

About

WinMProf DOCUMENTATION

Manual For MPROF Rietveld Refinement Program

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TABLE of CONTENTS

Introduction to WinMProf

How to run MPROF in WinMProf ?

Possible formats for experimental profile data

D1A format
PDS format
FR1 format
FR2 format
PHI format

Refinement methods

Rietveld method
Le Bail Method

The Possible Parameters

Overall Parameters

- 1) Wavelength of the diffracted radiation
- 2) Unit cell dimensions
- 3) Zero-point correction
- 4) Scale factor
- 5) Lorentz-Polarization factor
- 6) Overall isotropic temperature factor
- 7) Peak shape function parameters
- 8) Correction factors for preferred orientation
- 9) Absorption and micro-absorption correction
- 10) Correction for asymmetry
- 11) Refinable background functions

Atomic Parameters

Facilities offered by the MPROF refinement program

A Note on the Format of the Input Data

Input data for MPROF profile refinement program

Line :

- 1) Title
- 2) Overall Refinement Options
- 3) Preprofile preparation options
- 4) Excluded regions values (optional)
- 5) Experimental datafile name, range of calculation, FDS or VDS mode
- 6) Background values (optional)
- 7) Output options

Keyworded Input

- 8) Constraints Indicators

The set of lines 9 to 14 must be supplied for each phase

- 9) Text
- 10) Refinement Type and Preferred Orientation option
- 11) Unique Magnetic axis (optional)
- 12) Structure Indicators
- 13) Space group symbol
- 14) Symmetry operators (optional)

15) Wavelength(s) and Refinement Regulators

Input of scattering factors

- 16) Atomic parameters
- 17) Scale factor and overall temperature Factor for each phase
- 18) Zero-point, specimen displacement, absorption parameter and depolarisation factor
- 19) Micro-absorption coefficients (optional)
- 20) Halfwidth and shape Parameters for each phase
- 21) Cell Parameters for each phase
- 22) Preferred Orientation parameters for each phase (optional)
- 23) Asymmetry parameters (optional)
- 24) Background parameters (optional)
- 25) Background parameters (optional)

Refinement Codewords

- 26) Codewords for Atomic Parameters
- 27) Codewords for Scale(s) and overall temperature factor for each phase
- 28) Codewords for Zero-point, Specimen Displacement, absorption and depolarisation factors
- 29) Codewords for Micro-absorption coefficients (optional)
- 30) Codewords for Halfwidth and shape Parameters for each phase
- 31) Codewords for Cell parameters for each phase
- 32) Codewords for Preferred Orientation Parameters for each phase (optional)
- 33) Codewords for Asymmetry parameters (optional)
- 34) Codewords for Background parameters (optional)
- 35) Codewords for Background parameters (optional)

Constrained refinement

- 36) Strict constraints (optional)
- 37) Chemical constraints (optional)

Other associated programs

MFOURS
MBONDS

Examples of input for WinMProf

Synchrotron radiation
Cu Kalpha radiation
Neutron diffraction
Other data

Acknowledgements

Enquiries About the Programs

Disclaimer

Introduction to WinMProf

WinMProf is a Windows 9x / NT based program developed in combined Visual C++ and Visual Fortran. WinMProf is both a general GUI for MPROF Rietveld profile refinement program and a viewing software for experimental and calculated powder diffraction patterns. It can also be used as GUI for other associated programs (Fourier difference, bond distances calculation). WinMProf has all the features of a conventional Windows application using the mouse to select menus, tools in the toolbar, to resize and to move windows etc...

When a powder diffraction pattern is displayed in the graphic window, several options are available in the menus bar (Options) as well as by clicking on the right mouse button to call a context menu : zoom, copy, selection of background points, visualisation of (hkl) indices etc...

An internal text editor (Wordpad class) is included in WinMProf, which allows to create or edit the input control file (*.pro) required for executing the MPROF Rietveld program, as well as to display the output text files (*.lis and others).

The main WinMProf features are described using an online help system. The emphasis is especially put on the part concerning MPROF, in particular with a detailed description line by line of the input data which have to be included in the control file.

Reference information

You can reference the use of WinMProf by :

A. Jouanneaux

« WinMProf : a visual Rietveld software », CPD newsletter, **21**, p 13 (1999)

or

A. Jouanneaux, X. Le Gonidec and A.N. Fitch

« WinMProf : a visual Rietveld software »

Material Science Forum, Proceedings of EPDIC 7, in press

WinMProf is freely available from :

<http://lpec.univ-lemans.fr/winmprof/>

Or via the CCP14 site

<http://www.ccp14.ac.uk/ccp/web-mirrors/winmprof/WinMProf/>

WinMProf has been developed X. Le Gonidec, student at the IUP MIME (Université du Maine) during a training period of two months (supervisor : Dr. A Jouanneaux.).

How to run MPROF in WinMProf ?

An input control file (*.pro) must always be created before using the MPROF refinement program. Information required for MPROF is given below in the topic « Input data for MPROF Profile Refinement Program ». Once this control file (*.pro) has been edited and modified by the user, two ways for running MPROF are then possible :

- 1) This way is normally used when modifications are needed in the input control file (*.pro)

Open the input control file (*.pro).

After modifications in this file, click in the menu bar on « Run MProf ». The control file is then automatically saved and closed. All the other files open at this time are also closed and the refinement process with MPROF is started.

During the refinement sequence, Dialog boxes giving the evolution of R-factors values appear after each cycle. The final Dialog box can be closed by clicking on « OK ».

If the refinement proceeds without problem until the last cycle, the message « MPROF finished normally » is indicated in the final dialog box . Two output files are then automatically opened : the output lineprinter file MProf.lis and as well as the plot file (default : Rietplot.dif) containing the obs., calc. & Dif. Profiles and position of the reflections.

If the calculation crashes before the end, the dialog box indicates the message « MPROF finished abnormally » and only mprof.lis is opened. At the end of this file, an error message can be found giving diagnostic information. The control file .pro can then be reopened and modified appropriately.

- 2) This way to run MPROF does not require editing of the control file. It can be used for example when a refinement has not fully converged and the user wants simply to re-run MPROF using the updated control file.

In the menu bar, click on « Tools / MProf ».

Select an input control file. MPROF is then directly executed.

Note 1 : In both cases, when clicking on « Run MProf » or « Tools / MProf » options, all open files (e.g. MProf.lis, Rietplot.dif and any others) are automatically closed (it is therefore not required to close all open files before (re)running MPROF).

Note 2 : the associated programs MFOURS and MBONDS can be run by the same way.

Possible formats for experimental profile data

Five possible formats of experimental input data may be read in by MPROF, and subsequently by the plotting program in WinMProf. The format is recognised by the extension of the data filename, which must be imperatively one of D1A, PDS, FR1, FR2 or PHI. The angle step has to be constant.

D1A format

The data are formatted as follows :

Title (80 characters maximum)

Start angle, angle step, finish angle (in degrees)

Number of counters & counts formatted in format 10 (I2, I6)

-1000 and -10000 define the end of file.

The angular values (start, step and finish) may contain up to 3 decimal places.

An example :

```
BaGaF5 2H2O Daresbury Station 2.3 1.30098A
 7.000 0.010 80.000
1 2636 1 2669 1 2647 1 2667 1 2505 1 2563 1 2544 1 2609 1 2533 1 2558
1 2747 1 2550 1 2651 1 2607 1 2620 1 2658 1 2531 1 2683 1 2617 1 2672
1 2689 1 2581 1 2558 1 2552 1 2635 1 2517 1 2760 1 2609 1 2519 1 2661
1 2584 1 2599 1 2644 1 2588 1 2532 1 2597 1 2582 1 2771 1 2689 1 2733
1 2706 1 2764 1 2677 1 2870 1 2993 1 2935 1 2854 1 2970 1 3109 1 3179
1 3366 1 3582 1 3860 1 4450 1 4946 1 5926 1 7916 1 10326 1 13344 1 17999
1 22873 1 27498 1 27872 1 22705 1 13926 1 8258 1 5201 1 3942 1 3528 1 3100
```

etc...

```
1 564 1 558 1 583 1 551 1 581 1 563 1 532 1 542 1 489 1 483
1 477 1 456 1 436 1 444 1 460 1 468 1 394 1 391 1 397 1 435
1 430 1 398 1 398 1 366 1 402 1 397 1 399 1 399 1 405 1 413
1 394 1 423 1 425 1 419 1 393 1 409 1 406 1 402 1 419 1 391
1 417 1 422 1 421 1 416 1 395 1 442 1 410 1 402 1 435 1 404
1 446 1 442 1 436 1 430 1 435 1 422 1 396 1 424 1 414 1 393
1 367 1 0 1 0 1 0 1 0 1 0 1 0 1 0
-1000
-10000
```

PDS format

Powder diffraction data collected at ESRF or Daresbury Laboratory.

FR1 format

Input data in Free format (type 1) :

Title (80 characters maximum)

Angle in degrees and number of counts (unformatted)

The angular values may contain up to 3 decimal places.

An example :

```
BaGaF5 2H2O Daresbury Station 2.3 1.30098A
 7.000    2636
 7.010    2669
 7.020    2647
 7.030    2667
 7.040    2505
 7.050    2563
 7.060    2544
 7.070    2609
 7.080    2533
 7.090    2558
 7.100    2747
 7.110    2550
```

etc...

```
79.900    446
79.910    442
79.920    436
79.930    430
79.940    435
79.950    422
79.960    396
79.970    424
79.980    414
79.990    393
80.000    367
```

FR2 format

Input data in Free format (type 2) :

Title (80 characters maximum)
Start angle, angle step, finish angle (in degrees)

Number of counts (unformatted)

The angular values (start, step and finish) may contain up to 3 decimal places.

An example :

```
BaGaF5 2H2O Daresbury Station 2.3 1.30098A
 7.000  0.010  80.000
2636.
2669.
2647.
2667.
2505.
2563.
2544.
2609.
2533.
2558.
2747.
2550.
```

etc...

```
446.
442.
436.
430.
435.
422.
396.
424.
414.
393.
367.
```


Refinement methods

Rietveld Method.

Where extensive overlap occurs between adjacent reflections in a powder diffraction pattern, it is not possible to obtain directly the integrated intensity of each of the contributing reflections. H.M. Rietveld in his paper « A Profile Refinement Method for Nuclear and Magnetic Structures », *J. Appl. Cryst.* 2, 65–71 (1969), describes the method which allows the maximum amount of structural information to be extracted from the detailed profile of the composite peaks of the powder diffraction pattern.

Rather than considering the individual integrated intensities of the Bragg peaks for structural refinement, the Rietveld method uses the method of least-squares to fit a calculated diffraction profile to the measured diffraction profile. The profile is calculated as a sum of overlapping peaks which are described by an assumed peak-shape function. The position of each peak is governed by the refined values of the unit-cell parameters (and the instrumental zero-point and any other geometric corrections such as specimen displacement etc.), the full-width at half maximum height follows a simple angular function, controlled by refinable values, and the integrated intensity of each peak depends on the structure factor, and hence on the atomic parameters. The profile can therefore be described by the equation :

$$y(i) = \sum_{np} S \sum_k [C(k) \cdot F(k) \cdot \text{PSF}(2\theta(i), k)] + B(i) \quad (1)$$

Where :

$y(i)$ is the calculated profile at each point (i).

$2\theta(i)$ is the Two-theta value at each point (i).

The first summation is the sum over all phases contributing to the profile.

S is the scale factor relating the observed and calculated diffraction profiles.

The second one is the sum over all reflections that contribute at each point (i).

$F(k)$ is the structure factor squared of each reflection (k).

$\text{PSF}(k)$ is the peak shape function of each reflection (k).

$C(k)$ is a modification term taking into account factors such as the Lorentz, polarisation, preferred orientation & asymmetry parameters etc.

$B(i)$ is the calculated background at each point (i).

Thus the least-squares method can be used to obtain the best fit between observed and calculated profiles, by refining the values of the lattice parameters (zero-points etc.), the halfwidth parameters, and the atomic parameters. The quality of the fit is judged by the value the ratio of the « Weighted profile » & « Expected » R-factors, the « Chisq » value. For a good fit « Chisq » should be close to 1.0.

Le Bail Method.

The Rietveld method is for the refinement of a crystal structure. When solving structures from powder data it is necessary to extract the intensities of the overlapping peaks without a structural model. The Le Bail method allows this to be done, given a starting set of unit cell parameters, and a list of possible reflections. The method is similar to Rietveld in that a calculated profile is refined by least squares against the observed diffraction pattern. Hence lattice parameters, peak widths, peak-shape parameters are allowed to vary. The intensities are, however, unknown. In the Rietveld method, at the end of the least-squares cycles, overlapping intensity can be partitioned between the reflections in the ratios predicted by the structural model. In the Le Bail method, the intensity is partitioned between overlapping peaks from arbitrarily assigned starting values – all equal say. At the end of the first cycle, the peaks no longer have equal intensities. The strong peaks will be strong, and the weak peaks weak. The process is repeated. The overlapping intensity is now partitioned using the new intensities such that the strong peaks take a larger fraction and another new set of intensities results. The process is cycled until a stable refinement is obtained. Hence the Le Bail method uses the observed intensities directly to partition the intensity between overlapping peaks.

Note that the Le Bail method may be used with neutron nuclear diffraction, synchrotron and conventional X-ray diffraction only (not for magnetic scattering).

Refinement procedure.

Computationally, both methods may be divided into two parts : before powder profile refinement can be successfully carried out, it is necessary to determine (from consideration of the lattice parameters, zero-point, halfwidth parameters and peak-shape function) which reflections from the specimen contribute to which part of the powder profile pattern. This is the preparation or « pre-profile » stage (which is actually transparent for the user), and is carried out just before least squares refinement since it involves considerable reorganisation of data which must be regrouped in the most convenient form. The value of the least-squares weight assigned to each profile point is also calculated in this stage. This task must be carried out more than once during the course of refinement because alteration of the unit cell and profile parameters will change the relationship between the reflections and the observed profile. It is recommended that the profile preparation stage should be repeated whenever significant changes in the unit cell or profile parameters occur.

The refinement of the structure or extraction of the intensities using the data prepared in the previous stage is then carried out. It is necessary to calculate the intensity expected at each point in the observed powder diffraction profile, and also the derivatives of that intensity with respect to the parameters.

