), (-110), (1-10), (-1-10), (101), (-101), (10-1), (-10-1), (011), (0-11), (01-1), (0-1-1) → Equivalent

Multiplicity Factor = 12

In general for a cubic system where the Miller indices are n_1, n_2 and n_3 (all unequal) the multiplicity factors M_{hkl} are:

$n_1 00$ (i.e. 100) → M = 6	$n_1 n_1 n_1$ (ie 111) → M = 8
$n_1 n_1 0$ (i.e. 110) → M = 12	$n_1 n_2 0$ (ie 210) → M = 24
$n_1 n_1 n_2$ (i.e. 221) → M = 24	$n_1 n_2 n_3$ (ie 321) → M = 48

The multiplicities are lower in lower symmetry systems. For example in a tetragonal crystal the (100) is equivalent with the (010), (-100) and (0-10), but not with the (001) and the (00-1).

Lorentz Factor

There are a number of factors that lead to a theta dependence of the peak intensities (integrated intensities).

- Diffraction can occur for angles slightly different from the value predicted by Bragg's Law $\rightarrow I \alpha 1/\sin(2\theta)$
- The number of crystals oriented in such a way as to satisfy Bragg's Law is highest for low angles $\rightarrow I \alpha \cos(\theta)$
- The fraction of the diffraction cone that intersects the detector is highest at low angles $\rightarrow I \alpha 1/\sin(2\theta)$

When combine these considerations and do some trigonometric manipulation we get the Lorentz Factor:

$$\mathbf{I \alpha 1/(4\sin^2\theta \cos\theta)}$$

Polarization and the LP Factor

An X-ray propagating in the x-direction will have an electric vector oriented in the yz plane. The y and z components of the X-ray will be scattered differently because the angle between the scattered beam and the electric field gradient will differ, as derived by Thompson. This leads to the polarization factor:

$$I \alpha (1+\cos^2 2\theta)/2$$

Typically the Lorentz and Polarization terms are combined to give the Lorentz-Polarization (LP) factor.

$$I \alpha (1+\cos^2 2\theta)/(8\sin^2\theta \cos\theta)$$

Temperature Factor

The vibrations of atoms in a crystal lead to an angle dependent effect on the diffracted peak intensities. The more an atom vibrates the scattering power is decreased, because the scattering power of the atom is smeared out. As an approximation we can assume that all atoms vibrate equally. In that case the TF can be expressed by the equation:

$$TF(\theta) = \exp\{B(\sin\theta/\lambda)^2\}$$

Where the coefficient B is the isotropic temperature factor.

- B is proportional to the mean squared displacement of the atoms
- Typical values for inorganic extended solids range from 0.5 to 1.5.
- The temperature factor has its biggest impact at high angles.

More sophisticated treatments assume

- Different values of B for each crystallographically independent atom
- Anisotropic vibrations (elliptical in shape rather than spherical).

The **Nelson-Riley function** to find the accurate cell constant of a crystalline system is given by the following equation;

$$\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$$

The obtained cell values should be plotted w.r.to the NR function (x-axis) as calculated and outputted in ONR file. The extrapolation of cell parameter to x=0 will give the accurate cell value of the system.

DIAMOND

About the program

This is a refinement program (to refine the single crystal/powder XRD experimental data to (i) match the observed and calculated structure factors (ii) to refine the Debye-Waller factor (iii) hence to find experimental mean square amplitudes. Applicable to diamond (single element) type systems.

This program can process the observed X-ray structure factors of diamond structure. Diamond structure factors will be CALCULATED and the observed and calculated structure factors will be matched using least-squares refinement method. The (i) Debye-Waller factor and (ii) the scale factor are the prime parameters refined in this program. The output file will contain the results of refinement in each least-squares refinement.

Also, the listing will have the h k l values of the reflections, FOBS (observed) structure factor, FCAL (calculated) structure factor, the difference DELF, error as the % (ERR), atomic scattering factor of the atom involved SF(I,1), the Bragg angle THETA, and sin(theta)/Lambda (SINT)

The observed powder XRD intensities from a powder data set can be utilized. First, the observed X-ray intensities should be converted into observed X-ray structure factors. The supplied SCAT771 program can be used for this purpose. Or any other method can be used to get the observed structure factors of each reflection from the observed intensities. The prime corrections to be applied to convert the X-ray intensities into X-ray structure factors are (i) multiplicity and (ii) Lorentz-polarization corrections. SCAT771 program can do this.

After, converting the X-ray intensities into structure factors using SCAT771, the input file for running RE_DI_HA should be prepared.

Input

Prepare an input file for running RE_DI_HA. The input is FORMAT sensitive. Hence adhere to the spacings and other syntaxes. The input file name should be india. (without full-stop)

A typical input will be as follows;

```
Refinement of Germanium parameters
  1 20  1  3
 1.540560 5.657000 2.000000 0.700000
16.5410 1.5680 3.7280 3.3450 6.7850 2.8670 0.012013.432058.8660 0.2110 0.0190
-1.0890 0.8860
  1  1  1    0.614
  2  2  0    0.659
  3  1  1    0.467
  4  0  0    0.499
  3  3  1    0.329
  4  2  2    0.481
  5  1  1    0.321
  4  4  0    0.302
  5  3  1    0.284
  6  2  0    0.276
  5  3  3    0.210
  4  4  4    0.214
  5  5  1    0.202
 99
  4  4  0
  4  4  4
  4  0  0
```

First line is the title line

Second line, I parameter 1 indicates the number of species of atoms (allowed value is 1, since the program is for diamond monoatomic system).

Second line, II parameter 20 indicates user inputted number of cycles of least-squares refinement, typically 10 to 20 enough for convergence.

Second line, III parameter 1 indicates Wilson plot analysis is done for finding Debye-Waller factor using Fobs and Fcal. 0 will not do Wilson plot analysis.

Second line, IV parameter 3 indicates the no. of observed reflections to be omitted from refinement process (in this case 3). This can be decided after initial refinements and checking the results for reflections with large differences in Fobs and Fcal.

Third line, I parameter (1.54056) indicates the wavelength of X-rays used for XRD powder data recording.

Third line, II parameter (5.657) indicates the cell constant of the diamond system (in this case Ge with cell constant 5.657 angstrom).
Third line, III parameter (2.0) indicates the initial scale factor to be used in the refinement to match Fobs and Fcal. Any random value is OK so that refinement converges.

Third line, IV parameter (0.7) indicates the initial B value (Debye-Waller factor of fe atom) to be used in the refinement to match Fobs and Fcal. A small value is enough.

Fourth line indicates the analytical co-efficients (5 parameter model) to calculate the atomic scattering factors of the (here, Ge atom) atom. A1, A2, A3, A4, A5, B1, B2, B3, B4, B5, and C. A total of 11 coefficients are to be used. These values are listed in international tables for X-ray crystallography. But, if you use SCAT771 program you can find these values in one of the output files (PAR1) and use them in the input for BCC.

Fifth line indicates (-1.0890 0.8860) two values, the anomalous dispersion corrections terms of the atom (here, Ge) for the X-ray wavelength used. These values are listed in international tables for X-ray crystallography. But, if you use SCAT771 program you can find these values in one of the output files (DIS1) and use them in the input for RE_DI_HA.

In this input examples, the next 6 lines indicate the h k l values and the observed structure factors (FOBS) derived from SCAT771 program.

In the last line 99 indicates the parameter to terminate the reading of the input.

Output

The output file name is outdia. All the inputted values are listed first. Then, a typical output cycle shows as follows.

```
---------------
CYCLE NUMBER= 2
---------------
 SCALE FACTOR=  0.40661E-02   +OR-       0.00020
 B OF AN ION    =  0.10257E+01   +OR-       0.28979
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.78631E+00
    RMINIMUM=  0.066631
```

These results are self-explanatory. RMINIMUM will show the Reliability index at each cycle.

At the end of 20th cycle (here, the no. of cycles is 20 in this example), you can see the following.

** 2 RMINIMUM=0.0666 ,

2 RMINIMUM=0.0666 indicates that the minimum R factor occurs at 5th cycle and the R value is 6.66 %. The parameter listed in the 2nd cycle are the refined parameter.

Note, the most successful results can be obtained through a large no. observations. That is - good statistics only will lead to convincing results.

A typical output is as follows;

```
                Refinement of Germanium parameters
  1 20  1  3
 1.540560 5.657000 2.000000 0.700000
16.5410 1.5680 3.7280 3.3450 6.7850 2.8670 0.012013.432058.8660 0.2110 0.0190
-1.0890 0.8860
  1  1  1     0.614
  2  2  0     0.659
  3  1  1     0.467
  4  0  0     0.499
  3  3  1     0.329
  4  2  2     0.481
  5  1  1     0.321
  4  4  0     0.302
  5  3  1     0.284
  6  2  0     0.276
  5  3  3     0.210
  4  4  4     0.214
  5  5  1     0.202
 99  0  0     0.000

         TOTAL NO OF REFLECTIONS=   10

        TOTAL OMITTED REFLECTIONS=  3
        RMINIMUM=515.795898
    ---------------
   CYCLE NUMBER= 1
   ---------------
    SCALE FACTOR=  0.40660E-02   +OR-       1.14230
    B OF AN ION =  0.70066E+00   +OR-       3.43031
    CORRELATION BETWEEN SCALE AND B OF ANION = 0.78633E+00
        RMINIMUM=  0.067176
    ---------------
   CYCLE NUMBER= 2
   ---------------
    SCALE FACTOR=  0.40661E-02   +OR-       0.00020
    B OF AN ION =  0.10257E+01   +OR-       0.28979
    CORRELATION BETWEEN SCALE AND B OF ANION = 0.78631E+00
        RMINIMUM=  0.066631
```

CYCLE NUMBER= 3

 SCALE FACTOR= 0.40707E-02 +OR-   0.00015
 B OF AN ION = 0.10462E+01 +OR-   0.23907
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77985E+00
    RMINIMUM= 0.066836

CYCLE NUMBER= 4

 SCALE FACTOR= 0.40707E-02 +OR-   0.00016
 B OF AN ION = 0.10463E+01 +OR-   0.23973
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM= 0.066836

CYCLE NUMBER= 5

 SCALE FACTOR= 0.40707E-02 +OR-   0.00016
 B OF AN ION = 0.10463E+01 +OR-   0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM= 0.066836

CYCLE NUMBER= 6

 SCALE FACTOR= 0.40707E-02 +OR-   0.00016
 B OF AN ION = 0.10463E+01 +OR-   0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM= 0.066836

CYCLE NUMBER= 7

 SCALE FACTOR= 0.40707E-02 +OR-   0.00016
 B OF AN ION = 0.10463E+01 +OR-   0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM= 0.066836

CYCLE NUMBER= 8

 SCALE FACTOR= 0.40707E-02 +OR-   0.00016
 B OF AN ION = 0.10463E+01 +OR-   0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM= 0.066836

CYCLE NUMBER= 9

 SCALE FACTOR= 0.40707E-02 +OR-   0.00016
 B OF AN ION = 0.10463E+01 +OR-   0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM= 0.066836

CYCLE NUMBER=10

 SCALE FACTOR= 0.40707E-02 +OR-   0.00016
 B OF AN ION = 0.10463E+01 +OR-   0.23974

```
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM=  0.066836
 ---------------
CYCLE NUMBER=11
---------------
 SCALE FACTOR=  0.40707E-02   +OR-      0.00016
 B OF AN ION =  0.10463E+01   +OR-      0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM=  0.066836
 ---------------
CYCLE NUMBER=12
---------------
 SCALE FACTOR=  0.40707E-02   +OR-      0.00016
 B OF AN ION =  0.10463E+01   +OR-      0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM=  0.066836
 ---------------
CYCLE NUMBER=13
---------------
 SCALE FACTOR=  0.40707E-02   +OR-      0.00016
 B OF AN ION =  0.10463E+01   +OR-      0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM=  0.066836
 ---------------
CYCLE NUMBER=14
---------------
 SCALE FACTOR=  0.40707E-02   +OR-      0.00016
 B OF AN ION =  0.10463E+01   +OR-      0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM=  0.066836
 ---------------
CYCLE NUMBER=15
---------------
 SCALE FACTOR=  0.40707E-02   +OR-      0.00016
 B OF AN ION =  0.10463E+01   +OR-      0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM=  0.066836
 ---------------
CYCLE NUMBER=16
---------------
 SCALE FACTOR=  0.40707E-02   +OR-      0.00016
 B OF AN ION =  0.10463E+01   +OR-      0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM=  0.066836
 ---------------
CYCLE NUMBER=17
---------------
 SCALE FACTOR=  0.40707E-02   +OR-      0.00016
 B OF AN ION =  0.10463E+01   +OR-      0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM=  0.066836
 ---------------
CYCLE NUMBER=18
---------------
 SCALE FACTOR=  0.40707E-02   +OR-      0.00016
 B OF AN ION =  0.10463E+01   +OR-      0.23974
```

```
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM=  0.066836
 ---------------
CYCLE NUMBER=19
---------------
 SCALE FACTOR=  0.40707E-02   +OR-       0.00016
 B OF AN ION =  0.10463E+01   +OR-       0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00
    RMINIMUM=  0.066836
 ---------------
CYCLE NUMBER=20
---------------
 SCALE FACTOR=  0.40707E-02   +OR-       0.00016
 B OF AN ION =  0.10463E+01   +OR-       0.23974
 CORRELATION BETWEEN SCALE AND B OF ANION = 0.77946E+00


                              ** 2 RMINIMUM=0.0666  ,
 -------  ----      ----       ----    --- ------- ------  -----
H  K  L  FOBS      FCAL       DELF    ERR SF(I,1) THETA     SINT
-------  ----      ----       ----    --- ------- ------  -----
1  1  1   151.004   145.204     5.8   3.8 26.2932 13.6413  0.0234
2  2  0   162.071   170.568    -8.5  -5.2 22.7325 22.6518  0.0625
3  1  1   114.852   110.344     4.5   3.9 21.3036 26.8467  0.0859
3  3  1    80.913    89.429    -8.5 -10.5 18.4087 36.4076  0.1484
4  2  2   118.295   112.226     6.1   5.1 17.0029 41.8409  0.1875
5  1  1    78.945    74.096     4.8   6.1 16.2622 45.0342  0.2109
5  3  1    69.846    62.273     7.6  10.8 14.5721 53.6641  0.2734
6  2  0    67.878    79.439   -11.6 -17.0 13.6817 59.4490  0.3125
5  3  3    51.646    52.895    -1.2  -2.4 13.1971 63.2383  0.3359
5  5  1    49.679    45.325     4.4   8.8 12.0569 76.5088  0.3984

      --------------------------------
      WILSON PLOT FOR  Refinement of Germanium parameters
      --------------------------------
 -------    ----       -----       ----       ---          ----       ---------
H  K  L    FOBS       FCALC       DELF       ERR          SINT       LN(FO/FC)
-------    ----       -----       ----       ---          ----       ---------
  THERMAL PARAMETERS FROM WILSON PLOT =   -0.982270       +OR-       0.166004
  Y AXIS INTERCEPT FROM WILSON PLOT =   -0.001915     +OR-         0.039196
```

DremAbLp

About the program

The observed X-ray single crystal intensity data collected using an automatic diffractometer can be converted in to observed structure factors using this program.

The raw intensities (or raw structure factors) will be corrected for (i) left and right background intensities (ii) absorption of X-rays (iii) polarization correction for X-rays. Then, the intensities will be converted into observed structure factors applying the above corrections. The observed sigma(Fobs) values will be converted into the weight factor (w). The program will be useful to get single crystal structure factors from raw diffractometer intensity data.

Input

This program uses two input files, (i) Sfac_file (ii) absorp.

(i) Sfac_file :

Should contain the raw structure factors. The Raw Ssructure factor file to be processed can be selected by clicking |File|S.Factor File| from the main menu bar. The format of raw structure factor file is as below;

h k l Fobs Sig(Fobs). (Free format)')
The final line should be 99 0 0 0.0 0.0
e.g. lines are given below;

```
-11 -1 -1   489.06  17.83
-11 -1  1   495.15  16.84
-11  1 -1   425.00  17.03
-11  1  1   462.62  17.52
 99  0  0     0.00   0.00
```

(ii) absorp :

The file containing absorption correction values can be selected by clicking |File|Abs.Corr File| from the main menu bar. The format of absorption correction file is as below;

It has two columns. First column contains the angle (starting from 0). The second column contains the absorption correction value for sample used (sphere or thickness

of the sample) listed in International tables. A total of 19 lines are allowed. The Bragg angles of inputted reflections will be evaluated using the supplied information (a,b,c etc.) and the absorption and Lorentz-Polarization factor will be calculated for the Bragg angle of the observed reflection using the supplied absorption corrections w.r.t angle.