The least squares equations used during refinement are constructed as follows. Let the number of parameters being refined (variables) be « n », and the parameters themselves be represented by the symbol « p ». There are then a series of variables « p(1) » to « p(n) » and each of these must be assigned a number between 1 and « n » which specifies which of the least squares equations refers to that parameter. For each profile point, contributions to the matrix equation :

$$A \cdot s = d \quad (2)$$

must be evaluated. « A » is a symmetric, positive definite matrix of order « n », the elements, « A(i,j) », of which are :

$$\sum \left[w \cdot \left(\frac{d y_{\text{calc}}}{d p(i)} \right) * \left(\frac{d y_{\text{calc}}}{d p(j)} \right) \right] \quad (3)$$

where « $d y_{\text{calc}} / d p(i)$ » is the partial derivative of the calculated profile intensity with respect to parameter « p(i) ». « d » is a column vector of order « n » the elements, « d(i) », of which are :

$$\sum \left[w \cdot \left(\frac{d y_{\text{calc}}}{d p(i)} \right) * (y_{\text{obs}} - y_{\text{calc}} \cdot \text{scale}) \right] \quad (4)$$

and « s » is a column vector which is to be calculated after the inversion of the matrix « A ». The summations indicated are carried out over all profile points. The elements of « s », « s(i) », are the shifts which are to be applied to the refined parameter « p (i) » in order to yield better estimates of their true value. The ESD's of the refined parameters are then given by :

$$\text{ESD}(j) = \sqrt{A^{-1}(j,j) \cdot \sum \left[w * (y_{\text{obs}} - y_{\text{calc}} * \text{scale})^2 \right] / (N - n + C)} \quad (5)$$

A^{-1} is the inverted matrix, N the total number of observations, n the number of refined parameters and C the number of constraint terms.

A more complete discussion of the least squares method is given by J. S. Rollett in « Computing Methods in Crystallography », Pergamon Press, 1965, pp. 32–37. The following documentation describes the computer program MPROF written in FORTRAN and performing the functions required for both stages. This program is extensive modifications of that originally described by Rietveld and later modified by A. W. Hewat at AERE Harwell, P. Clarke at Oxford and also M. Thomas (Harwell) and P. Bendall (Oxford) for multiphase refinement and finally A.D. Murray (London College, UK) and A.N. Fitch (Keele University, UK).

The possible Parameters for a trial structure

The parameters needed to refine by the Rietveld method a model for a crystal structure may, in the case of powder diffraction data, include the following :

Overall Parameters

1) Wavelength of the diffracted radiation.

2) Unit cell dimensions

The unit-cell dimensions of the diffracting material, a , b , c , α , β , γ are defined in Angstroms and degrees respectively. Actually in the refinement procedure are refined the components of the reciprocal metric tensor A , B , C , D , E and F and not the direct cell constants. These components are defined as :

$$\begin{aligned} A &= (a^*)^2 & B &= (b^*)^2 & C &= (c^*)^2 \\ D &= 2.b^*.c^*.\cos \alpha^* & E &= 2.a^*.c^*.\cos \beta^* & F &= 2.a^*.b^*.\cos \gamma^*. \end{aligned}$$

The « * » denotes reciprocal values. The reciprocal d -spacing d^* is then given by :

$$d_{hkl}^* = \sqrt{A.h^2 + B.k^2 + C.l^2 + D.kl + E.hl + F.hk} \quad (6)$$

3) Zero-point correction

A zero-point correction and corrections for peak-shifts caused by displacement of the sample from the axis of the diffractometer.

4) Scale factor

The scale factor relating the observed and calculated diffraction profiles (S value in equation (1)).

5) Lorentz-Polarisation factor.

For powders, the Lorentz factor is defined as :

$$L = \frac{1}{2 \cdot \sin^2 \theta \cdot \cos \theta} \quad (7)$$

For neutrons, there is no polarisation factor, just the Lorentz factor.

For X-ray diffraction, the incident X-ray beam can be polarised or non-polarised. The form adopted in WinMProf for the polarisation factor P is :

$$P = 1 + \cos^2 2\theta_m \cdot \cos^2 2\theta \quad (8)$$

where $\cos^2 2\theta_m$ is the monochromator polarisation correction.

For an unpolarised beam, $\cos^2 2\theta_m = 1$. With a pre or post sample monochromator, the $\cos^2 2\theta_m$ value must be specified. For instance, with a graphite monochromator and Cu-Kalpa radiation, $\cos^2 2\theta_m = 0,7998$.

For synchrotron radiation when the beam is 100% polarised in the plane perpendicular to the incident and diffracted beams, $\cos^2 2\theta_m = 0$.

6) Overall isotropic temperature factor.

7) Peak shape function parameters.

Nine functions to describe the peak shape are currently available :

a) Gaussian

$$G(2\theta(i)) = \sqrt{\frac{4\text{Ln}2}{\pi}} \cdot \frac{1}{H(k)} \cdot \exp\left(-4\text{Ln}2 \cdot (X/H(k))^2\right)$$

Where : $X = 2\theta(i) - 2\theta(k)$ (9)

$$H(k) = \sqrt{U \cdot \tan^2 \theta(k) + V \cdot \tan \theta(k) + W + P / \cos^2 \theta(k)} \quad (10)$$

$2\theta(i)$ is the two theta value of each profile point (i).

$2\theta(k)$ is the expected two theta value for each reflection (k).

$H(k)$ is the full width at half maximum for each reflection (k).

U, V, W and P are the « halfwidth » parameters.

Refinable parameters : U, V, W, P

b) Variable Lorentzian (Pearson VII)

$$L(2\theta(i)) = \frac{\sqrt{C}}{\pi \cdot H(k)} \cdot \left(1 / \left[1 + C \cdot (X/H(k))^2\right]^m\right)$$

$$C = 4 \cdot \left(2^{1/m} - 1\right) \quad (11)$$

m is the Lorentzian order which varies between 0 and infinity.

m = 1.0 gives the « pure » Lorentzian function.

m = 1.5 gives the « intermediate » Lorentzian function.

m = 2.0 gives the « modified » Lorentzian function.

H(k) is defined by equation (10).

Refinable parameters : U, V, W, P, m

c) Pseudo-Voigt

$$p - V(2\theta(i)) = n \cdot L(2\theta(i)) + (1 - n) \cdot G(2\theta(i)) \quad (12)$$

n is the mixing parameter which varies between 0 and 1.

L(2θ(i)) is the « pure » Lorentzian function and H(k) is defined by equation (10).

Refinable parameters : U, V, W, P, n

d) Split Pearson VII

H. Toraya (1986) J. Appl. Cryst. 19, 440

$$PVII(2\theta(i)) = \frac{Q}{H(k)} \cdot \left(\left[1 + \left(\frac{1+As}{As} \right)^2 \cdot C1 \cdot (X/H(k))^2 \right]^{Lo} \right)^{-1}$$

for $2\theta(i)$ less than or equal to $2\theta(k)$

$$PVII(2\theta(i)) = \frac{Q}{H(k)} \cdot \left(\left[1 + (1+As)^2 \cdot C2 \cdot (X/H(k))^2 \right]^{Ho} \right)^{-1}$$

for $2\theta(i)$ greater than $2\theta(k)$

$$C1 = 2^{1/Lo} - 1 \quad \text{and} \quad C2 = 2^{1/Ho} - 1$$

$$As(\theta(k)) = As(1) + As(2) / \sin \theta(k) + As(3) / \sin^2 \theta(k)$$

$$Lo(\theta(k)) = Lo(1) + Lo(2) / \sin \theta(k) + Lo(3) / \sin^2 \theta(k)$$

$$Ho(\theta(k)) = Ho(1) + Ho(2) / \sin \theta(k) + Ho(3) / \sin^2 \theta(k) \quad (13)$$

Q is a function of As, Lo and Ho and H(k) is defined by equation (10).

Refinable parameters : U, V, W, P, As(1-3), Lo(1-3), Ho(1-3)

e) Variable pseudo-Voigt

$$p - V(2\theta(i)) = nV \cdot L(2\theta(i)) + (1 - nV) \cdot G(2\theta(i))$$

$$nV(\theta(k)) = p(1) \cdot \tan^2 \theta(k) + p(2) \cdot \tan \theta(k) + p(3) \quad (14)$$

Refinable parameters : U, V, W, P, p(1-3)

f) Parameterised pseudo-Voigt

P. Thompson, D.E. Cox & J.B. Hastings (1987) J. Appl. Cryst. 20, 79

$$p - V(2\theta(i)) = n \cdot L(2\theta(i)) + (1 - n) \cdot G(2\theta(i))$$

$$n = 1.36603 \cdot (Y_L / Y) - 0.47719 \cdot (Y_L / Y)^2 + 0.11116 \cdot (Y_L / Y)^3$$

$$Y = \left[Y_G^5 + 2.69269 \cdot Y_L \cdot Y_G^4 + 2.42843 \cdot Y_L^2 \cdot Y_G^3 + 4.47163 \cdot Y_L^3 \cdot Y_G^2 + 0.07842 \cdot Y_L^4 \cdot Y_G + Y_L^5 \right]^{1/5}$$

Gaussian part $Y_G(\theta(k)) = \sqrt{U \cdot \tan^2 \theta(k) + V \cdot \tan \theta(k) + W + P / \cos^2 \theta(k)}$

Lorentzian part $Y_L(\theta(k)) = X \cdot \tan \theta(k) + Y / \cos \theta(k) + Z \quad (15)$

Refinable parameters : U, V, W, P, X, Y, Z

g) Anisotropic variable pseudo-Voigt

A. Le Bail & A. Jouanneaux (1997) J. Appl. Cryst. 30, 265

$$p - V(2\theta(i)) = nV_{hk\ell} \cdot L(2\theta(i)) + (1 - nV_{hk\ell}) \cdot G(2\theta(i))$$

$$H(k) = \sqrt{U_{hk\ell} \cdot \tan^2 \theta(k) + V_{hk\ell} \cdot \tan \theta(k) + W_{hk\ell}} \quad (16)$$

$$U_{hk\ell} = d_{hk\ell}^2 \cdot (U_{11} \cdot h^2 \cdot a^{*2} + U_{22} \cdot k^2 \cdot b^{*2} + U_{33} \cdot \ell^2 \cdot c^{*2} + 2 \cdot U_{12} \cdot hk \cdot a^* \cdot b^* + 2 \cdot U_{13} \cdot h\ell \cdot a^* \cdot c^* + 2 \cdot U_{23} \cdot k\ell \cdot b^* \cdot c^*) \quad (17)$$

$$nV_{hk\ell}(\theta(k)) = pU_{hk\ell} \cdot \tan^2 \theta(k) + pV_{hk\ell} \cdot \tan \theta(k) + pW_{hk\ell} \quad (18)$$

and similar expressions as (17) for $V_{hk\ell}$, $W_{hk\ell}$, $pU_{hk\ell}$, $pV_{hk\ell}$, $pW_{hk\ell}$.

Refinable parameters : U_{11} , U_{22} , U_{33} , U_{12} , U_{13} , U_{23}
and V_{ij} 's, W_{ij} 's, pU_{ij} 's, pV_{ij} 's, pW_{ij} 's.

h) Anisotropic variable Pearson VII

A. Le Bail & A. Jouanneaux (1997) J. Appl. Cryst. 30, 265

The function is defined as in equation (9) with $H(k)$ given by equation (14) and m is a function of $(hk\ell)$:

$$m_{hk\ell}(\theta(k)) = pU_{hk\ell} \cdot \tan^2 \theta(k) + pV_{hk\ell} \cdot \tan \theta(k) + pW_{hk\ell} \quad (19)$$

Refinable parameters : U_{11} , U_{22} , U_{33} , U_{12} , U_{13} , U_{23}
and V_{ij} 's, W_{ij} 's, pU_{ij} 's, pV_{ij} 's, pW_{ij} 's.

i) Anisotropic parameterised pseudo-Voigt

P.W. Stephens (1999) J. Appl. Cryst. 32, 281

This function is derived from the Thompson, Cox & Hastings parameterised pseudo-Voigt.

$$p - V(2\theta(i)) = n \cdot L(2\theta(i)) + (1-n) \cdot G(2\theta(i))$$

$$n = 1.36603 \cdot (Y_L / Y) - 0.47719 \cdot (Y_L / Y)^2 + 0.11116 \cdot (Y_L / Y)^3$$

$$Y = \left[Y_G^5 + 2.69269 \cdot Y_L \cdot Y_G^4 + 2.42843 \cdot Y_L^2 \cdot Y_G^3 + 4.47163 \cdot Y_L^3 \cdot Y_G^2 + 0.07842 \cdot Y_L^4 \cdot Y_G + Y_L^5 \right]^{1/5}$$

$$\begin{aligned} \text{Gaussian part} \quad Y_G(\theta(k)) &= \sqrt{U \cdot \tan^2 \theta(k) + V \cdot \tan \theta(k) + W + (1-\xi)^2 \Gamma_A^2(hkl)} \\ \text{Lorentzian part} \quad Y_L(\theta(k)) &= X \cdot \tan \theta(k) + Y / \cos \theta(k) + \xi \Gamma_A(hkl) \end{aligned} \quad (20)$$

The anisotropic contribution is included in the $\Gamma_A(hkl)$ expression :

$$\Gamma_A(hkl) = \sqrt{\sigma^2(M_{hkl})} \cdot \tan \theta(k) / M_{hkl} \quad (21)$$

Where $\sigma^2(M_{hkl})$ is the variance of $M_{hkl} = 1/d_{hkl}^2$

$$\sigma^2(M_{hkl}) = \sum_{HKL} S_{HKL} \cdot h^H \cdot k^K \cdot l^L \quad \text{with } H+K+L = 4 \quad (22)$$

Refinable parameters : U, V, W, X, Y, ξ

and $S_{400}, S_{040}, S_{004}, S_{220}, S_{202}, S_{022}, S_{211}, S_{121}, S_{112}, S_{310}, S_{130}, S_{301}, S_{103}, S_{031}, S_{013}$

Restrictions on anisotropic strain parameters depending on the Crystal system :

Cubic $S_{400} = S_{040} = S_{004} ; S_{220} = S_{202} = S_{022}$

Tetragonal $S_{400} = S_{040} ; S_{202} = S_{022}$
 $S_{004} ; S_{220}$

Orthorhombic $S_{400} ; S_{040} ; S_{004} ; S_{220} ; S_{202} ; S_{022}$

Monoclinic $S_{400} ; S_{040} ; S_{004} ; S_{220} ; S_{202} ; S_{022}$

Trigonal (R3 etc.) $S_{301} ; S_{121} ; S_{103}$

Rhombohedral indices :

$$S_{400} = S_{040} = S_{004} ; S_{220} = S_{202} = S_{022}$$

$$S_{211} = S_{121} = S_{112}$$

$$S_{310} = S_{130} = S_{301} ; S_{103} = S_{031} = S_{013}$$

Hexagonal indices :

$$S_{400} = S_{040} = S_{310} / 2 = S_{130} / 2 = S_{220} / 3$$

$$S_{202} = S_{022} = S_{112} ; S_{004}$$

$$S_{301} / 2 = -S_{031} / 2 = S_{211} / 3 = -S_{121} / 3$$

Hexagonal, Trigonal (P3 etc.) $S_{400} = S_{040} = S_{310} / 2 = S_{130} / 2 = S_{220} / 3$

$$S_{202} = S_{022} = S_{112} ; S_{004}$$

Triclinic All 15 S_{HKL} allowed

8) Correction factors for preferred orientation in the sample.

a) March–Dollase function

$$\left[G^2 \cdot \cos^2 \alpha + \sin^2 \alpha / G \right]^{-3/2} \quad (23)$$

where α is the acute angle between the scattering vector and the preferred orientation axis. The correction assumes a Gaussian distribution of the preferred orientation axes of the individual crystallites about the axis of the sample. G is the refinable parameter ($G = 1$: no preferred orientation).

b) Donnet–Jouanneaux function (purely empirical function).

$$1 + \frac{D \cdot \cos 2\alpha}{1 + (G - 1) \cdot \sin^2 \alpha} \quad (24)$$

Refinable parameters : G, D ($D = 0$: no preferred orientation).