Example file is given below;

```
  0 49.449
  5 47.282
 10 42.459
 15 36.536
 20 31.102
 25 26.446
 30 21.789
 35 17.701
 40 17.312
 45 15.334
 50 13.845
 55 12.556
 60 11.556
 65 10.756
 70 10.064
 75  9.557
 80  9.180
 85  8.960
 90  8.871
```

Output

THIS PROGRAM PRODUCES 3 OUTPUT FILES AS FOLLOWS; (File names can be given through key board).

First file Lists,
H K L A*(ABS.CORR) LP FOBS SIGF WTG

Second file lists,
H K L FOBS SIGF

Third file lists,
H K L FOBS SIGF WGT

LP = Lorentz-Polarization factor applied
A* = Absorption correction applied
WTG = Weight of the particular Fobs.

SIGF = Sigma value of the Fobs

Typical outputs are;

test

	6.0000	6.0000	6.0000	90.0000	90.0000	90.0000	0.7000	12.2000

0 49.449
5 47.282
10 42.459
15 36.536
20 31.102
25 26.446
30 21.789
35 17.701
40 17.312
45 15.334
50 13.845
55 12.556
60 11.556
65 10.756
70 10.064
75 9.557
80 9.180
85 8.960
90 8.871

H	K	L	A*	LP	FOBS	SIGF	WTG
-11	-1	-1	17.189	0.71936	108.10	1.97	0.25753
-11	-1	1	17.189	0.71936	108.77	1.85	0.29229
-11	1	-1	17.189	0.71936	100.77	2.02	0.24532
-11	1	1	17.189	0.71936	105.14	1.99	0.25230
0	0	0	0.000	0.00000	0.00	0.00	0.00000

Second output

H	K	L	FOBS	SIGF
-11	-1	-1	108.10	1.97
-11	-1	1	108.77	1.85
-11	1	-1	100.77	2.02
-11	1	1	105.14	1.99
0	0	0	0.00	0.00

Third output

H	K	L	FOBS	SIGF	WGT
-11	-1	-1	108.10	1.97055	0.25753
-11	-1	1	108.77	1.84966	0.29229
-11	1	-1	100.77	2.01900	0.24532
-11	1	1	105.14	1.99085	0.25230
0	0	0	0.00	0.00000	0.00000

FCC

About the program

This is a refinement program (to refine the single crystal/powder XRD experimental data to (i) match the observed and calculated structure factors (ii) to refine the Debye-Waller factor (iii) hence to find experimental mean square amplitudes. Applicable to FCC (single element) type systems.

This program can process the observed X-ray structure factors of FCC structure. FCC structure factors will be CALCULATED and the observed and calculated structure factors will be matched using least-squares refinement method. The (i) Debye-Waller factor and (ii) the scale factor are the prime parameters refined in this program. The output file will contain the results of refinement in each least-squares refinement.

Also, the listing will have the h k l values of the reflections, FOBS (observed) structure factor, FCAL (calculated) structure factor, the difference DELF, error as the % (ERR), atomic scattering factor of the atom involved SF(I,1), the Bragg angle THETA, and sin(theta)/Lambda (SINT).

The observed powder XRD intensities from a powder data set can be utilized. First, the observed X-ray intensities should be converted into observed X-ray structure factors. The supplied SCAT771 program can be used for this purpose. Or any other method can be used to get the observed structure factors of each reflection from the observed intensities. The prime corrections to be applied to convert the X-ray intensities into X-ray structure factors are (i) multiplicity and (ii) Lorentz-polarization corrections. SCAT771 program can do this.

After, converting the X-ray intensities into structure factors using SCAT771, the input file for running FCC should be prepared.

Input

Prepare an input file for running FCC. The input is FORMAT sensitive. Hence adhere to the spacings and other syntaxes. The name should be in_fcc. (without full-stop)

A typical input will be as follows;

```
Refinement of FCC parameters (eg. fcc-Al)
  1 10  1  0
 1.540560 4.049000 2.000000 0.200000
  4.731  2.314  1.542  1.118  3.155  3.629 43.051  0.096108.932  1.556  0.140
  0.213  0.2455
  1  1  1   0.8913
  2  0  0   0.8348
  2  2  0   0.6165
  3  1  1   0.5445
  2  2  2   0.5300
  4  0  0   0.3495
  3  3  1   0.3351
  4  2  0   0.3250
  4  2  2   0.2608
 99
```

First line is the title line

Second line, I parameter 1 indicates the number of species of atoms (allowed value is 1, since the program is for FCC monoatomic system)

Second line, II parameter 20 indicates user inputted number of cycles of least-squares refinement, typically 10 to 20 enough for convergence. (here 10 is given)

Second line, III parameter 1 indicates Wilson plot analysis is done for finding Debye-Waller factor using Fobs and Fcal. 0 will not do Wilson plot analysis.

Second line, IV parameter 0 indicates the no. of observed reflections to be omitted from refinement process (in this case 0). This can be decided after initial refinements and checking the results for reflections with large differences in Fobs and Fcal.

Third line, I parameter (1.54056) indicates the wavelength of X-rays used for XRD powder data recording.

Third line, II parameter (4.049) indicates the cell constant of the FCC system (in this case Al with cell constant 4.049 angstrom).

Third line, III parameter (2.0) indicates the initial scale factor to be used in the refinement to match Fobs and Fcal. Any random value is OK so that refinement converges.

Third line, IV parameter (0.2) indicates the initial B value (Debye-Waller factor of Al atom) to be used in the refinement to match Fobs and Fcal. A small value is enough.

Fourth line indicates the analytical co-efficients (5 parameter model) to calculate the atomic scattering factors of the (here, Al atom) atom. A1, A2, A3, A4, A5, B1, B2, B3, B4, B5, and C. A total of 11 coefficients are to be used. These values are listed in international tables for X-ray crystallography. But, if you use SCAT771 program you can find these values in one of the output files (PAR1) and use them in the input for FCC.

Fifth line indicates (-1.133 3.197) two values, the anomalous dispersion corrections terms of the atom (here, Fe) for the X-ray wavelength used. These values are listed in international tables for X-ray crystallography. But, if you use SCAT771 program you can find these values in one of the output files (DIS1) and use them in the input for FCC.

In this input examples, **the next 9 lines indicate the h k l values and the observed structure factors (FOBS)** derived from SCAT771 program.

In the **last line 99 indicates** the parameter to terminate the reading of the input.

Output

The output file name is out_fcc. All the inputted values are listed first. Then, a typical output cycle shows as follows.

```
---------------
CYCLE NUMBER= 1
---------------
 SCALE FACTOR = 0.25932E-01     +/-    0.13649E+01
 B OF ANION     =  0.21752E+00    +/-    0.37618E+01
 CORRELATION BETWEEN  1 AND 2 IS  =  0.83639485
 RMINIMUM       =  0.304534
```

These results are self-explanatory. RMINIMUM will show the Reliability index at each cycle. At the end of 10th cycle (here, the no. of cycles is 10 in this example), you can see the following.

```
************************
************************
** 3R  MINIMUM=0.0317**
************************
```

3R MINIMUM=0.0317, indicates that the minimum R factor occurs at 3rd cycle and the R value is 3.17 %.

The parameter listed in the 3rd cycle are the refined parameter as follows.

```
---------------
CYCLE NUMBER= 3
---------------
 SCALE FACTOR = 0.26650E-01     +/-     0.10474E-02
 B OF ANION       = 0.19860E+01     +/-     0.25914E+00
 CORRELATION BETWEEN  1 AND 2 IS  =  0.81680983
 RMINIMUM         =  0.031689
```

Note, the most successful results can be obtained through a large no. observations. That is - good statistics only will lead to convincing results.

GRAIN

About the program

There are principally three types of broadening that can happen in the powder diffraction profiles.

I. Size Broadening

Broadening due to the crystallite size distribution [1], given by

$$B = \frac{K\lambda}{d\cos\theta} \qquad (1)$$

B is the FWHM (Full Width at Half Maximum) in radians.

K is a constant - usually 0.9. (For a spherical sample of cubic symmetry, K = 0.89 if the FWHM used is integral width. The integral breadth is (i) The area under the peak/the peak height or (ii) The width of a rectangle having the same area and the same height as the peak. K= 0.94 for a spherical crystals with cubic symmetry if FWHM is used. The average of 0.89 and 0.94 is 0.915. In general, K varies from 0.2 to 2.08).

λ is the wavelength used.

d is the crystallite size (size of the coherently diffracting domain – different from particle size).

θ is the Bragg angle of the reflection.

II. Strain Broadening

Broadening due to strains in the sample (due to lattice displacements of atoms from their original positions, surface strains, dislocations, impurities, non-stoichiometry in mixed systems, etc.- usually predominant in thin films, low order and nano structures).

$$B = 4e\tan\theta \qquad (2)$$

B is the FWHM

e is the strain

θ is the Bragg angle of the reflection.

III. Instrumental Broadening

Broadening due to instrument (due to offset optics, dispersionn due to wavelength used, divergence of the beam, other detector based errors).

$$B = \beta \tag{3}$$

The total broadening can be represented (convolution of all the above broadenings) as below;

$$B_{Total}^2 = \left[\frac{K\lambda}{d\cos\theta}\right]^2 + \left[4e\tan\theta\right]^2 + \beta^2 \tag{4}$$

***There is no other way to account for instrumental broadening, except to measure the diffraction pattern of a standard sample for which the particle size is sufficiently large (to eliminate the size effect) under the same experimental conditions at which the diffraction pattern of the sample of interest is measured.**

The correction for instrumental broadening can be made as follows;

1.Measure the diffraction profile of the two samples (sample to be analyzed and the reference sample, e.g., Si, or Ge – probably single crystal made into powders).

2. Fit the FWHM of the two samples (with respect to 2θ) and get the 2 polynomial equations.

3. Interpolate the FWHM values of the two curves at the same 2θ values (these 2θ values may be Bragg angles of the samples to be analyzed).

4. Find $B_{corrected} = \sqrt{B^2 - B_{\text{Re}\,ference}^2}$

5. Use this $B_{corrected}$ value in the equation $B_{corrected} = \left[\frac{K\lambda}{d\cos\theta}\right] + [4e\tan\theta]$, which can be fitted to a straight line.

($B_{corrected} = \left[\frac{K\lambda}{d\cos\theta}\right] + [4e\tan\theta]$

$B_{corrected} = \left[\frac{K\lambda}{d\cos\theta}\right] + \left[4e\frac{\sin\theta}{\cos\theta}\right]$

$\cos\theta B_{corrected} = \left[\frac{K\lambda}{d}\right] + [4e\sin\theta]$)

Plotting $\sin\theta$ (vs) $\cos\theta B_{corrected}$ will give a linear plot with 4e as the slope and $\frac{K\lambda}{d}$ as the y-intercept.

(The broadening due to crystallite size, instrumental broadening and micro strain will be larger at large Bragg angles).

Reference

[1].P. Scherrer, "Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen," *Nachr. Ges. Wiss. Göttingen* **26** (1918) pp 98-100.

[2].J.I. Langford and A.J.C. Wilson, "Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size," *J. Appl. Cryst.* **11** (1978) pp 102-113.

Steps to run this program ('grain')

I(1). This program can be executed without giving any entry in the window panel of the program, just by checking box corresponding to (i) 'All the information from file?'

(ii) then selecting the 'All info file' from the file menu (click file select All info file. A new window will open from which you can browse the input file prepared in the format given below) and (iii) clicking OK button.

I(2). If the above mode is selected, the input file should be prepared as follows (without the separating lines above and below);

```
#Enter a title in the following line
Test
#Enter the lambda value below
0.7107
#Enter the K value (usually 0.9)
0.9
#Enter the number of data sets
4
#Enter the data (2Theta and FWHM)
15.6 2.025
26.8 2.028
35.6 1.831
47.3 2.024
#Enter the crystallite size model (1 or 2)
#(1=Size broadening;2=Size+Strain)
2
#Enter the output file name (LIMITED TO 4 ALPHABETS)
o1
```

I(3). For all the other modes of operation of this program, panel entry of values is required.

II. Give the name of the output file in the box provided (not needed if the 'All info from file' mode selected).

III(1). The sets of 2thetas and FWHMs values alone can be inputted through a file if intended. For this, check the box 'Input (thetas and FWHMs only) from file?' and click the file menu to open the '2Theta, FWHM File'. (A new browsing window will open from which you can select the file containing 2theta and FWHM values. The format of this file is as follows; (2theta FWHM (in degrees))

34.5667 1.2356

46.2788 1.6782

III(2). All the other values in this mode should be entered through the spaces allocated.

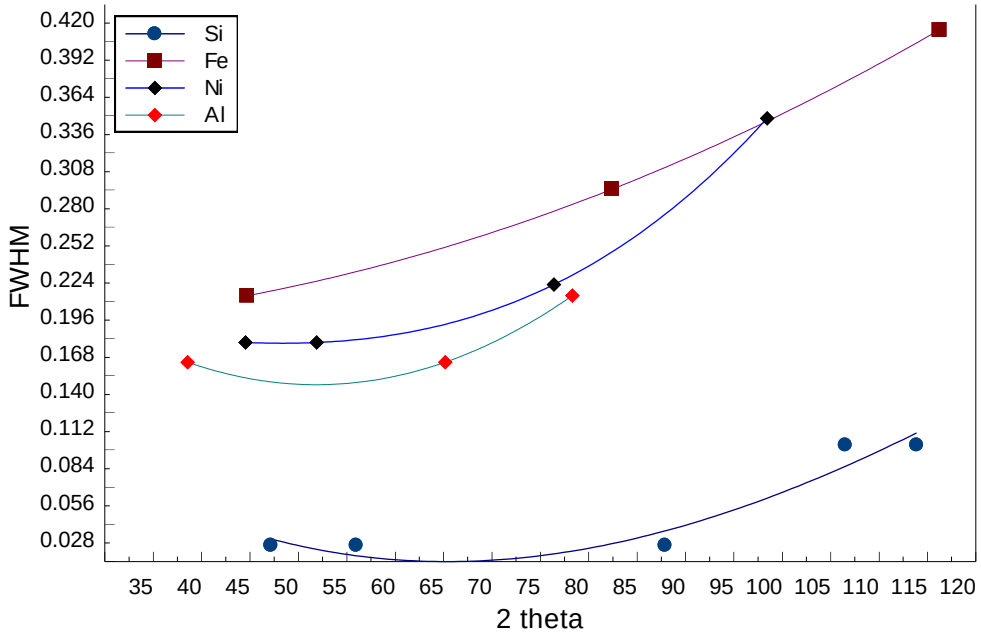
III(3). Do not forget to give the output file name for this mode.

IV(1). If you do not check both the boxes (All info file mode and Theta_FWHM file mode), still the input theta and FWHM can be inputted through the keyboard. For this, don't check both the boxes. Enter all the required values in the program panel. Give an output file name. Select a size model (ST1 or ST2). Click OK. A new window should open in which you can enter one set of 2theta and FWHM value (in degrees). Click OK. The same window will open again for entering the next set of 2theta and FWHM values. The process will be repeated until the total number of (2theta FWHM) sets is completed.

V. For all the three modes (All_info_file, theta_FWHM_file and keyboard input), any one of the models (ST1 or ST2) can be selected according to your sample.

VI. The output can be viewed in the file with name given as the output file name.

The full-width at half maximum plotted for various metals is shown in the following figure.