9) Absorption and micro-absorption correction

In WinMProf, absorption correction can be applied for various geometries ; ($\mu.R$) or ($\mu.t$) is the refinable parameter, depending on the experimental setting.

The micro-absorption correction (W. Pitsche, N. Mattern & H. Hermann (1993) Powder Diff. 8, 223) takes the form :

$$1 - P_0 - \frac{C \cdot \tau}{\sin \theta} \cdot \left[1 - \frac{\tau}{\sin \theta} \right] \quad (27)$$

Refinable parameters : P_0, C, τ

Note : actually it is not recommended to refine the first parameter P_0 which is strongly correlated to the scale factor.

10) Correction for asymmetry in the peak shape

a) Howard's correction

(C.J. Howard (1982) J. Appl. Cryst. 15, 615)

The correction employs the Simpson's or Bode's integration rule and is applied in the form of a sum of n peaks, n being the number of integration ordinates. For instance, if Pseudo-Voigt function P-V is used, the corrected peak shape function PSF will be defined as :

$$\text{PSF}(2\theta(i)) = \sum_{\ell=1}^n g_{\ell} \text{P-V}[2\theta(i) - f_{\ell}(\alpha) \cdot P / \tan(2\theta(k))] \quad (25)$$

P is the asymmetry parameter ($P = 0$: no correction). The values of the Simpson's or Bode's rule coefficients, f_{ℓ} and g_{ℓ} , depend on the number of terms in the summation. $f_{\ell}(\alpha)$ is related to the ordinates positions ; α is a refinable parameter which enables the positions to be not only equidistant. In WinMProf, the correction can be applied with all peak shape functions except with the Split Pearson VII function.

Refinable parameters : P, α .

b) Finger, Cox & Jephcoat's correction

(L.W. Finger, D.E. Cox & A.P. Jephcoat (1994) J. Appl. Cryst. 27, 892)

This correction is the most physically appropriate ; it is expressed as a function of three parameters : i) L , the distance between the sample and the detector, ii) $2H$, the aperture of the detector slit and iii) $2S$, the beam size on the sample or alternately the sample size if the beam is larger. For X-ray powder diffraction, $2H$ is the horizontal width of the detector slit and $2S$ is the horizontal beam size. For neutron diffraction, $2H$ is the vertical width of the slit and $2S$ is the vertical beam size.

Refinable parameters : the ratios $S/L, H/L$.

c) Bézar & Baldinozzi's function

(J.F. Bézar & G. Baldinozzi (1993) J. Appl. Cryst. 26, 128)

The asymmetry correction, which works well for weak asymmetry, takes the form :

$$1 + \left[P_1 + 2 \cdot P_2 \cdot (2z^2 - 3) \right] \cdot \frac{F_a(z)}{\tan \theta(k)} + \left[P_3 + 2 \cdot P_4 \cdot (2z^2 - 3) \right] \cdot \frac{F_a(z)}{\tan 2\theta(k)} \quad (26)$$

where $z = \frac{2\theta(i) - 2\theta(k)}{H(k)}$ and $F_a(z)$ a function of z only.

Refinable parameters : P_1, P_2, P_3, P_4 ($P_i = 0, i = 1, 4$: no correction)

11) Refinable Background functions

Five empirical background functions are available.

a) 7th order polynomial function.

$$B(i) = BK0 + BK1.[2\theta(i)/bkpos - 1] + \dots + BK7.[2\theta(i)/bkpos - 1]^7 \quad (28)$$

B(i) is the calculated background at each point (i).

$2\theta(i)$ and $bkpos$ are in Degrees. $bkpos$ is the origin of the polynomial.

Refinable parameters : BK_j ($j=0, 7$)

b) Fourier series.

$$B(i) = BK0 + BK1.\cos 2\theta(i) + \dots + BK11.\cos(11 * 2\theta(i)) \quad (29)$$

Refinable parameters : BK_j ($j=0, 11$)

c) Double 5th order polynomial function.

$$B(i) = BK0A + BK1A.[2\theta(i)/bkpos - 1] + \dots + BK5A.[2\theta(i)/bkpos - 1]^5 \quad (30)$$

if $2\theta(i) < bkpos$

$$B(i) = BK0B + BK1B.[2\theta(i)/bkpos - 1] + \dots + BK5B.[2\theta(i)/bkpos - 1]^5 \quad (31)$$

if $2\theta(i) > bkpos$.

$bkpos$ (in Degrees) is the origin of both polynomial functions.

Refinable parameters : BK_{jA} ($j=0, 5$), BK_{jB} ($j=0, 5$)

d) Mixed background function (with 7th order polynomial function)

$bkpos$ (in degrees) is a limit angle defined by the user. It is also the origin of the polynomial. When $2\theta(i) < bkpos$, the $B(i)$ values are calculated from estimated values. Background counts at intermediate points are obtained by linear interpolation. When $2\theta(i) > bkpos$, $B(i)$ is calculated using equation (28).

Refinable parameters : BK_j ($j=0, 7$)

e) Mixed background function (with Fourier series)

As in d) when $2\theta(i) < bkpos$ (limit angle in degrees defined by the user). When $2\theta(i) > bkpos$, $B(i)$ is calculated using equation (29).

Refinable parameters : BK_j ($j=0, 11$)

Atomic Parameters

Atomic parameters which may be specified include :

- 1) The Atomic Scattering Factor which may include both nuclear and magnetic scattering for neutron diffraction, or real and anomalous scattering for X-ray diffraction.
- 2) The Site Occupation Factor, which may reflect genuine defects in the occupancy of a particular atomic site, or, more usually, is employed to produce correct structure factor contributions from atoms situated on crystallographic symmetry elements.
- 3) The Coordinates within the unit cell expressed relative to the possibly non-orthogonal unit cell axes in terms of fractions of the unit cell edge.
- 4) The Thermal vibration parameters, which may describe either isotropic or anisotropic vibration. The isotropic temperature correction to the calculated structure factor is :

$$\exp \left[- B \cdot (\sin \theta / \lambda)^2 \right] \quad (32)$$

where « B » is the temperature factor expressed in \AA^2 . The anisotropic correction for reflection (hkl) is :

$$\exp - \left[h^2 \cdot \beta(11) + h^2 \cdot \beta(22) + \ell^2 \cdot \beta(33) + 2 \cdot hk \cdot \beta(12) + 2 \cdot h\ell \cdot \beta(13) + 2 \cdot k \cdot \ell \cdot \beta(23) \right] \quad (33)$$

where $\beta(11)$ to $\beta(23)$ are the unique elements of the symmetric tensor describing the thermal vibration ellipsoid.

- 5) The components of the magnetic vector along each of the unit cell axes. If these parameters are supplied, additional symmetry information is required in order to determine the direction of the magnetic vector for each of the magnetic atoms in the unit cell. The calculation of the magnetic scattering cross section may be greatly simplified if the structure possesses either uniaxial or cubic spin configurational symmetry (see G. Shirane, *Acta Crystallographica* 1959, volume 12, pp. 282–287).

Facilities Offered by the MPROF Refinement Program

This version of the program allows calculation and refinement with contributions from up to three phases, with possibility of combining Rietveld and/or Le Bail methods. Quantitative phase analysis may be performed in Rietveld mode (see below).

In Rietveld mode, all of the structure parameters described above, with the exception of the scattering length and radiation wavelength, may be refined. For neutron diffraction, in the absence of magnetic scattering, the atomic scattering length may be effectively refined by varying the site occupation parameter which is completely correlated with it.

Symmetry relations among the atom parameters may be maintained during refinement by manipulation of refinement codewords described later. Two types of constrained refinement may be carried out. The first of these, involving « strict » constraints, allows specification of an equation relating various parameters, all but one of which must be refined. The terms in the equation may not exceed quadratic in order. The second type of constraint, « slack », Bayesian, chemical constraints, allows restrictions to be placed, with a reliability specified by the user, on interatomic distances and bond angles.

After calculation, MPROF automatically produces an output file in DIF format recognised by WinMProf (default name : Rietplot.dif) containing the observed and calculated profiles as well as the reflections positions. Various optional forms of output of structure factors and profile intensities are available, including that required for difference Fourier calculations. Different forms of output files can also be generated for various other programs (SHELXS or SHELXL, EXPO (SIRPOW), PLATON, ORTEP, STRUVIR or WinSTRUPLO, WinPLOT, GFOUR).

Simple calculation mode is also possible, without reference to observed profile data (« Calculation mode »). An output file (DIF format) containing the calculated profile and reflections positions (default name : LazyPulv.dif) is produced.

Calculation is possible with data collected with either Fixed Divergence Slits (FDS) or Variable Divergence Slits (VDS). In VDS mode, the correction factor involving illumination length, goniometer radius and divergence angle is constant for all data points and is finally included in the scale factor. Therefore, calculated intensities are simply corrected by $\sin\theta$.

Quantitative phase analysis

Quantitative phase analysis can be performed on multi-phase samples using the formalism described by R.J. Hill & C.J. Howard (J. Appl. Cryst., 20, 467, 1987). The general scattering cross-section for Bragg scattering is proportional to N/V , where N is the number of unit cells contributing to the scattering and V is the unit cell volume. The scale factor, S , in equation (1) is then proportional to N/V .

The weight fraction of phase p can then be derived as :

$$W_p = \frac{(S.Z.M.V)_p}{\sum_{i=1}^{np} (S.Z.M.V)_i} \quad (34)$$

where S is the scale factor, Z is the number of formula units per unit cell, M is the molecular weight of the formula unit, V is the unit cell volume and i is an index running over all phases. It is worth noting that $S.V$ is proportional to the number of unit cells diffracting (N) and $Z.M$ is just the molecular weight of the unit cell, hence $S.V.Z.M$ is proportional to the weight of the diffracting sample.

A Note on the Format of the Input Data

In MPROF, all of the input instructions are read in a « free-format » mode, in which all numeric values must be terminated by at least one space character or a comma. Certain defined values are expected to be integers and should therefore not include decimal points, but there is no requirement to insert a decimal point in a decimal value unless there are figures following it. The program also recognises simple fractions (e.g. 1/2, 1/6) and exponential format (1.6D-10, -3.2E+4).

For the most part, the program scans one line of input data at a time searching for a definite number of values (this is defined as « input mode 0 »). If not all of these values are found (that is not all of them have been provided), then those not specified are set to zero. Hence, if the program expects to read five decimal values from a line of input data, the following representations are equivalent :

```
1 2
1 2 0 0 0
1.0 2.0 0.0 0.0 0.0
```

as are the combinations possible with or without decimal points :

```
1 2.0
etc.
```

In the above example, note that the specification of the fifth value, but not the third or fourth, would require one of the following :

```
1 2 0 0 3
1.0 2.0 0.0 0.0 3.0
```

An alternative mode of input, which is used for magnetic scattering factors or atoms requiring magnetic vector components or anisotropic temperature factors, allows the data to be spread over more than one line of input. In this case, all the values to be input must be provided, even if they are zero. The program will continue to input values until the required number of these has been read. (This is defined as « input mode 1 »). If it is required to input three values in input mode 1, the following examples are equivalent :

```
1 2 0

1
2
0

1          2
      0
```

The use of input mode 1 is restricted to those cases where not all the required values can be given on one line owing to the limit of 80 characters per line in the data, or where a definite number of generally non-zero values must be input. In the majority of cases it is not necessary to provide all of the values which may be inserted on a line of data.

Lines beginning with a « # » symbol are treated as comments and will normally be ignored by the program. Comments cannot be included in the input diffraction data.

In the description of the input data required by the program given in the remainder of this document, the following conventions are used :

- ivalue indicates that input of an integer value is required.
- value indicates that input of a real (floating point) number is required.
- char indicates that input of a character string is required.

Lines (or group of lines) marked « For Each phase » must be repeated for every phase that is required.

Input data for MPROF Profile Refinement Program

Line 1. Title

A title consisting of up to 80 characters which will be used as a heading for printed output, or, up to twenty lines of 80 characters each, preceded by a line whose first five characters are TITLE, and terminated by a line whose first three characters are END.