INPUT

The input file (2theta) is as follows;

```
38.57   0.15040
44.81   0.10027
65.19   0.15040
78.32   0.20054
82.53   0.20054
99.09   0.20054
```

The input file (allinfo) is as follows;

```
#Enter a title in the following line
Example3
#Enter the lambda value below
1.5418
#Enter the K value (usually 0.9)
0.9
#Enter the number of data sets
6
#Enter the data (2Theta and FWHM)
38.57   0.15040
44.81   0.10027
65.19   0.15040
78.32   0.20054
82.53   0.20054
99.09   0.20054
#Enter the cryatllite size model (1 or 2)
#(1 = Size broadening; 2 = Size + Strain)
2
#Enter the output file name (LIMITED TO 4 ALPHABETS)
ST2
```

OUTPUT

A typical output file is as follows;

```
Example3
---------------------------------------------

 THE WAVELENGTH =  1.54180
  THE CONSTANT K (IN SHERRERS FORMULA) IS =   0.9000
  THE TOTAL NUMBER OF OBSERVATIONS =   6
-------------------
 2THETA      FWHM
-------------------
 38.5700   0.1504
 44.8100   0.1003
 65.1900   0.1504
```

```
 78.3200   0.2005
 82.5300   0.2005
 99.0900   0.2005
-------------------
  THE MODEL USED IS =   2
(1 = SIZE BROADENING ONLY
 2 = SIZE + STRAIN BROADENING)



----------------------
Least Squares Analysis
----------------------
  TOTAL NUMBER OF X VALUES =    6
 TOTAL NUMBER OF Y VALUES =    6
 SUMX       =     3.302
 SUMY       =     0.014
 SLOPE      =     0.001006445(     0.001070448)
 Y-INTERCEPT =     0.001766609(     0.000611393)
(SLOPE/4 IS THE STRAIN BROADENING)
----------------------
2THETA      FWHM(rad)
----------------------
   38.5700    0.0026
   44.8100    0.0018
   65.1900    0.0026
   78.3200    0.0035
   82.5300    0.0035
   99.0900    0.0035
----------------------
 THE CRYSTALLITE SIZE FROM LEAST SQUARES ANALYSIS IS  =     0.785470888E-07(
0.271837806E-07)(metre)
 THE STRAIN BROADENING FROM LEAST SQUARES ANALYSIS IS =     0.251611316E-03(
0.267612078E-03)

IF THE SLOPE IS ZERO OR NEGATIVE, YOUR SAMPLE IS STRESS FREE.

IF THE esd OF ANY PARAMETER IS LARGER THAN THE  PARAMETER VALUE
ITSELF, THEN THAT PARAMETER ESTIMATE IS NOT DEDUCEABLE FROM YOUR DATA.
```

KCL

About the program

This is a refinement program (to refine the single crystal/powder XRD experimental data to (i) match the observed and calculated structure factors (ii) to refine the Debye-Waller factor (iii) hence to find experimental mean square amplitudes. Applicable to NaCl (diatomic, FCC) type systems.

This program can process the observed X-ray structure factors of NaCl (diatomic, FCC) type structure. NaCl structure factors will be CALCULATED and the observed and calculated structure factors will be matched using least-squares refinement method. The (i) Debye-Waller factor and (ii) the scale factor are the prime parameters refined in this program. The output file will contain the results of refinement in each least-squares refinement.

Also, the listing will have the h k l values of the reflections, FOBS (observed) structure factor, FCAL (calculated) structure factor, the difference DELF, error as the % (ERR), atomic scattering factor of the atom involved SF(I,1), the Bragg angle THETA, and sin(theta)/Lambda (SINT).

The observed powder XRD intensities from a powder data set can be utilized. First, the observed X-ray intensities should be converted into observed X-ray structure factors. The supplied SCAT771 program can be used for this purpose. Or any other method can be used to get the observed structure factors of each reflection from the observed intensities. The prime corrections to be applied to convert the X-ray intensities into X-ray structure factors are (i) multiplicity and (ii) Lorentz-polarization corrections. SCAT771 program can do this.

After, converting the X-ray intensities into structure factors using SCAT771, the input file for running KCl should be prepared.

Input

Prepare an input file for running KCl. The input is FORMAT sensitive. Hence adhere to the spacings and other syntaxes. The name should be in_b_kcl. (without full-stop)

A typical input will be as follows;

```
Refinement of KBr parameters (eg. fcc-KBr)
 2 20  1  1
 1.540560 6.600000 9.000000 1.200000 0.7000 3.0
 8.164  7.147  1.070  0.877  1.486 12.816  0.809 210.327 39.598  0.053  0.254
 0.3868 1.0657
17.551  5.412  3.937  3.881  6.708  2.119 16.557   0.002 42.164  0.162 -2.492
-0.676  1.281
 1  1  1    0.187
 2  0  0    0.701
 2  2  0    0.564
 3  1  1    0.175
 2  2  2    0.519
 4  0  0    0.493
 3  3  1    0.122
 4  2  0    0.400
 4  2  2    0.346
 5  1  1    0.150
 4  4  0    0.231
 5  3  1    0.084
 6  0  0    0.540
 6  2  0    0.246
 5  3  3    0.123
 6  2  2    0.213
 4  4  4    0.209
 7  1  1    0.117
 6  4  0    0.164
 6  4  2    0.134
 7  3  1    0.073
 8  0  0    0.183
 8  2  0    0.110
99
 6  0  0
```

First line is the title line

Second line, I parameter 1 indicates the number of species of atoms (allowed value is 2, since the program is for KCl - diatomic system)

Second line, II parameter 20 indicates user inputted number of cycles of least-squares refinement, typically 10 to 20 enough for convergence. (here 20 is given)

Second line, III parameter 1 indicates Wilson plot analysis is done for finding Debye-Waller factor using Fobs and Fcal. 0 will not do Wilson plot analysis.

Second line, IV parameter 1 indicates the no. of observed reflections to be omitted from refinement process (in this case 1). This can be decided after initial refinements and checking the results for reflections with large differences in Fobs and Fcal. In this example 6 0 0 reflection has been omitted.

Third line, I parameter (1.54056) indicates the wavelength of X-rays used for XRD powder data recording.

Third line, II parameter (6.6) indicates the cell constant of the KBr system (in this case KBr with cell constant 6.6 angstrom).

Third line, III parameter (9.0) indicates the initial scale factor to be used in the refinement to match Fobs and Fcal. Any random value is OK so that refinement converges.

Third line, IV parameter (1.2) indicates the initial B value of **first atom** (Debye-Waller factor of K atom) to be used in the refinement to match Fobs and Fcal. A small value is enough.

Third line, VI parameter (0.7) indicates the initial B value of **second atom** (Debye-Waller factor of Br atom) to be used in the refinement to match Fobs and Fcal. A small value is enough.

Fourth line indicates the analytical co-efficients (5 parameter model) to calculate the atomic scattering factors of the **first** atoms. A1, A2, A3, A4, A5, B1, B2, B3, B4, B5, and C. A total of 11 coefficients are to be used. These values are listed in international tables for X-ray crystallography. But, if you use SCAT771 program you can find these values in one of the output files (PAR1) and use them in the input for KCl.

Fifth line indicates (0.3868 1.0657) two values, the anomalous dispersion corrections terms of the **first** atom for the X-ray wavelength used. These values are listed in international tables for X-ray crystallography. But, if you use SCAT771 program you can find these values in one of the output files (DIS1) and use them in the input for KCl.

Sixth line indicates the analytical co-efficients (5 parameter model) to calculate the atomic scattering factors of the **second** atoms. A1, A2, A3, A4, A5, B1, B2, B3, B4, B5, and C. A total of 11 coefficients are to be used. These values are listed in international tables for X-ray crystallography. But, if you use SCAT771 program you can find these values in one of the output files (PAR1) and use them in the input for KCl.

Seventh line indicates (-0.676 1.281) two values, the anomalous dispersion corrections terms of the **second** atom for the X-ray wavelength used. These values are listed in international tables for X-ray crystallography. But, if you use SCAT771 program you can find these values in one of the output files (DIS1) and use them in the input for KCl.

In this input examples, **the next 23 lines indicate the h k l values and the observed structure factors (FOBS)** derived from SCAT771 program.

Next line 99 indicates the parameter to terminate the reading of the input.

The last line (in this example) 6 0 0 indicates the reflection to be omitted (omit = 1 in this example – see second line 4th parameter)

Output

The output file name is out_b_kcl. All the inputted values are listed first. Then, a typical output cycle shows as follows.

```
---------------
CYCLE NUMBER= 1
---------------
 SCALE FACTOR = 0.40245E-02     +/-     0.31926E+01
 B OF ANION   = 0.12005E+01     +/-     0.21172E+01
 B  OF CATION =  0.70079E+00    +/-    .47E+01
 CORRELATION BETWEEN  1AND 3 IS  =    0.66234559
    RMINIMUM=  0.243239
```

This 0.243239 is the Reliability factor R at the beginning of the refinement.