Line 2. Overall Refinement Options

- ivalue(2.1) number of refinement cycles.
If specified as zero, then structure factors and profile intensities will be calculated and may be output.
(Maximum 99)
- ivalue(2.2) number of phases.
(Maximum 3)
- ivalue(2.3) number of parameters to be refined.
(Maximum 300)
- ivalue(2.4) a non-zero value indicates that an asymmetry parameter is to be applied to the pattern and requires inclusion of value(2a.1) and optional line 23.
allowed values of this parameter are :
- 1 Finger, Cox & Jephcoat method. This method may be applied only when pseudo-Voigt functions are used (i.e. when ivalue(10.2) equals 2, 4, 5, 6 or 8).
 - 2 Berar & Baldinazzi function.
 - N with ($3 \leq N \leq 11$) : Howard's method using Simpson's or Bode's integration rule
N is the number of ordinates. This method can be applied with any of the peak shape functions except the Split Pearson VII function (i.e. when ivalue(10.2) equals 3).
- ivalue(2.5) allowed values of this parameter are :
- 0 a normal single zero-point correction will be applied. A non-zero value leads to the application of a correction to the peak positions arising from displacement of the sample from the axis of the diffractometer.
 - 1 Debye-Scherrer geometry,
 $\Delta 2\theta = a/R \cdot \cos\theta - b/R \cdot \sin 2\theta$
 - 2 Flat plate, $\theta / 2\theta$ geometry,
 $\Delta 2\theta = b/R \cdot \cos\theta$
 - 3 Flat plate at fixed sample angle alpha,
 $\Delta 2\theta = b/R \cdot \sin 2\theta / \sin(\alpha)$
 - 4 Flat plate transmission geometry,
 $\Delta 2\theta = -a/R \cdot \sin 2\theta$
- Where a and b are sample displacement in the directions parallel with and perpendicular to the incident beam, respectively, and R is the sample to detector distance. The parameters to be entered are value(18.1) and possibly values(18.2) and (18.3). Option 3 additionally requires the sample angle alpha, value(2a.2).
- ivalue(2.6) A non-zero value leads to calculation of an empirical background.
allowed values are :
- 0 The background value is calculated from estimated values. Background counts at intermediate points are obtained by linear interpolation. This option requires inclusion of a non-zero value for ivalue(3.5) and of optional line 6.
 - 1 The background is calculated as a 7th order polynomial function

- 2 Cosine Fourier series.
- 3 Double 5th order polynomial function.
- 4 Mixed background function (with 7th order polynomial function).
- 5 Mixed background function (with Fourier series).

Options 1 to 5 require inclusion of optional lines 24 and 25. Options 1, 3, 4 and 5 require inclusion of optional value(2a.3). Options 4 and 5 require inclusion of a non-zero value for ivalue(3.5) and of optional line 6.

- ivalue(2.7) a non-zero value leads to the application absorption correction.
allowed values are :
- 0 Debye-Scherrer geometry, or a fully absorbing flat plate specimen in $\theta/2\theta$ geometry. No correction for absorption is applied.
 - 1 Partially absorbing flat plate specimen in $\theta/2\theta$ geometry.
 - 2 Fully absorbing flat plate specimen at fixed sample angle alpha.
 - 3 Partially absorbing flat plate specimen at fixed sample angle alpha.
 - 4 Symmetric scanning transmission geometry.
 - 5 Transmission geometry at fixed sample angle alpha.
 - 6 Capillary Sample.
 - 7 Micro-absorption correction in flat plate $\theta/2\theta$ geometry.
- All non-zero options (except 2 and 7) require input of the absorption parameter (value(18.4)). Options 2, 3 and 5 additionally require the sample angle alpha, value(2a.2). Option 7 requires micro-absorption coefficients (optional line 19).
- ivalue(2.8) a non-zero value leads to correction for depolarisation of the incident synchrotron radiation, when the beam is not 100% polarised in the plane perpendicular to the incident and diffracted beams.
- 0 incident beam is 100% plane polarised.
 - 1 incident radiation is on average value(18.5)x100% depolarised.
 - 2 incident radiation is on average value(18.5)x100% depolarised and the diffracted beam is incident upon an analyser crystal (whose normal lies in the plane of the incident and diffracted radiation) which acts as a receiving slit before the detector. Option requiring the further input of the 2θ angle of the analyser crystal, value(2a.4). Note this option only applies to synchrotron radiation.
- ivalue(2.9) a non-zero value leads to Fourier filtering of the residual background and requires inclusion of values(2a.5) to (2a.8).
If ivalue(2.9) equals 2 the values from a previous refinement will be read in from the file (see keyword options).
- ivalue(2.10) a non-zero value leads to the following options :
- 1 correction to the intensities arising from absorption of a covering film over a flat plate sample, and requires the absorption parameter of the film value(2a.9).
 - 2 correction to the intensities in flat plate geometry when the cross section of the sample is lower than the beam dimensions at low angles.
- ivalue(2.11) a non-zero value leads to minimisation using proportionate discrepancies. This option should be set when performing a multipattern refinement using different scale factors for each phase, when refining conventional alpha 1-alpha 2 X-ray radiation, and is set automatically when refining a background function.
- ivalue(2.12) weighting schemes
- 0 $w(i) = 1 / Y_{obs}(i)$
 - 1 $w(i) = 1 / Y_{calc}(i)$

Optional line set 2a.

- value(2a.1) the 2θ angle in degrees below which the asymmetry correction is to be applied. To be supplied only when ivalue(2.4) is non-zero.
- value(2a.2) the fixed angle in degrees of a flat plate specimen. To be supplied only if ivalue(2.5) equals 3, or ivalue(2.7) equals 2, 3 or 5.
- value(2a.3) When ivalue(2.6) equals 1, 3 or 4, value(2a.3) is the 2θ angle in degrees corresponding to the origin of the background polynomial. For option 4, this angle is both the origin of the polynomial function and the angle above which the empirical background is calculated. When ivalue(2.6) equals 5, value(2a.3) is the 2θ angle above which the empirical Fourier series is calculated.
- value(2a.4) the 2θ angle in degrees of the analyser crystal before the detector when synchrotron radiation is used. To be supplied only when ivalue(2.8) equals 2.
- value(2a.5) starting value for the summation in real space for Fourier filtering (in Angstrom – recommended value = 0.0).
- value(2a.6) end value for the summation.
- value(2a.7) step value for the summation.
- value(2a.8) number of data points To be used in the inverse Fourier transform (a zero value uses all profile points).
- Values(2a.5) – (2a.8) are to be supplied only if ivalue(2.9) is non-zero.
- value(2a.9) the absorption parameter (μ^*t) of the covering film only when ivalue(2.10) is equal to 1. When ivalue(2.10) equals 2, the θ_0 angle in degrees at which the sample intercepts completely the X-ray beam.

Line 3. Preprofile preparation options

- value(3.1) the 2θ range over which a reflection is assumed to yield a significant contribution to the profile is calculated from : $2*\text{value}(3.1)*H(k)$, where $H(k)$ is the halfwidth at half maximum.
- value(3.2) the monochromator polarisation constant, $\cos^2 2\theta_m$. For neutron or synchrotron radiation, value(3.2) must be set to zero.
- ivalue(3.3) a non-zero value allows the preparation stage to be carried out and yields output of the lineprinter file mprep.lis containing the main informations related to this stage.
This step consists in the determination (from consideration of the lattice parameters and profile parameters) of which reflections may contribute to each of the observed points in the powder diffraction profile. Values(3.1) and (3.2) and excluded regions (ivalue(3.4)) are also used in this step. The reorganised data will be regrouped in a convenient form in a binary file (default filename : fort.3) which will be used in the next least-squares refinement stage.
- When ivalue(3.3) is zero, the binary file is read in from a previous refinement and no lineprinter file is produced.
- ivalue(3.4) number of excluded regions.
(Maximum 9)
- ivalue(3.5) number of background estimates.
(Maximum 99)
This value must be non-zero when ivalue(2.6) is equal to 0, 4 or 5.

Optional Line set 4. Excluded regions values

To be supplied only if value(3.4) is non-zero

- value(4.1) lowest 2θ value (in degrees) of the excluded region
- value(4.2) highest 2θ value (in degrees) of the excluded region
- Value(3.4) lines are to be supplied.

Line 5. Experimental datafile Name, range of calculation, FDS or VDS mode

Char(5.1) <Filename> (30 characters maximum)

where <Filename> is the name of the file containing the experimental profile data ; the filename extension must be imperatively one of the five possible extensions, D1A, PDS, FR1, FR2 or PHI, depending on the format of the profile data.

value(5.2) start angle for reading the data from the file.

value(5.3) finish angle for reading the data from the file (angles in degrees)

When Values(5.2) or (5.3) are input as zero, the start or finish angles are read directly from the experimental data file.

When char(5.1) is input as the word « calculation », a simple calculation without reference to observed data is carried out by the program. In that case, several control codes, such as ivalue(2.1), (2.3) etc..., are automatically set to zero. In « calculation mode », the angular range of calculation is defined by values(5.2) and (5.3) , and the angular step by value(5.4). These 3 values are to be supplied imperatively.

value(5.4) to be supplied only when char(5.1) is specified as the word « calculation ». The angular step of calculation (in degrees).

ivalue(5.5) This parameter must be non-zero for a diffraction pattern collected in flat-plate geometry with Variable Divergence Slits (VDS). Calculated intensities will be corrected by $\sin\theta$.

Optional Line set 6. Background values

To be supplied only if value(3.5) is non-zero

value(6.1) 2θ in degrees.

value(6.2) background count at 2θ equals value(6.1).

Value(3.5) lines are to be supplied. The first background value should be given either before or at the point where the first profile intensity was measured. Background counts at intermediate points are obtained by linear interpolation.

Note that background values may be given even if ivalue(2.6) equals 1,2 or 3. They will be read in but not used by the program.

Line 7. Output Options

- ivalue(7.1) Allowed values of this parameter are :
- 0 : no action.
 - 1, 2 or 3 (depending on ivalue(2.2), number of phases present in the pattern) : output of a file containing the final observed and calculated structure Factors for phase number ivalue(7.1) in a form suitable for input to the associated Fourier program MFOURS (default filename : mfours.mfs) (see also keyword option ASYU).
 - 11, 12 or 13 (depending on ivalue(2.2)) : output for phase number [ivalue(7.1)–10] of both files in a form suitable for input to the Fourier program GFOUR (default filenames : GFourier.inp and GFourier.fou).
 - 1, –2 or –3 (depending on ivalue(2.2)) : output of a file containing the final observed structure Factors squared for phase number abs[ivalue(7.1)] in a form suitable for input to the program SHELXL (default filename : shelx.hkl) (see also ivalue(7.3)).
- This option acts only when the selected phase is refined in normal Rietveld calculation mode (i.e. when ivalue(12.7) of the corresponding phase equals 0).
- ivalue(7.2) a non–zero value produces output of the final observed and calculated peak intensities (and optionally, profile intensities) to the lineprinter file.
- allowed values are:
- 1 output peak intensities.
 - 2 output structure factor squared.
 - 1 output peak intensities and observed and calculated profiles.
 - 2 output structure factor squared and observed and calculated profiles.
- ivalue(7.3) Allowed values of this parameter are :
- 0 : no action.
 - Positive value : output of calculated bond lengths and angles to the lineprinter file (see keyword option BOND) for phase number ivalue(7.3).
 - Negative value :
 - When phase number abs[ivalue(7.3)] is refined in normal Rietveld calculation mode (i.e. when ivalue(12.7) of the corresponding phase equals 0), this option produces output of a file containing useful data in a form suitable for input to the programs SHELXL (possible combination with a negative value for ivalue(7.1)).
 - When phase number abs[ivalue(7.3)] is refined in LeBail decomposition mode (i.e. when ivalue(12.7) is not equal to zero), this option produces output of both files containing required data in a form suitable for input to the program SHELXS (ivalue(12.8) positive) or EXPO (SIRPOW) (ivalue(12.8) negative). The default filenames are : shelx.inp and shelx.hkl for SHELXS output and sirpow.exp and sirpow.hkl for EXPO output.
- ivalue(7.4) a non–zero value leads to output of a file in a form suitable for input to the program WinPLOTTR (.PRF format) containing the observed and calculated profiles as well as the reflections positions.
- ivalue(7.5) Allowed values of this parameter are :
- 0 : no action.
 - Positive value : output of a file containing useful data for phase number ivalue(7.5) in a form suitable for input to the program STRUVIR or WinSTRUPLO.
 - Negative value : output of a file in SHELX format containing useful data for phase number abs[ivalue(7.5)] in a form suitable for input to the programs PLATON or ORTEP.

- ivalue(7.6) To be supplied only if ivalue(2.9) is non-zero.
A non-zero value leads to output of the Fourier filtered residuals in a form suitable for re-input or plotting (DIF format).
- ivalue(7.7) To be supplied only if ivalue(2.9) is non-zero.
A non-zero value leads to output of the radial distribution function from Fourier filtering in a form suitable for plotting (with EXCEL or other equivalent softwares).
- ivalue(7.8) Correlation matrix output key.
Allowed values of this parameter are :
Negative output of the final correlation matrix to the lineprinter file.
0 no action
Positive output of the correlation coefficients greater than ivalue(7.8)/100 to the lineprinter file.
- ivalue(7.9) a non-zero value produces output of the final variance-covariance matrix to the lineprinter file.

Keyworded Input

Optional keyworded input can be supplied. The format of this input is :

KEYWORD parameter list

If any keyword is not supplied, the default values shown will be used.

Allowed keywords are :

- ASYU xmin xmax ymin ymax zmin zmax
The asymmetric unit coordinates used by the associated program MFOURS. This option acts only when ivalue(7.1) is positive. Default values are : 0 1 0 1 0 1.
- BOND ivalue1 value2 value3 value4
Calculate bond lengths and bond angles for atoms in phase ivalue1 at a distance apart within the range value2 to value3, and contact distances only for atoms separated by value3 - value4.
Default values : value2 = 0.8 ; value3 = 2.0 ; value4 = 2.8.
This keyword is used only when ivalue(7.3) is positive.
- CHEC check validity of input data only. No refinement or calculation of intensities will be carried out.
- FFIN filename (30 characters)
Fourier filtered input will be read from file filename.
- FFOU Fourier filtered output will be written to file filename.
Default values : FFIN = FFOU = fort15.dif.
- INPU filename (30 characters)
Binary input file generated in the preparation stage.
Default : fort.3

NEWF	filename (30 characters) with extension (.pro) MPROF produces systematically output of an updated input control file (default filename : newfile.pro). Option NEWF allows this filename to be changed. Note that the same filename as the initial one may be given.
PLOT	filename (30 characters) with extension (.dif) Output file for observed and calculated profiles. Default : Rietplot.dif in Rietveld mode ; LazyPulv.dif in calculation mode.
RDFP	filename (30 characters) Output file for Fourier filtered radial distribution function. Default : rdf.dat
FOUR	filename (30 characters) File for output of observed and calculated structure factors for input to Fourier programs GFOUR or associated MFOURS (for this latter program, use an extension .mfs) or of observed structure factors squared for input to SHELXL. Default filenames are respectively shelx.hkl, GFourier.fou and mfours.mfs for SHELXL, GFOUR and MFOURS.
GINP	filename (30 characters) Output File of the control file for GFOUR program. Default : GFourier.inp.
SHEL	filename (30 characters) Default : shelx.inp for SHELXL / SHELXS or sirpow.exp for EXPO output This option acts only when ivalue(7.3) is negative.
SIRP	filename (30 characters) Default : shelx.hkl for SHELXS or sirpow.hkl for EXPO (SIRPOW) output. This option acts only when ivalue(7.3) is negative.
STRU	filename (30 characters) Output File for the programs STRUVIR or WinSTRUPLO (Default : struvir.dat) or PLATON or ORTEP (Default : Plat_Ort.dat).