These results are self-explanatory. RMINIMUM will show the Reliability index at each cycle. At the end of 20th cycle (here, the no. of cycles is 20 in this example), you can see the following.

```
**********************
**********************
** 3R  MINIMUM=0.0890**
**********************
**********************
```

3R MINIMUM=0.0890, indicates that the minimum R factor occurs at 3rd cycle and the R value is 8.90 %.

The parameter listed in the 3rd cycle are the refined parameter as follows.

```
---------------
CYCLE NUMBER= 3
---------------
 SCALE FACTOR = 0.41111E-02     +/-     0.13762E-03
 B OF ANION       = 0.26059E+01     +/-     0.22291E+00
 B  OF CATION    =  0.29634E+01    +/-    .63E+00
 CORRELATION BETWEEN  1 AND 3 IS  =    0.68714958
    RMINIMUM=  0.088967
```

The final list of Fobs, Fcal etc are given in the order as follows;

H K L FOBS FCAL DELF ERR SF(I,1) SF(I,2) THETA SINT

FOBS = Observed structure factor
FCAL = Calculated structure factor
DELF = FOBS- abs(FCAL)
ERR = (DELF/FOBS)*100
SF(I,1) = atomic scattering factor of first atom
SF(I,2) = atomic scattering factor of second atom
THETA = Bragg angle
SINT = (sin (theta)/Lambda)**2

Note, the most successful results can be obtained through a large no. observations. That is - good statistics only will lead to convincing results.

SARAAA

About the program

This is a program to refine parameters in the harmonic, anharmonic and charge transfer Approximations of the XRD data of ZnS type structures. It can refine individual thermal, scale, extinction parameters and the charge transfer from one atom to the other in ZnS type structures. It calculates the real and imaginary phase parts FA and FB of the structure factors. It includes Bijvoet differences in the analysis. It averages the Bijvoet equivalent reflections.

The observed structure factors of ZnS type structures can be used for getting a numerous parameters from refinement. It is applicable to single crystal or powder XRD data. The powder intensities are to be converted into structure factors for which the supplied SCATT771 can be used.

This program can process data of mixed systems also, for e.g., Zn1-xCdxTe, etc. It can make Wilson plot analysis to get the thermal parameters. It can correct the single crystal data for extinction, absorption and TDS (temperature diffuse scattering). It can refine the individual harmonic thermal parameters. Also it can refine anharmonic thermal parameter using Mc Intyre's approach or Cooper's approach. It can find the charge transferred from one atom to other atom in ZnS structure.

Input

The input file name should be in_saraaa_m.

A typical input will be as follows;

```
Gallium Arsenide AFC7R
 IREF   =  0
 ICHRG  =  0
 IBIJ1  =  1
 NC     =  1
 JJJJJJ =999
 JJKKLL =  0
 JPARA  =  2
 NCYCL  = 15
 IWILS  =  1
```

NOMIT = 0
IWGT = 0
IDATA = 0
NRDAT = 0
IAVE = 0
ICOO = 1
BETXY =0.0001
BETAA =0.0110
BETAC =0.0110
CHRG =0.1000
C11 =-0.847
C22 =-2.984
THEM =6.0694
RADIS =0.1150
BAN =1.4500
BCAT =1.7500
CTDS =0.0200
XFRAC =0.0000
YFRAC =0.0000
ALMDA =0.7107
GIM = 0.0000
CELL1 = 5.6500
CELL2 = 5.6500
CELL3 = 5.6500
SCALE = 91.2000
TEMP =298.0000
GIVE THE NUMBER OF INDIVIDUAL ATOMS IN THE CELL BELOW THIS LINE IN FREE FORMAT
4 4
SCATTERING FACTORS (OR COEFFICIENTS) IN THE FOLLOWING 2 LINES (FREE FORMAT)
15.759 6.841 4.121 2.715 2.395 3.122 0.226 12.482 66.204 0.007 -0.847
-1.285 0.776
17.026 4.503 3.716 3.937 6.790 2.598 0.003 14.272 50.438 0.193 -2.984
-0.930 1.005
GIVE THE ATOMIC COORDINATES OF ALL THE ATOMS IN THE UNIT CELL BELOW(FREE FORMAT)
0.0 0.0 0.0
0.0 0.5 0.5
0.5 0.0 0.5
0.5 0.5 0.0
0.25 0.25 0.25
0.75 0.75 0.25
0.25 0.75 0.75
0.75 0.25 0.75
H K L VALUES,THE STRUCTURE FACTORS,SIGFO AND WEIGHT
0 -2 -10 481.68253 6.91714
-2 0 -10 476.28763 6.83586
2 0 -10 473.52798 7.01862
0 2 -10 476.51230 7.01862
-3 -3 -9 355.84000 7.76151
-1 -3 -9 386.48456 8.05823
……
……..
99
ERROR = 2.0
NOMIT (GIVE THE H K L OF REFLECTIONS TO BE OMITTED)

The parameter-wise information has been given below.

IREF = TYPE OF REFINEMENT.
IREF = 0 - HARMONIC REFINEMENT.
(SCALE,EXTINCTION,INDIVIDUAL ISOTROPIC THERMAL FACTORS).
IREF = 1 - ANHARMONIC REFINEMENT.
(SCALE,EXTINCTION,INDIVIDUAL ISOTROPIC THERMAL FACTORS, OVERALL ANHARMONIC THERMAL FACTOR).
IREF = 2 - ANHARMONIC REFINEMENT.
(SCALE,EXTINCTION,INDIVIDUAL ISOTROPIC THERMAL FACTORS, INDIVIDUAL ANHARMONIC THERMAL FACTORS).
ICHRG = 0 TRANSFERRED CHARGE NOT REFINED.
ICHRG = 1 TRANSFERRED CHARGE REFINED.
IBIJ1 = POLARITY CHANGE OF STRUCTURE FACTORS. IBIJ1= 0 OR 1.
JJKKLL=INTEGER EQUAL TO (H**2+K**2+L**2).
JJKKLL IS THE UPPER LIMIT OF THE H + K + L = 4N+2 TYPE REFLECTIONS TO BE INCLUDED IN THE ANALYSIS. JJKKLL CAN BE ZERO OR ANY INTEGER WHEN ICHRG=0.
BUT JJKKLL SHOULD NOT BE ZERO WHEN ICHRG=1.
JJKKLL FACILITATES THE INCLUSION OR EXCLUSION OF H+K+L=4N+2 REFLECTIONS EVEN WHEN CHARGE IS NOT REFINED.
NC=NUMBER OF DATA SETS TO BE REFINED. NC=1 (USUALLY)
BETXY=INITIAL VALUE OF OVERALL BETA (THE ANHARMONIC THERMAL VIBRATION).
BETAA=INITIAL BETA OF ANION.
BETAC=INITIAL BETA OF CATION.
CHRG=INITIAL CHARGE TRANSFER PARAMETER. ANY FRACTIONAL VALUE.
C11 AND C22 = THE CONSTANTS C.
ANALYTICAL CONSTANTS OF INT. TABLES CAN BE USED WITH 9 PARAMETER MODEL)
FOR CATION AND ANION.
JPARA=NUMBER OF ELEMENTS IN THE SYSTEM (e.g; JPARA FOR GaAs IS 2).
NCYCL=NUMBER OF CYCLES FOR THE REFINEMENT.
IWILS = 1, THEN WILSON PLOT ANALYSIS WILL BE CARRIED OUT.
= 0, SKIP.
IWILS MAY BE USEFUL FOR CHECKING EXTINCTION EFFECTS.
NOMIT= NUMBER OF REFLECTIONS TO BE OMITTED FROM THE REFINEMENTS.
THIS CAN BE DECIDED AFTER ANALYSING INITIAL REFINEMENT RESULTS.
IWGT= WEIGHT TO BE USED IN THE ANALYSIS.
IF IWGT=0, THEN UNIT WEIGHTS WILL BE USED.
IF IWGT=1, THEN THE GIVEN WEIGHTS WILL BE USED.
IDATA AND NRDAT ARE THE SIGNALS INCLUDED FOR DATA REDUCTION PART OF THIS PROGRAM WHICH IS UNDER CONSTRUCTION.
IAVE=O OR 1. IF IAVE=1, THEN AVERAGING (AFTER REFINEMENT) OF STRUCTURE FACTORS, EXTINCTION, TDS ETC. OF EQUIVALENT REFLECTIONS WILL BE CARRIED OUT.
THEM=THE MONOCHROMATOR ANGLE IN DEGREES.
GIM=THE INITIAL EXTINCTION PARAMETER.
AMU=THE LINEAR ABSORPTION COEFFICIENT OF THE MATERIAL
(NOT USED IN THE CALCULATIONS, JUST USED TO BE PRINTED OUT).
RADIS=RADIUS OF THE SPHERICAL SAMPLE.
IF THE SAMPLE IS NOT PERFECT SPHERE, YOU ARE NOT ENTITLED TO USE THIS PROGRAM !!.
NATOM(I)=NUMBER OF ATOMS OF EACH SPECIES IN THE SYSTEM.
FOR e.g, FOR GaAs, NATOM(I)= 4 4.
ALMDA=WAVELENGTH USED FOR THE INTENSITY DATA COLLECTION.
,CELL2,CELL3=CELL DIMENSIONS OF THE SYSTEM.
SCALE=INITIAL OVERALL SCALE FACTOR.
BAN=INITIAL DEBYE WALLER FACTOR OF ANION.
BACT=INITIAL DEBYE WALLER FACTOR OF CATION.