Line 8. Constraints Indicators

- ivalue(8.1) a non-zero value indicates that ivalue(8.1) « strict » constraint function(s) will be supplied, and requires the inclusion of optional line set 36.
- ivalue(8.2) a non-zero value indicates that chemical constraint function(s) will be supplied, and requires the inclusion of optional line set 37.

The set of lines 9 to 14 must be supplied For Each phase

Line set 9. Text and data for quantitative phase analysis

- Char(9.1) Up to 16 characters (no space) which will be used as a heading on output.
- value(9.2) the product (Z.M), where Z is the number of formula units per unit cell and M is the (molar) mass of the formula unit. When value(9.2) is input as zero, no quantitative analysis is performed.
- value(9.3) the Brindley coefficient which accounts for micro-absorption effects (useful for quantitative phase analysis). This value is reset to 1.0 if input as zero.

Line set 10. Refinement Type and Preferred Orientation Option

- ivalue(10.1) refinement type indicator.
Allowed values of this parameter are :
- 0 neutron nuclear scattering only.
 - 1 neutron nuclear scattering plus magnetic scattering calculated from the formula given by O. Halpern and M. H. Johnson (Physical Review 1939, vol. 55, p. 898).
 - 2 neutron nuclear scattering plus magnetic scattering calculated from the special formula for uniaxial configuration spin symmetry (Shirane, loc.cit. This option requires the inclusion of optional line 11.)
 - 3 neutron nuclear scattering plus magnetic scattering calculated from the special formula for cubic configurational spin symmetry (Shirane, loc. cit.).
 - 4 diffraction of synchrotron or of alpha-1 radiation.
 - 5 conventional X-ray diffraction with alpha-1 alpha-2 radiation.

Note : To account for magnetic scattering only when ivalue(10.1) equals 1, 2 or 3 (i.e. to remove the nuclear scattering contribution), ivalue(12.4) must be set to zero.

- ivalue(10.2) peak-shape function indicator.
Allowed values are :
- 0 Gaussian peak-shape.
 - 1 Variable Lorentzian (Pearson VII).
 - 2 Pseudo-Voigt.
 - 3 Split Pearson VII (Toraya).
 - 4 Variable pseudo-Voigt.
 - 5 Parameterised pseudo-Voigt (Thompson, Cox & Hastings).
 - 6 Anisotropic variable pseudo-Voigt (Le Bail & Jouanneaux).
 - 7 Anisotropic variable Pearson VII (Le Bail & Jouanneaux).
 - 8 Anisotropic parameterised pseudo-Voigt (Stephens).

- ivalue(10.3) a non-zero value leads to the application of the preferred orientation correction, and requires inclusion of optional values (10.4) to (10.6) and optional line 22.
allowed values are :
- 1 March-Dollase function
 - 2 Donnet-Jouanneaux function

The three following values are to be supplied only when ivalue(10.3) is non-zero.

- value(10.4) >
>
value(10.5) > Zone axis of the preferred orientation axis.

value(10.6) >
>

ivalue(10.7) acts only when ivalue(3.3) is non-zero. When ivalue(10.7) is non-zero, the reflections are not generated by the program in the preparation stage, but read in from existing file patti.hkl where i is the serial number of the phase.

Optional line set 11. Unique Magnetic Axis.

To be supplied when ivalue(10.1) is equal to 2.

value(11.1) >

>

value(11.2) > Zone axis of the unique magnetic axis.

>

value(11.3) >

Line set 12. Structure Indicators

ivalue(12.1) [non] centrosymmetric key.
 allowed values of this parameter are :
 0 the symmetry operators information will be internally retrieved by the program from the space group symbol read in line 13.
 1 the structure is non-centrosymmetric.
 2 the structure is centrosymmetric.

For magnetic refinements (ivalue(10.1) equals 1, 2 or 3), ivalue(12.1) must be non zero.

ivalue(12.2) to be supplied only when ivalue(12.1) is non-zero.
 the number of spacegroup symmetry operators which define the nuclear structure. Exclude the identity operation (x,y,z), operations related by a centre of symmetry and those due to centred cells. The maximum number of operators which may be supplied is therefore 23.
 When ivalue(12.2) is non-zero, optional line set 14 must be supplied.

ivalue(12.3) the number of atoms contained in the asymmetric unit of the structure. (Maximum 99).

ivalue(12.4) the number of different types of atom which give rise to neutron nuclear scattering. (Maximum 8).

ivalue(12.5) the number of different types of atom which give rise to neutron magnetic or normal X-ray scattering, or to neutron paramagnetic background scattering. (Maximum 8).

ivalue(12.6) applicable only when the structure gives rise to neutron magnetic scattering (ivalue(12.6) must be set to zero when ivalue(10.1) is equal to 0, 4 or 5).
 The number of rotation matrices associated with each of the ivalue(12.2) spacegroup symmetry operators (for magnetic scattering, ivalue(12.1) must be non zero). These rotation matrices are applied to the magnetic vectors in order to transform them from the reference position in the asymmetric unit to other sites which are structurally, but not necessarily magnetically, related. When ivalue(12.6) is non-zero, optional line set 14a must be supplied.

ivalue(12.7) Rietveld (structure constraint) or Le Bail (full pattern matching) option.
 Allowed values are :
 0 Normal Rietveld calculation mode with structural model.
 1 Cell constrained profile fitting procedure (Le Bail decomposition method or Full pattern matching). This option acts only when ivalue(10.1) equals 0, 4 or 5.
 This option produces output of a file profi.hkl (i is the serial phase number) which can be used either for re-input for MPROF or for output in a form suitable for input to the SHELXS or EXPO (SIRPOW) programs (see ivalue(7.3) option).

ivalue(12.8) applicable only when ivalue(12.7) is non-zero (i.e. for the Le Bail method).
 allowed values of this parameter are :
 1 initial structure factors squared are read in from the file profi.hkl or generated by MPROF if that file does not exist.
 2 initial structure factors squared calculated from atomic coordinates entered.

When ivalue(12.7) and ivalue(12.8) are combined with a negative value for ivalue(7.3), output files are produced respectively in SHELXS format (ivalue(12.8) positive) or EXPO (SIRPOW) format (ivalue(12.8) negative).

Line 13. Space group symbol(e.g. : p2(1)/m ; r-3m ; P6(3)/mmc ; pbnm)

Char(13.1) <Space Group symbol>

When ivalue(12.1) is set as zero, the space group symbol is used for both generating the reflections and retrieving symmetry operators information. When ivalue(12.1) equals 1 or 2, it is used for the reflections generation only.

The program can generate h,k,l reflection lists for any unit cell, i.e. for triclinic, monoclinic (any axis unique), orthorhombic, tetragonal, trigonal (including the use of either rhombohedral or hexagonal unit cells for rhombohedral spacegroups), hexagonal, and cubic systems. For tetragonal and hexagonal unit cells, the z-axis must be unique. All the information needed to determine extinction conditions and the multiplicities of the reflections is determined solely from the spacegroup symbol.

From the space group symbol, the code for [non] centrosymmetry and the symmetry operators are retrieved by MPROF using Prof. Burzlaff's routine. In principle, any space group should work with the following restrictions in case of multiple settings.

Are then recognised :

- a) Orthorhombic symmetry : the setting with « Origin -1 » only.
- b) Tetragonal symmetry : the setting with « Origin -1 » or « Origin 2/m » only.
- c) Trigonal (Rhombohedral) symmetry : hexagonal setting only for rhombohedral space groups.
- d) Cubic symmetry : the setting with « Origin -3 » or « Origin -3m » only.

Optional line set 14. Symmetry operators.

To be supplied only when ivalue(12.2) is non zero.

ivalue(12.2) symmetry operators must be supplied in verbatim form according to the keyworded scheme :

e.g.

Spacegroup n° 64, C m c a

SYMM X, -Y, -Z

SYMM X, 0.5-Y, 0.5+Z

SYMM X, 0.5+Y, 0.5-Z

The identity symmetry operation should never be specified, but is given a serial number 1. Then, each time the keyword « SYMM » is encountered, the serial number of the symmetry operation is incremented by one.

Optional line set 14a. Magnetic Vector Rotation matrices.

To be supplied only when ivalue(12.6) is non zero.

Value(14a.1) until value(14a.9) are the elements of a matrix describing the rotation or reflection which must be applied to the magnetic vector to transform to the space group position immediately preceding the matrix. Values of ivalue(12.6) greater than one allow different magnetic vector rotation matrices to be applied to different atoms, since the serial number of the magnetic vector rotation matrix must be specified for each atom (optional ivalue(16.9)). In the case where there are two spacegroup symmetry operations plus the magnetic vector rotation matrices, the structure of the input data for line set 14 is :

Space group symmetry operator (1)
 Magnetic vector rotation matrix (1.1)
 Magnetic vector rotation matrix (1.2)
 Space group symmetry operator (2)
 Magnetic vector rotation matrix (2.1)
 Magnetic vector rotation matrix (2.2)

If « Kx », « Ky », « Kz » are the components of the magnetic vector along the x, y, z crystallographic axes respectively, then the matrix multiplication carried out on transforming to a new space group position is :

$$\begin{aligned} Kx' &= \text{value}(14a.1)*Kx + \text{value}(14a.2)*Ky + \text{value}(14a.3)*Kz \\ Ky' &= \text{value}(14a.4)*Kx + \text{value}(14a.5)*Ky + \text{value}(14a.6)*Kz \\ Kz' &= \text{value}(14a.7)*Kx + \text{value}(14a.8)*Ky + \text{value}(14a.9)*Kz \end{aligned}$$

(Note : rotation matrices may also be supplied in verbatim form as in line set 14).

Line 15. Wavelength(s) and Refinement Regulators.

- value(15.1) the neutron or synchrotron wavelength, or the wavelength of the alpha-1 radiation for X-ray refinement.
- value(15.2) The wavelength of the alpha-2 radiation.
To be supplied only when conventional X-ray diffraction with alpha-1 alpha-2 radiation refinement is carried out (ivalue(10.1) equals 5)
Note: this value should not be supplied when refining with data from synchrotron radiation.
- value(15.3) Intensity ratio $I(\alpha-1) / I(\alpha-2)$.
To be supplied only when conventional X-ray diffraction with alpha-1 alpha-2 radiation refinement is carried out (ivalue(10.1) equals 5)
- value(15.4) the refinement will be terminated if all of the shifts in the refined parameters are less than the product of value(15.4) and the standard deviations of the parameters. A typical value is 0.3.

The remaining five values specify the fraction of the calculated shift which is To be applied to the type of parameters specified below. If any of these relaxation factors is input as zero, it is immediately set to 0.8.

- value(15.5) applies to atomic coordinates.
- value(15.6) applies to the temperature factors and the preferred orientation parameter.
- value(15.7) applies to the scale and site occupation factors, and to the components of the magnetic vector.
- value(15.8) applies to the zero-point and the halfwidth, cell, depolarisation, absorption and asymmetry parameters.
- value(15.9) applies to background parameters.

Input of Scattering Factors

The input of scattering factors is controlled by keyworded input. The three character keyword determines which type of scattering factor is to be read in. Termination of scattering factor input occurs when the keyword « END » is read in.

A) Neutron Nuclear Scattering lengths.

To be supplied only when ivalue(10.1) is less than 3.

Keyword – NEU

Example :

NEU Nb

Neu P

Neu 0.5803

The input of neutron scattering factors, independent of $\sin\theta/\lambda$, is controlled by the keyword « NEU ». Each time this keyword is encountered, the scattering factor number is incremented by one. The scattering length values can be supplied directly (in the example 0.5803 which is the value for oxygen atom) or are retrieved by the program (according to the values given by V.F. Sears, Neutron news, vol.3, pp 26–37, 1992) when the atom name (e.g. Nb and P) is given (all elements from hydrogen H to curium ^{244}Cm are recognised by MPROF. Deuterium is defined as « D »). Thus the value or atom symbol following the first « NEU » keyword constitutes scattering factor 1, values following the second « NEU » keyword constitute curve 2 etc. Only the first ivalue(12.4) values are read in.

B) Neutron magnetic Scattering curves

To be supplied only when ivalue(10.1) equals 1, 2 or 3 and ivalue(12.5) is greater than zero.

Keyword – MAG

The neutron magnetic scattering curves should be supplied according to the following scheme. The keyword, followed by an integer, <ipairs>, giving the total number of $\sin\theta/\lambda$ and F scattering factor pairs, is input on a single line. The following line(s) should contain <ipairs> pairs of $\sin\theta/\lambda$ and F values. The input may be spread over more than one line, but all values must be given even if they are zero (a total of 2 times <ipairs> values). The values to be input are therefore, alternately, $\sin\theta/\lambda$ followed by the value of F at that value of $\sin\theta/\lambda$, and so on (maximum value of <ipairs> is 49).

Neutron magnetic scattering factor curves should be normalised so that the value of F at $\sin\theta/\lambda = \text{zero}$ is 1 (unity). Each time the keyword « MAG » is encountered, the scattering curve number is incremented by one. The values following the first « MAG » keyword constitute curve 1, values following the second « MAG » keyword constitute curve 2 etc. the curves are assigned to individual atoms according to optional ivalue(16.8).

Example :

MAG 10

0.0	1.0	0.2	0.8	0.4	0.65	0.6	0.54	0.8	0.49
1.0	0.35	1.2	0.25	1.4	0.20	1.6	0.16	1.8	0.10

Values of F at intermediate values of $\sin\theta/\lambda$ are calculated by linear interpolation. If a reflection occurs at a value of $\sin\theta/\lambda$ lower than the first value input in the curve, an error occurs. If a reflection occurs at a value of $\sin\theta/\lambda$ higher than the last value supplied in a curve, the value of F at the highest value of $\sin\theta/\lambda$ given in the curve, will be used.

C) X-ray Atomic Scattering Factor Curves

To be supplied only when ivalue(10.1) is greater than 3 and ivalue(12.5) is greater than zero.

Keywords – XRA,F0, F1, F2

The input of X-ray scattering curves is controlled by above four keywords in the following manner. Each time the keyword « XRA » is encountered, the number of the scattering curve is incremented by one.

The X-ray scattering curve is defined as :

$$f(\sin\theta/\lambda) = f_0 + f' + if'' \quad (35)$$

where (f_0) is the atomic scattering factor, (f') and (f'') are the real and imaginary dispersion terms respectively.

In MPROF, values of (f_0) are calculated using the formula :

$$f_0(\sin\theta/\lambda) = \text{SUM} \left[a(i) \cdot \exp\left(-b(i) \cdot (\sin\theta/\lambda)^2\right) \right] + c \quad (i = 1, 4) \quad (36)$$

The nine coefficients $a(i)$, $b(i)$, $i = 1, 4$ & c can be either retrieved by the program simply by supplying the atom name just after the keyword « XRA » on the same line (neutral atoms and ions (e.g. as Sr^{2+} , O^{2-} etc.) are recognised by MPROF) or input by using the keyword F0. In that case, nothing should be given after the keyword « XRA » which must be supplied on a single line.

Input of Scattering factors (f_0)

Keyword – F0

The line following that with F0 must contain the nine values $a(i)$, $b(i)$, $i = 1, 4$ & c (even if some of them are zero). This keyword should normally not be used, since the nine coefficients can be directly retrieved by MPROF by supplying the atom name after the « XRAY » keyword on the same line.

The « XRA » keyword can be followed by none, one or two of the remaining keywords controlling the input of respectively the real dispersion term (f') and the imaginary dispersion term (f'').

Input of Real X-ray Dispersion Curves (f')

Keyword – F1

The keyword, followed by an integer, <ipairs>, giving the total number of $\sin\theta/\lambda$ and f' scattering factor pairs, is input on a single line. The following line(s) should contain <ipairs> pairs of $\sin\theta/\lambda$ and f' values. The input may be spread over more than one line, but all values must be given even if they are zero (a total of 2 times <ipairs> values). The values to be input are therefore, alternately, $\sin\theta/\lambda$ followed by the value of f' at that value of $\sin\theta/\lambda$, and so on. Values of f' at intermediate values of $\sin\theta/\lambda$, are calculated by linear interpolation. If <ipairs> is given as 1, the f' curve is assumed to be flat, i.e. constant at the value input.

Imaginary X-ray Dispersion Terms (f'')

Keyword – F2

The keyword, followed by the value of the X-ray imaginary dispersion term, independent of $\sin\theta/\lambda$, are supplied on a single line.

Note : when using Kalpha X-ray radiation for copper, keywords F1 and F2 may be not supplied, because the corresponding dispersion terms values are internally known by MPROF.

Examples

For $\lambda = 1.300$ Angstroms.

XRA Ba

F1 1

0.0 -0.555

f2 6.41

XRA

O

F0

3.0485 13.2771 2.2868 5.7011 1.5463 0.3239 0.867 32.9089 0.2508

F1 10.0 0.032

F2 0.023

END

$\lambda = 1.5406$ Angstroms.

XRA Ba

XRA O

END

D) « END » Keyword

One END keyword must be supplied to terminate the input of scattering factors. After the « END » keyword, the next line of the input data should be the atomic parameters, line 16.

A unit value for ivalue(16.13) converts the input to « input mode 1 » and requires input of optional values (16.14) to (16.19). These data may be spread over more than one line, but all values must be given even if they are zero.

Values (16.14) to (16.19) should only be supplied when ivalue(16.13) is equal to 1.

value(16.14)	>	< $\beta(11)$
	>	<
value(16.15)	>	< $\beta(22)$
	>	<
value(16.16)	>	< $\beta(33)$
	> Components of the anisotropic temperature	<
value(16.17)	> factor according to equation (33)	< $\beta(12)$
	>	<
value(16.18)	>	< $\beta(13)$
	>	<
value(16.19)	>	< $\beta(23)$

Line set 17. Scale and Overall Temperature Factors for Each phase.

value(17.1)	scale factor for neutron diffraction data, or X-ray alpha 1 radiation or synchrotron radiation.
value(17.2)	overall isotropic temperature factor, applied to each atom in addition to any individual atomic temperature factor specified in line set 16.

Line 18. Zero-point, Specimen Displacement, Absorption parameter and Depolarisation Factor

value(18.1)	the zero-point error relating the true 2θ value to that indicated by the counter arm scale (in units of hundredths of a degree). The zero point error is subtracted from the counter reading in calculating the true 2θ value.
value(18.2)	To be supplied only if ivalue(2.5) is equal to 1 or 4. a/R as described in line 2.
value(18.3)	To be supplied only if ivalue(2.5) is equal to 1, 2 or 3. b/R as described in line 2.
value(18.4)	To be supplied only when ivalue(2.7) is neither equal to 0 nor to 2, nor to 7. Sample absorption parameter μ^*t for a flat-plate specimen (options 1, 3, 4, 5) or μ^*r for a capillary specimen (option 6), where μ is the linear absorption coefficient of the powder, t is the thickness of the sample, r is the radius of the capillary.
value(18.5)	depolarisation fraction. To be supplied only when ivalue(2.8) is non-zero.

Optional line 19. Micro-absorption coefficients

To be supplied only when ivalue(2.7) is equal to 7.

value(19.1)	>	< P_0
	>	<
value(19.2)	> micro-absorption coefficients	< C
	> according to equation (27)	<
value(19.3)	>	< τ

Line set 20. Halfwidth and shape Parameters for Each phase.

Optional line set 20a.

To be supplied only when $ivalue(10.2)$ is neither equal to 6 nor to 7.

Halfwidth parameters (in units of hundredths of a degree) according to equation (10). When $ivalue(10.2)$ is equal to 5 or 8, U, V, W are also the halfwidth parameters for the Gaussian part of the parameterised pseudo-Voigt function as defined in equations (15) or (20).

value(20a.1) – value(20a.3) U, V, W parameters

value(20a.4) To be supplied only when $ivalue(10.2)$ is equal to 1 or 2.
The Lorentzian order parameter m as described in equation (119) or the mixing parameter n of the pseudo-Voigt function as defined in equation (12).

value(20a.5) halfwidth parameter P, according to equations (10) or (15).

Optional line set 20b, c, d.

To be supplied only when $ivalue(10.2)$ is equal to 3

Split Pearson VII parameters as defined by equations (13).

value(20b.1) – value(20b.3) asymmetry parameters, $As(1-3)$.

value(20c.1) – value(20c.3) low angle order parameters, $Lo(1-3)$.

value(20d.1) – value(20d.3) high angle order parameters, $Ho(1-3)$.

Optional line set 20e.

To be supplied only when $ivalue(10.2)$ is equal to 5

Halfwidth parameters (in units of hundredths of a degree) of the Lorentzian part of the parameterised pseudo-Voigt function as defined by equation (15).

value(20e.1) – value(20e.3) X, Y and Z parameters.

Optional line set 20f.

To be supplied only when $ivalue(10.2)$ is equal to 4

Variable pseudo-Voigt parameters as defined by Equation (14).

value(20f.1) – value(20f.3) mixing parameters, $p(1-3)$.

Optional line set 20g, h, i, j, k, l.

To be supplied only when `ivalue(10.2)` is equal to 6 or 7.

Tensor components (in units of hundredths of a degree) describing anisotropic halfwidth of anisotropic variable Pearson VII or pseudo–Voigt functions as defined by equations (16) and (17).

`value(20g.1) – value(20g.6)` U11, U22, U33, U12, U13, U23 parameters

`value(20h.1) – value(20h.6)` V11, V22, V33, V12, V13, V23 parameters

`value(20i.1) – value(20i.6)` W11, W22, W33, W12, W13, W23 parameters

Tensor components describing the anisotropic Lorentzian order parameter m (equations (17) and (19)) or the mixing parameter n of the pseudo–Voigt function as described in equations (17) and (18).

`value(20j.1) – value(20j.6)` pU11, pU22, pU33, pU12, pU13, pU23 parameters

`value(20k.1) – value(20k.6)` pV11, pV22, pV33, pV12, pV13, pV23 parameters

`value(20l.1) – value(20l.6)` pW11, pW22, pW33, pW12, pW13, pW23 parameters

Optional line set 20m, n, o, p.

To be supplied only when `ivalue(10.2)` is equal to 8.

Halfwidth parameters (in units of hundredths of a degree) of the Lorentzian part of the parameterised pseudo–Voigt function and ξ parameter as defined by equation (20).

`value(20m.1) – value(20m.3)` X, Y, ξ parameters.

Anisotropic parameters as described in equations (21) and (22).

`value(20n.1) – value(20n.6)` $S_{400}, S_{040}, S_{004}, S_{220}, S_{202}, S_{022}$ parameters

`value(20o.1) – value(20o.3)` $S_{211}, S_{121}, S_{112}$ parameters

`value(20p.1) – value(20p.6)` $S_{310}, S_{130}, S_{301}, S_{103}, S_{031}, S_{013}$ parameters

Line set 21. Cell Parameters for Each phase.

value(21.1) – value(21.6) a, b, c, α , β , γ

where the cell edges a, b, c are in Angstroms, and the angles α , β and γ in degrees.

Optional line 22. Preferred Orientation parameters for Each phase

To be supplied only when ivalue(10.3) is non-zero

value(22.1) the parameter G (see equations (23) and (24)).

value(22.2) To be supplied only when ivalue(10.3) is equal to 2.
the parameter D (see equation (24)).

Optional line 23 Asymmetry Parameters

To be supplied only when ivalue(2.4) is non-zero.

value(23.1) –value(23.2) the asymmetry parameters S/L and H/L (Finger, Cox & Jephcoat correction)
or the asymmetry parameters P and α (Howard's method, see equation (25))
or the asymmetry parameters P1 and P2 (see equation (26))

value(23.3) – value(23.4) To be supplied only when ivalue(2.4) is equal to 2.
the parameters P3 and P4 (see equation (26)).

Optional line set 24a. Background Parameters.

To be supplied only when ivalue(2.6) is equal to 1 or 4.

value(24a.1) – value(24a.4) background coefficients, BK0–BK3 (as described by equation (28)).

Optional line set 24b. Background Parameters.

To be supplied only when ivalue(2.6) is equal to 2, 3 or 5.

value(24b.1) – value(24b.6) background coefficients BK0–BK5 (options 2 or 5) (see equation (29)) or BK0A–BK5A (option 3) (see equation (30)).

Optional line set 25a. Background Parameters.

To be supplied only when ivalue(2.6) is equal to 1 or 4.

value(25a.1) – value(25a.4) background coefficients, BK4–BK7 (as described by equation (28)).

Optional line set 25b. Background Parameters.

To be supplied only when ivalue(2.6) is equal to 2, 3 or 5.

value(25b.1) – value(25b.6) background coefficients BK6–BK11 (options 2 or 5) (see equation (29)) or BK0B–BK5B (option 3) (see equation (31)).

Refinement Codewords

The program provides the user with the facility to relate directly the parameters being refined and the way in which the least squares matrix is calculated. This is achieved by requiring the user to specify which row of the least squares matrix is associated with which of the structure parameters. Parameters which are independent of one another are assigned different row numbers, (irow), whereas parameters which are linearly dependent are assigned the same row number. The number of row numbers supplied must be equal to the number of variables (ivalue(2.3)), but the row numbers may take on any value, and need not be sequentially ordered. In order to allow simple linear relationships to be maintained between parameters, the user is also required to specify for each parameter a shift multiplier (frac) by which the shift calculated from the least squares equations will be multiplied before it is applied to the parameter to which it refers. This shift multiplier is given in addition to the blanket relaxation factors supplied for different types of parameter on line 15. The row number in the least squares matrix and the shift multiplier are combined to form a refinement codeword (code) for each parameter according to :

$$\text{code} = [\text{irow} * 10 + \text{abs}(\text{frac})] * \text{sign}(\text{frac}) \quad (37)$$

where « abs (frac) » means the absolute value of « frac » and « sign(frac) » is +1 if frac is positive, and -1 if frac is negative. A zero codeword means that the parameter with which it is associated will not be refined.

If two parameters of the structure are related by :

$$\text{parameter}(1) = f * \text{parameter}(2) + \text{constant} \quad (38)$$

This relationship may be preserved during refinement by allocating each parameter the same row number (say, « ir ») in the least squares matrix, and setting the appropriate codewords to :

$$\begin{array}{ll} \text{for parameter}(1) : & \text{code} = 10 * \text{ir} + 1.0 \\ \text{(that is apply the calculated shift directly to parameter}(1)\text{)}. & \end{array} \quad (39)$$

$$\begin{array}{ll} \text{for parameter}(2) : & \text{code} = (10 * \text{ir} + \text{abs}(f)) * \text{sign}(f) \\ \text{(that is apply (the calculated shift)*f to parameter}(2)\text{)}. & \end{array} \quad (40)$$

Note that the codewords are constructed without reference to the constant term in equation (38).

A common situation in which codewords are of use is that in which an atom resides on a special position such as (x, 2x, z). In this case, the x and y coordinates are linearly dependent and must be given the same row number in the least squares matrix. In order to maintain the relationship « y = 2x », the shift applied to y must be twice that applied to x. If x is designated the 5th parameter of the refinement, and z the 6th, then the codewords required for the coordinates x, y, and z respectively are : 51; 52; and 61 or 50.5 ; 51 ;61.

Anisotropic temperature factors assigned to an atom on a special position present another situation where correct manipulation of the codewords is vital. For example, in position 16(f) of spacegroup I4(1)/acd (no. 142, origin on -1), the relations between the anisotropic thermal parameters are (see H. A. Levy, Acta Crystallographica 1956, volume 9, p. 679) :

$$\beta(11) = \beta(22) ; \beta(13) = -\beta(23) ; \beta(12), \beta(33) \text{ independent.}$$

Accordingly, $\beta(11)$ and $\beta(22)$ must be assigned the same row number in the least squares matrix, as must $\beta(13)$ and $\beta(23)$, but for the latter pair, the shift multiplier must take account of the negative sign in the relationship. If $\beta(11)$ is taken as parameter 3 of the refinement, $\beta(33)$ as 5, $\beta(12)$ as 6, and $\beta(13)$ as 4 then the codewords required are :

$\beta(11)$	$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(23)$
31	31	51	61	41	-41

A third case requiring correctly specified codewords is exemplified by refinement of the cell parameters in a hexagonal crystal. In this case, the cell parameters (see equation (6)) are related by :

$$D = E = 0 ; A = B = F ; C \text{ independent.}$$

thus D and E should not be refined, and A, B, and E should be given the same codeword.