CTDS=TDS CORRECTION FACTOR.
XFRAC=IF THE SYSTEM IS QUARTERNARY MIXED, GIVE THE COMPOSITION OF X.
YFRAC=IF THE SYSTEM IS TERNARY MIXED, GIVE THE COMPOSITION OF Y.
A(J,I) AND B(J,I)= ATOMIC SCATTERING FACTORS.
ATOMIC SCATTERING FACTORS WITH RESPECT TO SIN(THETA)/LAMBDA.
A(J,I)=SIN(THETA)/LAMBDA AND B(J,I)=SCATTERING FACTORS.
DISP1(J) AND DISP2(J) = REAL AND IMAGINARY DISPERSION CORRECTION TERMS.
X1(J),Y1(J),Z1(J)=ATOMIC COORDINATES OF THE FIRST SPECIES (ANION).
X2(J),Y2(J),Z2(J)=ATOMIC COORDINATES OF THE SECOND SPECIES (CATION).
IH(I,J), FO(I), SIGF(I), WGT1(I) = H, K, L VALUES, OBSERVED STRUCTURE
FACTORS (LP AND ABSORPTION CORRECTED), SIGMA FO VALUES AND WEIGHT OF EACH
OBSERVATION. ONE REFLECTION PER LINE. AT THE END OF STRUCTURE FACTOR DATA,
GIVE 99 OR 99 0 0 FOR HKL IN 3I3 FORMAT.
J,K,L= IF NOMIT IS ANY NUMBER, GIVE THE H,K,L VALUES (REFLECTION TO BE
OMITTED) UPTO NOMIT TIMES. ONE H,K,L PER LINE.

FOR MIXED SYSTEMS LIKE Ga(x) Al(1-x) As, GIVE THE X=COMPOSITION WITH OTHER
APPROPRIATE PARAMETERS. GIVE THE ATOMIC COORDINATES OF THE Ga AND Al SITES
THE SAME VAULES. GIVE THE SAME NUMBER OF ATOMS FOR THESE ATOMS. THE PROGRAM
WILL TAKE CARE THE REST OF ANALYSIS.
THE BETA VALUES ARE IN UNITS OF 10**(-12) ERG. ANG.**(-3). B VALUES ARE INC
UNITS OF ANG.**2
THAT'S ALL !!!

Output

THIS PROGRAM PRODUCES 4 OUTPUT FILES AS FOLLOWS

(1) TAPE3 : LISTING OF OBSERVED (EQUIVALENTS AVERAGED) AND CALCULATED STRUCTURE FACTORS

(2) TAPE4 :(i) LISTING OF OBSERVED AND CALCULATED STRUCTURE FACTORS, FO-FC, ERR, SCATTERING FACTORS OF THE ELEMENTS, THETA, (SIN(THETA/LAMBDA)**2), EXTINCTION
PARAMETER AND TDS (ii) LISTING OF FO, FC, SIGMAFO/FO, EXTINCTION AND TDS (THIS LISTING MAY BE SUBMITTED FOR PUBLICATION (iii) LISTING OF FO, FC, REAL AND IMAGINARY PARTS OF STRUCTURE FACTOR AND SIGMA FO (MAY BE USED FOR ELECTRON DENSITY ANALYSIS)

(3) TAPE7 : LISTING OF THE OMITTED REFLECTIONS AND THE EXTINCTION CORRECTED AND UNCORRECTED STRUCTURE FACTORS WITH RESPECT TO (SIN(THETA/LAMBDA))**2. THIS OUTPUT CAN BE USED FOR PLOTTING.

(4) TAPE8 : LISTING OF ALL THE INPUT PARAMETERS AND THE REFINED PARAMETERS IN EACH CYCLE WITH R FACTOR AND Rw. exc, AND exn ARE OUTPUTS WITH AND WITH EXTINCTION CORRECTION FOR STRUCTURE FACTORS AND WITHOUT AVERAGING EQUIVALENTS.

SCAT771

About the program

Processing of observed X-ray intensities

1. Generates reflections and thier structure factors using the Supplied atomic coordinates and the analytical coefficients.

2. Can process the observed X-ray intensities and convert them into observed structure factors.

3. Using the observed and calculated structure factors, can generate data for Wilson plot to find the thermal vibration parameter of the system.

If you want to use (1) fractional atomic coordinates from file and (2) cell parameters from file check appropriate boxes.

Then, if fractional coordinates file is needed in the main menu bar click |file-coordinates|. A new window will be opened from where you can browse for the coordinate file and select it. Similarly, you can browse for the cell parameter file by clicking |file-cell values| from the main menu bar.

The intensity file to be processed can be selected by clicking |file-Intensity| from the main menu bar. Or it can be given through key board by checking the box below.

The format of **cell values** file is as below;
a b c alpha beta gamma.

This means numerical values separated by at least one space.
See example below.

5.4307 5.4307 5.4307 90.0 90.0 90.0

The format of **coordinates file** is as below;
First line - Number of different kinds of species in the system (n).
Second line - Name_of_the_atom Number_of_atoms_of_this_kind_(m)
Fractional_composition_for_this_atom.

Third line same for next species. Susequent lines for and upto n species.
After n lines, fractional atomic coordinates x, y, z of m atoms of first species (m lines).
Then, x,y,z for for m atoms of second species and so on upto n species.
See example below.

```
2
Na  4  1.0
Cl   4  1.0
0.00 0.00 0.00
0.50 0.50 0.00
0.00 0.50 0.50
0.50 0.00 0.50
0.50 0.50 0.50
0.50 0.00 0.00
0.00 0.50 0.00
0.00 0.00 0.50
```

The format of **intensity** file is as below;
h k l Iobs (in a single line). Upto N lines (Total number of observations or simulation).
See example below.

```
1 1 1  50.0
2 0 0 150.0
2 2 0  76.0
3 1 1  24.0
4 0 0 128.0
```

OUTPUT

Atypical output is as follows;

```
---------------------------------------------
 Al SF
---------------------------------------------
 Input h k l values and observed Intensities
------------------
 h k l   Intensity
------------------
 1 1 1   100.0000
 2 0 0    47.0000
 2 2 0    22.0000
 3 1 1    24.0000
 2 2 2     7.0000
 4 0 0     2.0000
 3 3 1     8.0000
 4 2 0     8.0000
 4 2 2     8.0000
-----------------------------------------------------------------------------------------------
THE OUTPUT DATA
Al
 LAMDA=   Cu
 CELL1=    4.0490
 CELL2=    4.0490
 CELL3=    4.0490
```