The codewords for the structure parameters are specified in the same order as the parameters themselves. All of the codewords are omitted when ivalue(2.1) is zero.

Line 26. Codewords for Atomic Parameters

Codewords must be supplied for each of the atoms as follows :

value(26.1) > < x-coordinate.
> <

value(26.2) > codeword for < y-coordinate.
> <

value(26.3) > < z-coordinate.

value(26.4) codeword for the isotropic temperature factor.

value(26.5) codeword for the site occupation factor.

Values (26.6) to (26.8) should only be supplied when the atom contributes to neutron magnetic scattering (that is when ivalue(10.1) is equal to 1, 2, or 3, and ivalue(16.8) is non-zero).

value(26.6) > < x
> <

value(26.7) > codeword for the magnetic < y
> vector components along <

value(26.8) > < z

When ivalue(16.13) is non-zero (that is when the atom has anisotropic temperature factors) the data given for line 26 should be immediately followed by that described under optional line 26a. There are then two lines of refinement codewords for anisotropic atoms.

value(26a.1) > < $\beta(11)$
> <

value(26a.2) > < $\beta(22)$
> <

value(26a.3) > < $\beta(33)$
> Codewords for anisotropic <

value(26a.4) > thermal parameters < $\beta(12)$
> <

value(26a.5) > < $\beta(13)$
> <

value(26a.6) > < $\beta(23)$

Note : None of the atomic parameter(s) may be refined in the Le Bail decomposition method.

Line set 27. Codewords for Scale and Overall Temperature factors for Each phase.

value(27.1) codeword for the scale factor for neutron or synchrotron diffraction or X-ray alpha-1 radiation.

value(27.2) Codeword for the overall isotropic temperature factor.

Note : the scale factor and Overall Temperature factor may not be refined in the Le Bail decomposition method.

Line 28. Codewords for Zero-point, Specimen Displacement, Absorption Parameter and Depolarisation Factor

value(28.1) codeword for zero-point error.

value(28.2) To be supplied only if ivalue(2.5) is equal to 1 or 4.
Codeword for a/R as described in line 2.

value(28.3) To be supplied only if ivalue(2.5) is equal to 1, 2 or 3.
Codeword for b/R as described in line 2.

value(28.4) To be supplied only when ivalue(2.7) is neither equal to 0 nor to 2, nor to 7.
Codeword for the flat plate sample absorption parameter μ^*t or for the capillary absorption coefficient μ^*r .

value(28.5) Codeword for the depolarisation fraction, to be supplied only when ivalue(2.8) is non-zero.

Optional line 29. Codewords for micro-absorption coefficients

To be supplied only when ivalue(2.7) is equal to 7.

value(29.1) > < P_0

> <

value(29.2) > codewords for < C

> <

value(29.3) > < τ

Note : actually it is not recommended to refine the first parameter P_0 which is strongly correlated to the scale factor.

Line set 30. Codewords for Halfwidth and shape Parameters for Each phase.

Optional line set 30a.

To be supplied only if $\text{ivalue}(10.2)$ is neither equal to 6 nor to 7.

$\text{value}(30a.1) - \text{value}(30a.3)$ codewords for U, V, W

$\text{value}(30a.4)$ To be supplied only when $\text{ivalue}(10.2)$ is equal to 1 or 2.
Codeword for the Lorentzian order parameter m as described in Equation (11) or for the mixing parameter n of the pseudo-Voigt function as defined in equation (12).

$\text{value}(30a.5)$ Codeword for halfwidth parameter P , according to equations (10) or (15).

Optional line set 30b, c, d.

To be supplied only when $\text{ivalue}(10.2)$ is equal to 3

Codewords for Split Pearson VII parameters as defined by equations (13).

$\text{value}(30b.1) - \text{value}(30b.3)$ codewords for asymmetry parameters, $A_s(1-3)$.

$\text{value}(30c.1) - \text{value}(30c.3)$ codewords for low angle order parameters, $L_o(1-3)$.

$\text{value}(30d.1) - \text{value}(30d.3)$ codewords for high angle order parameters, $H_o(1-3)$.

Optional line set 30e.

To be supplied only when $\text{ivalue}(10.2)$ is equal to 5

Codewords for Halfwidth parameters of the Lorentzian part of the parameterised pseudo-Voigt function as defined by equation (15).

$\text{value}(30e.1) - \text{value}(30e.3)$ codewords for X, Y and Z parameters.

Optional line set 30f.

To be supplied only when $\text{ivalue}(10.2)$ is equal to 4.

Codewords for Variable pseudo-Voigt parameters as defined by equation (14).

$\text{value}(30f.1) - \text{value}(30f.3)$ codewords for mixing parameters, $p(1-3)$.

Optional line set 30g, h, i, j, k, l.

To be supplied only when $\text{ivalue}(10.2)$ is equal to 6 or 7.

Codewords for the Tensor components describing anisotropic halfwidth of anisotropic variable Pearson VII or pseudo–Voigt functions as defined by equations (16) and (17).

$\text{value}(30g.1) - \text{value}(30g.6)$ Codewords for U11, U22, U33, U12, U13, U23 parameters

$\text{value}(30h.1) - \text{value}(30h.6)$ Codewords for V11, V22, V33, V12, V13, V23 parameters

$\text{value}(30i.1) - \text{value}(30i.6)$ Codewords for W11, W22, W33, W12, W13, W23 parameters

Codewords for the Tensor components describing the anisotropic Lorentzian order parameter m (equations (17) and (19)) or the mixing parameter n of the pseudo–Voigt function as described in equations (17) and (18).

$\text{value}(30j.1) - \text{value}(30j.6)$ Codewords for pU11, pU22, pU33, pU12, pU13, pU23 parameters

$\text{value}(30k.1) - \text{value}(30k.6)$ Codewords for pV11, pV22, pV33, pV12, pV13, pV23 parameters

$\text{value}(30l.1) - \text{value}(30l.6)$ Codewords for pW11, pW22, pW33, pW12, pW13, pW23 parameters

Optional line set 30m, n, o, p.

To be supplied only when $\text{ivalue}(10.2)$ is equal to 8.

Codewords for Halfwidth parameters of the Lorentzian part of the parameterised pseudo–Voigt function and ξ parameter as defined by equation (20).

$\text{value}(30m.1) - \text{value}(30m.3)$ Codewords for X, Y and ξ parameters.

Codewords for Anisotropic parameters as described in equations (21) and (22).

$\text{value}(30n.1) - \text{value}(30n.6)$ Codewords for $S_{400}, S_{040}, S_{004}, S_{220}, S_{202}, S_{022}$ parameters

$\text{value}(30o.1) - \text{value}(30o.3)$ Codewords for $S_{211}, S_{121}, S_{112}$ parameters

$\text{value}(30p.1) - \text{value}(30p.6)$ Codewords for $S_{310}, S_{130}, S_{301}, S_{103}, S_{031}, S_{013}$ parameters

Line set 31. Codewords for Cell Parameters for Each phase.

The cell parameters actually refined are the components of the reciprocal metric tensor defined in equation (6).

value(31.1) – value(31.6) Codewords for A, B, C, D, E, F.

Optional line 32. Codewords for the Preferred Orientation parameters for Each phase.

To be supplied only when ivalue(10.3) is non-zero

value(32.1) Codeword for the parameter G (see equations (23) and (24)).

value(32.2) To be supplied only when ivalue(10.3) is equal to 2.
Codeword for the parameter D (see equation (24)).

Note : the preferred orientation parameter(s) may not be refined in the Le Bail decomposition method.

Optional line 33. Codewords for Asymmetry Parameters

To be supplied only when ivalue(2.4) is non-zero.

value(33.1) – value(33.2) Codewords for the asymmetry parameters S/L and H/L (Finger, Cox & Jephcoat correction) or the asymmetry parameters P and α (Howard's method, see equation (25)) or for the asymmetry parameters P1 and P2 (see equation (26)).

value(33.3) – value(33.4) To be supplied only when ivalue(2.4) is equal to 2.
Codewords for the parameters P3 and P4 (see equation (26)).

Optional line set 34a. Codewords for Background Parameters.

To be supplied only when $\text{ivalue}(2.6)$ is equal to 1 or 4.

$\text{value}(34a.1) - \text{value}(34a.4)$ Codewords for the background coefficients, BK0–BK3 (as described by equation (28)).

Optional line set 34b. Codewords for Background Parameters.

To be supplied only when $\text{ivalue}(2.6)$ is equal to 2, 3 or 5.

$\text{value}(34b.1) - \text{value}(34b.6)$ Codewords for the background coefficients BK0–BK5 (options 2 or 5) (see equation (29)) or BK0A–BK5A (option 3) (see equation (30)).

Optional line set 35a. Codewords for Background Parameters.

To be supplied only when $\text{ivalue}(2.6)$ is equal to 1 or 4.

$\text{value}(35a.1) - \text{value}(35a.4)$ Codewords for the coefficients, BK4–BK7 (as described by equation (28)).

Optional line set 35b. Codewords for Background Parameters.

To be supplied only when $\text{ivalue}(2.6)$ is equal to 2, 3 or 5.

$\text{value}(35b.1) - \text{value}(35b.6)$ Codewords for the coefficients BK6–BK11 (options 2 or 5) (see equation (29)) or BK0B–BK5B (option 3) (see equation (31)).

Constrained Refinement

It is possible to perform two types of constrained refinement using either the « strict » constraints described by G. S. Pawley (Advances in Structure Research by Diffraction Methods 1972, volume 4, pp. 1–64.) or the « chemical » constraints first described by J. Waser (Acta Crystallographica 1963, volume 16, pp. 1091–1094. See also J. S. Rollett in « Crystallographic Computing », Munksgaard, 1970, p. 170, editor F. R. Ahmed). The mixing of « strict » and « chemical » constraints is possible but is not recommended.

« Strict » constraints enforce a precise relationship between various structural parameters, and are specified in the form of an equation with linear or quadratic terms relating the parameters to a constant term (the value of the constraint function). A common case where « strict » constraints may be of use is the constraining to unity of the sum of the site occupation factors for all the sites occupied by a disordered atom.

« Chemical » constraints impose less stringent requirements on the atomic parameters. Indeed, if they are in complete disagreement with the profile intensity data, they may not be obeyed at all. It is possible by means of « chemical » constraints to provide ideal values of derived quantities such as bond lengths and bond angles. These ideal values are treated as extra observed data, and contributions to the least squares equations are evaluated in rather the same way as for an intensity observation (see equations (2), (3) and (4)). However, each constraint has associated with it a standard deviation, also supplied by the user, this standard deviation is used to weight the contribution of the « chemical » constraints to the least squares equations, and its magnitude determines how well the constraint is obeyed. A small standard deviation yields a high weight and enhances the effect of the constraint on the refinement, whereas a large standard deviation will achieve the opposite. If, at the end of the refinement, a derived quantity differs significantly from the value to which it was constrained, then the validity of the constraint should be carefully considered.

« Strict constraints »

« Strict » constraints are input in the form of an equation relating the parameters to be constrained. The terms of the equation may be either linear or quadratic functions of the parameters, but one, and only one, of the parameters referred to must not be refined. This parameter will be adjusted after each refinement cycle to ensure that the constraint is obeyed. When the non-refined parameter appears multiplied by itself in a constraint equation, there are two possible solutions for this parameter when the equation is solved at the end of the refinement cycle. The solution chosen is that closest to the original value of the non-refined parameter.

Individual parameters are specified by two integers which refer to the following table :

icolumn	1	2	3	4	5	6	7	8	9	10	11	12	13	14
irow	x	y	z	B(iso)	site	Kx	Ky	Kz	$\beta(11)$	$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(14)$
.														
.														
n														

Note: In the above table the first ivalue(12.3) rows represent the parameters of the ivalue(12.3) atoms in the same order as the atoms were input.

To select a parameter in the above table, it is necessary to choose the correct values of « irow » and « icolumn ». For example, the two integers « 3, 7 » define the component of the magnetic vector along the y-axis (Ky) for the third atom of the input list (assuming ivalue(12.3) to be greater than two). The input data required to define a « strict » constraint equation is then :

Optional line set 36 « Strict » Constraints

To be supplied only when ivalue(8.1) is non-zero.

ivalue(8.1) constraint equations must be supplied. The following specifies the data to be given for each such equation. Each term in the equation occupies one line of the input, and the input of terms is terminated by a line whose first two characters are « EQ ». The next line contains the constraint value and the input of this terminates the constraint function.

value(36.1) the multiplier for the constraint term.

in determining the remaining values, refer to the above table.

ivalue(36.2) the row number for parameter (1).

ivalue(36.3) the column number for parameter (1).

Optional ivalues(36.4) and (36.5) are to be given only for quadratic terms.

ivalue(36.4) the row number for parameter (2).

ivalue(36.5) the column number for parameter (2).

The above five values are input for each of the terms comprising a constraint at the rate of one term per line, and the input of terms is terminated by a line whose first two characters is read as « EQ ».

value(36a.1) the value of the constraint function.

Some examples :

1) In a structure containing three atoms, the sum of the site occupation factors of atoms (1) and (3) may be constrained to equal 1.0 by the input :

```
1 1 5
1 3 5
EQUALS
1
```

The above data represent the equation : $1*\text{site}(1) + 1*\text{site}(3) = 1$

2) In a cubic crystal of edge 5 Angstroms, the distance between atoms 1 and 2 could be constrained to equal 1.54 Angstroms [$=\sqrt{2.3716}$] by the input :

```
25 1 1 1 1
-50 1 1 2 1
25 2 1 2 1
25 1 2 1 2
-50 1 2 2 2
25 2 2 2 2
25 1 3 1 3
-50 1 3 2 3
25 2 3 2 3
EQUALS
2.3716
```

The above data represent the equation :

$$25*[x(1)-x(2)]**2 + 25*[y(1)-y(2)]**2 + 25*[z(1)-z(2)]**2 = 2.3716$$

Note that in this example all the parameters in the constraint equation appear as the square. Consequently, solution of the constraint equation after refinement will be carried out by choosing the new value of the non-refined parameter which is closest to the original value.

Optional line set 37 « Chemical » Constraints

To be supplied only when ivalue(8.2) is greater than zero.

The application of « chemical » constraints involves modification of the least squares equations, and is best achieved when all of the parameters involved in the constraints are refined. However, the program will cope with « chemical » constraints in which this is not the case.

The input of « chemical » constraints is controlled by a series of directives which must be as shown. The available directives are detailed below.

Atom Specification

The input of directives all require the specification of definite atomic sites within the unit cell, and to this end it is possible to apply symmetry transformations to the coordinates given in line set 16. An atomic site is defined by the following line of input :

Name	is	tx	ty	tz
------	----	----	----	----

« name » is the identifier of the atom as given in line set 16 and is assumed to occupy the first four columns of the line. Lines with the first four columns blank are ignored and hence may be used to separate and clarify a list of atom specifications. « is » is the integer serial number of a spacegroup symmetry operation defined in optional line set 14. When the symmetry operations are retrieved by the program from the space group symbol, the serial numbers can be obtained in the lineprinter output file MProf.lis. The identity operation is given a serial number of 1. « tx », « ty », and « tz » are additional unit cell translations along the x, y, and z crystallographic axes respectively. The symmetry transformation applied to the coordinates given in line set 16 is :

$$x'' = q*\text{value}(14[\text{is}].1)*x + q*\text{value}(14[\text{is}].2)*y + q*\text{value}(14[\text{is}].3)*z + \text{value}(14[\text{is}].10) + \text{tx}$$

$$y'' = q*\text{value}(14[\text{is}].4)*x + q*\text{value}(14[\text{is}].5)*y + q*\text{value}(14[\text{is}].6)*z + \text{value}(14[\text{is}].11) + \text{ty}$$

$$z'' = q*\text{value}(14[\text{is}].7)*x + q*\text{value}(14[\text{is}].8)*y + q*\text{value}(14[\text{is}].9)*z + \text{value}(14[\text{is}].12) + \text{tz}$$

The value of the factor <q> is 1.0 when <is> is input as zero or a positive integer, and is -1.0 when <is> is input as a negative integer. The sign of <is> can therefore be employed to generate symmetry operations which are related by a centre of symmetry.

Examples :

```
O(2)
C(1) -1
S 3 0 0.5 0.5
```

In the above, the coordinates of atom « O(2) » will be used as given in line set 16, those of « C(1) » will be inverted through a centre of symmetry at the origin [since operation 1 is always (x,y,z)] and those of « S » will be transformed by spacegroup symmetry operation (3) and an additional translation of (0,0.5,0.5) applied.

DIST value esd

The « DIST » directive is immediately followed by the value to which distances are to be constrained and its standard deviation. Atom specifications are then input as a pair followed by an « END » directive.

An example :

```
DIST 1.67 0.01
S(1)
F(3) 2
END
```

Distance S(1)–F(3) is constrained to be equal to 1.67 Angstroms with a standard deviation of 0.01, F(3) is transformed by spacegroup symmetry operation (2) before the distance S(1)–F(3) is calculated.

SAME esd

The « SAME » directive is followed by the standard deviation within which the distances are to be constrained. Two pairs of atom specifiers (followed by an « END » directive) define the two distances which are constrained to be the same.

An example :

```
SAME 0.01
C(1)
O(1)
C(2)
O(2)
END
```

The distances C(1)–O(1) and C(2)–O(2) are constrained to be equal.

ANGL value esd

The « ANGL » directive is immediately followed by the value to which angles are to be constrained (in degrees) and its standard deviation. Three atom specifications are needed (terminated by an « END » directive) to define the angle, and the second atom is taken as the vertex.

An example :

```
ANGL 120 0.1
C(1)
C(2)
C(3)
END
```

The angle C(1)–C(2)–C(3) is constrained to be equal to 120 degrees with a standard deviation of 0.1.

END

The « END » directive terminates a list of atom specifications.

STOP

The « STOP » directive terminates the input of chemical constraints.

Line 38.

A blank line is recommended to help lubricate the program.

Output files produced by MPROF for other programs

Using specific codes in the input control file (*.pro) for MPROF can produce output file(s) for other programs. In this topic are given the list of these programs and the associated codes in MPROF.

SHELX

Author, WEB site :

SHELX-97

G. Sheldrick

<http://shelx.uni-ac.gwdg.de/SHELX/index.html>

Codes in MPROF : ivalue(7.1)

 ivalue(7.3)

see also keywords FOUR, SHEL and SIRP in the topic Keyworded Input

PLATON or ORTEP

Author(s), WEB site :

PLATON

A.L.Spek

<http://www.cryst.chem.uu.nl/platon/>

ORTEP - 3

M.N. Burnett & C.K. Johnson

<http://www.ornl.gov/ortep :ortep.html/>

WinGX single crystal suite (GUI WinORTEP, GUI WinStruplo, WinPlaton)

L. J. Farrugia

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

Code in MPROF : ivalue(7.5)

see also keyword STRU in the topic Keyworded Input

This option produces output of a file in SHELX format readable by PLATON or ORTEP.

EXPO (SIRPOW)

Authors, WEB site :

EXPO (SIRPOW)

A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna.

http://www.ba.cnr.it/IRMEC/SirWare_main.html

Code in MPROF : ivalue(7.3)

see also keywords SHEL and SIRP in the topic Keyworded Input

STRUVIR or WinSTRUPLO,

Author(s), WEB sites :

STRUVIR

A. LeBail

<http://www.cristal.org/vrml/struvir.html>

WinGX single crystal suite (GUI WinORTEP, GUI WinStruplo, WinPlaton)

L. J. Farrugia

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

WinSTRUPLO (MS-Windows version of STRUVIR)

L. J. Farrugia

<http://www.chem.gla.ac.uk/~louis/struplo/>

Code in MPROF : ivalue(7.5)

see also keyword STRU in the topic Keyworded Input

WinPLOTTR

Authors, WEB site :

WinPLOTTR

T. Roisnel and J. Rodríguez-Carvajal

<http://www-llb.cea.fr/winplotr/winplotr.htm>

Code in MPROF : ivalue(7.4)

This option produces output of a file in (.prf) format.

GFOUR

Authors, WEB site :

GFOUR

Gonzalez Platas and J. Rodriguez-Carvajal

http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/fullprof/pub/divers/progs_pc/fourier/

Code in MPROF : ivalue(7.1)

see also keywords FOUR and GINP in the topic Keyworded Input

Other associated programs

Program MFOURS

It allows Difference Fourier calculation to be carried out and yields output of a lineprinter file MFours.lis. The input data file (with an extension .mfs) is automatically generated by MPROF when ivalue(7.1) is positive.

An example of input file (file mfours.mfs in the examples folder) :

```

La2 Cu O4 Fmmm (without O2 at 1/4; 1/4; 0) X-rays Flat plate
# Cell constants
  5.3553  5.3991  13.1538  90.000  90.000  90.000
# Asymmetric unit
  0.00000  0.25000  0.00000  0.25000  0.00000  0.50000
# Symmetry
  2 4 F
SYMM X, Y, Z
SYMM X, -Y, -Z
SYMM -X, Y, -Z
SYMM -X, -Y, Z
#
# H K L F(OBS) F(CALC) COS(PHA.ANG) SIN(PHA.ANG) DELTA
  0 0 2 420.4311 104.5469 -1.0000 -1.2317 315.8842
  1 1 1 1080.8883 1075.6478 -1.0000 -0.3426 5.2405
  0 0 4 1802.6844 2163.9307 -1.0000 -0.2484 -361.2462
  1 1 3 2864.6489 2862.6494 1.0000 0.1805 1.9995
  0 2 0 3430.9661 3871.7251 1.0000 0.1529 -440.7590
  2 0 0 3521.5818 3876.9890 1.0000 0.1533 -355.4072
  0 2 2 457.0182 79.8898 -1.0000 -6.7582 377.1284
  2 0 2 363.3476 79.9828 -1.0000 -7.8989 283.3648
  0 0 6 2533.5112 2180.8889 1.0000 0.1384 352.6223

etc...

  1 5 9 296.0096 203.0566 1.0000 0.0433 92.9530
  1 1 15 1178.6334 1125.9457 -1.0000 -0.4134 52.6877
  5 1 9 212.3389 208.6951 1.0000 0.0435 3.6438
  2 6 0 1740.2646 1714.3197 1.0000 0.2882 25.9449
  0 4 12 516.7581 508.6273 -1.0000 -0.5218 8.1308
  4 0 12 519.3658 516.7589 -1.0000 -0.5224 2.6070
  6 2 0 1877.9569 1762.5164 1.0000 0.2901 115.4406
  2 6 2 64.1143 62.4540 1.0000 -40.5181 1.6602
  2 2 14 1615.1764 1577.2140 1.0000 0.3184 37.9624
  6 2 2 64.5711 64.5836 1.0000 -19.3928 -0.0125
999
  3
La 0.00000 0.00000 0.36134
Cu 0.00000 0.00000 0.00000
O1 0.00000 0.00000 0.18322
# Limits for Bondlengths and angles calculation
  0.010 2.000 2.900 10 parbond.mbs

```

All input data are in free format as described above for MPROF. The asymmetric unit coordinates can be supplied directly in the input control file (*.pro) by using the keyword *ASYU* or by modifying the default values in the (*.mfs) input file before running MFOURS.

A bond distances and angles calculation is also carried out by MFOURS using the three default values (in Angstroms) supplied on the last line of the (*.mfs) input file (the meaning of these values, which may be modified by the user, is given by the keyword option BOND in MPROF), involving all atoms included in phase ivalue(7.1) as well as the first five Fourier peaks found by MFOURS.

If a bond distances and angles calculation is needed with more than five Fourier peaks, this may be changed by using the fourth parameter of the last line (default value : 10). In that case, the coordinates of the first 10 Fourier peaks, of all atoms included in phase ivalue(7.1), and other useful information (cell constants, symmetry) are transferred to the output file parbond.mbs (default name). This file will then constitute the input control file for the other associated program MBONDS.

Program MBONDS

MBONDS is a very simple program to perform bond distances and angles calculation (no esd's). An lineprinter output file MBonds.lis is produced.

An example of input file (file parbond.mbs in the examples folder) :

```
La2 Cu O4 Fmmm (without O2 in 1/4; 1/4; 0) X-rays Flat plate
  2      4      F
# Symmetry operators
SYMM X, Y, Z
SYMM X,-Y,-Z
SYMM -X,Y,-Z
SYMM -X,-Y,Z
La      0.00000      0.00000      0.36134
Cu      0.00000      0.00000      0.00000
O1      0.00000      0.00000      0.18322
Q1      0.25000      0.25000      0.00000
Q2      0.25000      0.25000      0.50000
Q3      0.12500      0.11000      0.18500
Q4      0.12500      0.09750      0.23500
Q5      0.11000      0.11500      0.26000
Q6      0.09250      0.12000      0.28000
Q7      0.13000      0.09500      0.14000
Q8      0.06250      0.11750      0.29500
Q9      0.00000      0.11000      0.30000
Q10     0.13000      0.09000      0.13500
# Cell constants
      5.3553      5.3991      13.1538      90.000      90.000      90.000
# Limits for Bondlengths and angles calculation
      0.010      2.000      2.900
```

The meaning of the codes 2 4 F on the line just before # Symmetry operators is :

- 2 : code for centrosymmetry (1 for non-centrosymmetry)
- 4 : number of symmetry operations (including x, y, z)
- F : Bravais lattice type.

The 3 default values (in Angstroms) supplied on the last line of the (*.mbs) input file may be modified by the user (the meaning of these values is given by the keyword option BOND in MPROF).

Examples of input for WinMProf

Synchrotron radiation data

Example 1 Input control file : Nb5P7.pro
 Experimental Data File : R17668.pds

Description : synchrotron radiation
 Pseudo-Voigt function
 Background refined

Example 2 Input control file : Nb5P7_LB.pro
 Experimental Data File : R17668.pds

Description : synchrotron radiation
 Le Bail decomposition method (full pattern matching)
 Pseudo-Voigt function
 Background refined

Example 3 Input control file : BaGaF5.pro
 Experimental Data File : R10736.pds

Description : synchrotron radiation
 Multiphase refinement
 Anisotropic variable pseudo-Voigt function
 Preferred orientation correction
 Background refined

Example 4 Input control file : BaGaF5_calc.pro

Description : calculation mode only

Cu Kalpha radiation data

Example 1 Input control file : TiO2.pro
Experimental Data File : TiO2.phi

Description : Monochromatized Cu Kalpha1 radiation
Pre-sample monochromator
Background subtracted

Example 2 Input control file : Nac_V6V6.pro
Experimental Data File : Na2Ca3Al2F14.phi

Description : Cu Kalpha1 - Kalpha2 radiation
Post-sample monochromator
Parameterised pseudo-Voigt function
Variable Divergence Slits
Background subtracted

Example 3 Input control file : La2Cu.pro
Experimental Data File : La2CuO4.phi

Description : Cu Kalpha1 - Kalpha2 radiation
Post-sample monochromator
Split Pearson VII function
Anisotropic temperature factors
Output of Bond lengths and angles in the lineprinter file
Background subtracted

Example 4 Input control file : La2Cu_How.pro
Experimental Data File : La2CuO4.phi

Description : Cu Kalpha1 - Kalpha2 radiation
Post-sample monochromator
Pseudo-Voigt function
Anisotropic temperature factors
Background subtracted

Neutron diffraction data

Example 1 Input control file : CuPc_Nuc.pro
Experimental Data File : cc64.d1a

Description : Nuclear neutron diffraction
Multiphase mixed refinement (both Rietveld and LeBail)
Bayesian chemical constraints
Background refined

Example 2 Input control file : CuPc_Mag.pro
Experimental Data File : cc10.d1a

Description : Magnetic neutron diffraction
Multiphase mixed refinement (both Rietveld and LeBail)
Bayesian chemical constraints
Background refined

Other input data

- 1/ R10736.pds
R10736.d1a
R10736.phi the same experimental data file in the different available formats
R10736.fr1
R10736.fr2
- 2/ mfours.mfs Example of input control file for the associated Fourier program MFOURS.
- 3/ mbonds.mbs Example of input control file for the associated program MBONDS
(bond distances and angles calculation).

Acknowledgements

The FORTRAN programs authors are :

H.M. Rietveld → A.W. Hewat → P.J. Clarke → P.J. Bendall & M.W. Thomas

↓

A.N. Fitch, J.K. Cockcroft & A.D. Murray

↓

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The first version of the manual was typed by J. Lampard (26/08/89) and updated by A. Jouanneux (23/03/2001).

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Disclaimer

While the program has been tested by the authors, no guarantee is given concerning its proper functioning.