ALPHA= 90.0000
BETA = 90.0000
GAMMA= 90.0000
NO.OF ELEMENTS IN THE SYSTEM = 1
ATOM(S) INVOVLED IN THE SYSTEM ARE THE FOLLOWING; Al
THE FOLLOWINIG SYMBOLS FOR WAVELENGTHS ARE ALLOWED

TI (= 2.7485)
CR (= 2.2896)
FE (= 1.9360)
CO (= 1.7890)
CU (= 1.5405)
MO (= 0.7093)
AG (= 0.5594)
TA (= 0.2159)
AU (= 0.2090)
TI (= 0.1802)

THE WAVELENGTH USED IS = 1.540520

THE FOLLOWING ATOMS/IONS ARE ALLOWED

4 COLUMNS ALLOWED FOR EACH ATOM/ION NAME

H He Li Be B C N O F Ne Na Mg
Al Si P S Cl Ar K Ca Sc Ti V Cr
Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
In Sn Sb Te I Xe Cs Ba La Ce Pr Nd
Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf
Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po
At Rn Fr Ra Ac Th Pa U Np Pu Am Cm
Bk Cf H1- Li1+ Be2+ Cval O1- O2- F1- Na1+ Mg2+ Al3+
Siva Si4+ Cl1- K1+ Ca2+ Sc3+ Ti2+ Ti3+ Ti4+ V2+ V3+ V5+
Cr2+ Cr3+ Mn2+ Mn3+ Mn4+ Fe2 Fe3+ Co2+ Co3+ Ni2+ Ni3+ Cu1+
Cu2+ Zn2+ Ga3+ Ge4+ Br1- Rb1+ Sr2+ Y3+ Zr4+ Nb3+ Nb5+ Mo3+
Mo5+ Mo6+ Ru3+ Ru4+ Rh3+ Rh4+ Pd2+ Pd4+ Ag1+ Ag2+ Cd2+ In3+
Sn2+ Sn4+ Sb3+ Sb5+ I1- Cs1+ Ba2+ La3+ Ce3+ Ce4+ Pr3+ Pr4+
Nd3+ Pm3+ Sm3+ Eu2+ Eu3+ Gd3+ Tb3+ Dy3+ Ho3+ Er3+ Tm3+ Yb2+
Yb3+ Lu3 Hf4+ Ta5+ W6+ Os4+ Ir3+ Ir4+ Pt2+ Pt4+ Au3+
Hg1+ Hg2+ Tl1+ Tl3+ Pb2+ Pb4+ Bi3+ Bi5+ Ra2+ Ac3+ Th4+ U3+
U4+ U6+ Np3+ Np4+ Np6+ Pu3+ Pu4+ Pu6+

ATOMS MATCHING ?
Al Al
THE ANALYTICAL COEFFICIENTS (11 PARAMETER MODEL) ARE THE FOLLOWING FOR ATOM Al

A11 = 4.7308
A12 = 2.3140
A13 = 1.5420
A14 = 1.1176
A15 = 3.1548
B11 = 3.6289
B12 = 43.0512
B13 = 0.0960
B14 = 108.9324

B15 = 1.5559
C1 = 0.1395

ATOMIC WEIGHT OF THE ATOM Al IS 26.98000
THE DISPERSION CORRECTION TERMS fp AND fpp ARE THE FOLLOWING FOR THE ATOM Al
DIS1= 0.2130
DIS2= 0.2455

MOLECULAR WEIGHT OF THE SYSTEM = 26.9800

ATOMIC COORDINATES OF THE ATOMS

Atom	x	y	z
Al	0.0000	0.0000	0.0000
Al	0.5000	0.5000	0.0000
Al	0.0000	0.5000	0.5000
Al	0.5000	0.0000	0.5000

ISYS:
TRICILINIC (-1) = 1
MONOCLINIC (Z UNIQUE; 2/M) = 2
MONOCLINIC (Y UNIQUE; 2/M) = 3
ORTHORHOMBIC (MMM) = 4
TETRAGONAL(4/M) = 5
TETRAGONAL(4/MMM) = 6
CUBIC (M3) = 7
CUBIC (M3M) = 8
TRIGONAL (-3) = 9
TRIGONAL (-3M) = 10
HEXAGONAL (-3) = 11
HEXAGONAL (-3M) = 12
HEXAGONAL 6/M = 13
HEXAGONAL 6/MMM = 14

CHOSEN ISYM = 8

H	K	L	THETA	SIN0/Lambda	M	Lp	FOBS	FCAL	ln(Fo/Fc)
1	1	1	19.2382	0.2139	8	15.7346	0.8913	36.6704	-3.7170
2	0	0	22.3628	0.2470	6	11.2407	0.8348	34.8771	-3.7324
2	2	0	32.5520	0.3493	12	4.8240	0.6165	30.1655	-3.8904
3	1	1	39.1193	0.4096	24	3.3724	0.5445	27.5221	-3.9228
2	2	2	41.2230	0.4278	8	3.1144	0.5300	26.7283	-3.9205
4	0	0	49.5470	0.4939	6	2.7283	0.3495	23.8980	-4.2249
3	3	1	56.0180	0.5383	24	2.9683	0.3351	22.0856	-4.1882
4	2	0	58.2939	0.5523	24	3.1555	0.3250	21.5328	-4.1935
4	2	2	68.7417	0.6050	24	4.9007	0.2608	19.5468	-4.3168

VOLUME OF THE UNIT CELL = 66.3809 Angstrom**3
DENSITY OF THE SYSTEM = 2.69927 gm/cc

NUMBER OF REFLECTIONS = 9

One more output will like the following;

Al SF

---

h	k	l	FA	FB	Fcal
1	1	1	36.6704	0.0000	36.6704
2	0	0	34.8771	0.0000	34.8771
2	2	0	30.1655	0.0000	30.1655
3	1	1	27.5221	0.0000	27.5221
2	2	2	26.7283	-0.0001	26.7283
4	0	0	23.8980	0.0000	23.8980
3	3	1	22.0856	0.0000	22.0856
4	2	0	21.5328	0.0000	21.5328
4	2	2	19.5468	0.0000	19.5468

SFAC334

About the program

Calculation of X-ray structure factors of any structure, the real and imaginary parts of the (phases) structure factors, corresponding atomic scattering factors of each element in the structure.

1. Generates reflections and their X-ray structure factors using the Supplied atomic coordinates and the analytical coefficients.

2. Calculates the real and imaginary parts of the structure factors.

3. Calculates the individual atomic scattering factors of each element in the structure.

The input example is as follows;
The format of coordinates file is as below;
First line – Title (80 characters)
Second line – No. of different species in the system, e.g. GaAs – 2; Si-1; LaMnO3-3 etc.
Third line - a b c alpha beta gamma.
Fourth line – name_of_the_atom no_of_that_atom fractional_composition
Fifth line – name_of_the_atom no_of_that_atom fractional_composition and so on upto the no. of species
Next line – fractional atomic coordinate of first atom of first species
Next line – fractional atomic coordinate of second atom of first species
And so on.

Example input

```
Aluminium
1
4.04 4.04 4.04 90.0 90.0 90.0
Al 4 1.0
0.00 0.00 0.00
0.50 0.50 0.00
0.00 0.50 0.50
0.50 0.00 0.50
```

Second example

```
Sodium Chloride
2
6.04 6.04 6.04 90.0 90.0 90.0
Na  4  1.0
Cl  4  1.0
0.00 0.00 0.00
0.50 0.50 0.00
0.00 0.50 0.50
0.50 0.00 0.50
0.50 0.50 0.50
```

0.50 0.00 0.00
0.00 0.50 0.00
0.00 0.00 0.50

UV-Vis Band gap

About this sheet

Read the given reference (odms1.pdf). Give the optical absorption data (UV-Vis) in the first 2 columns of the supplied excel sheet (UvVis_Band_Gap.xls). That is - the wavelength in 1st column and the absorption data in the 2nd column. The next column (3rd) will calculate the following;

$$E = \frac{hc}{\lambda} = h\nu$$

The next (4th) column will calculate $(\alpha h\nu)$. (See given reference).

The next column (5th) will calculate $(\alpha h\nu)^2$. (See given reference).

The A plot of E and $(\alpha h\nu)^2$ (3rd and 5th columns) will give a curve. The straight line drawn along the straight portion of the curve intersecting y=0 will give the band gap of the material.