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Structure Refinement

The Rietveld method is a structure refinement technique for powder diffraction data which fits the whole powder pattern including peak shapes and background.

Stages in Rietveld Refinement

- (1) Decide on initial structural model
- (2) Refine background and overall scale
- (3) Refine Unit cell dimensions
- (4) Refine zero-point correction
- (5) Refine peak shape
- (6) Refine atomic coordinates
- (7) Refine thermal parameters and/or occupancies
- (8) Check model and closeness of fit

History

Prior to the 1960s. Structure refinement from powder diffraction data involved careful measurement of the Bragg intensities and extraction of Fobs from these after correction for multiplicity, Lorentz and Polarisation factors.

The problem lay in extracting intensities for overlapping peaks. To some extent this was overcome by increasing diffractometer resolution and higher wavelengths but the technique was mainly limited to small unit cell high symmetry structures.

In 1967 Hugo M Rietveld published his seminal paper on how to overcome these problems in neutron diffraction data.

Line Profiles of Neutron Powder-diffraction Peaks for Structure Refinement
H.M. Rietveld *Acta Crystallogr.*,**22** (1967) 151-2

A Profile Refinement Method for Nuclear and Magnetic Structures, H.M. Rietveld *J. Appl. Crystallogr.*,**2**, (1969). 65-71

The Rietveld Method R.A. Young, Oxford University Press, 1993



H.M. Rietveld

Basis of the Rietveld Method

A digitised powder diffraction profile is essentially a one dimensional x, y data set, where $y(obs)_i$ is the observed intensity of the i th point and x_i is the position of the i th point.

Increments of x are normally constant and measured in degrees 2θ , time of flight, d -spacing, energy or wavelength depending on the technique used.

In some cases additional data are stored such as weighting or error on the intensity.

The Rietveld method involves using structural information to calculate the intensity, $y(calc)_i$, at each point i on the profile, *i.e.*

$$y(calc)_i = F(x_i)$$

The function $F(x_i)$ incorporates structural, sample and instrumental parameters.

Because structural information is required the method is a structure refinement technique rather than one of structure determination.

The method involves a non-linear least squares refinement of model parameters minimising a weighted residual function S_y :

$$S_y = \sum_i w_i (y(obs)_i - y(calc)_i)^2$$

where

$$w_i = \frac{1}{y(obs)_i}$$

The function $F(x_i)$ is dependent not only on x , but also on various structural and experimental information. Therefore we can expand our $y(calc)_i$ equation as follows :

$$y(calc)_i = s \sum_{hkl} L_{hkl} |F_{hkl}|^2 \phi(2\theta_i - 2\theta_{hkl}) P_{hkl} A + y(back)_i$$

s = scale factor

L_{hkl} is a function containing Lorentz, polarisation and multiplicity factors

ϕ is the profile peak shape function

P_{hkl} is the preferred orientation function

F_{hkl} is the structure factor

$y(back)_i$ is the background intensity at point i .

A is an absorption correction factor.

Goodness of fit criteria

Refinement is normally continued until an acceptable fit is obtained or some convergence criteria have been met.

A number of criteria can be used to establish the quality of the fit.

The R or residual factors allow for comparison to single crystal refinements. Unfortunately R -factors are very much influenced by the statistics of the profile. For example the R_{wp} value is significantly affected by the signal to noise ratio, such that often a noisy profile will give better R -factors than one with a better signal to noise ratio.

R -pattern

$$R_p = \left\{ \frac{\sum_i |y(obs)_i - y(calc)_i|}{\sum_i y(obs)_i} \right\}$$

R -weighted pattern

$$R_{wp} = \left\{ \frac{\sum_i w_i (y(obs)_i - y(calc)_i)^2}{\sum_i w_i (y(obs)_i)^2} \right\}^{\frac{1}{2}}$$

The Bragg and structure factor R -factors allow direct comparison to single crystal refinements. Unfortunately because of the lack of certainty in estimating $I(obs)_{hkl}$ they are not always very helpful.

R -Bragg

$$R_B = \frac{\sum_{hkl} |I(obs)_{hkl} - I(calc)_{hkl}|}{\sum_{hkl} I(obs)_{hkl}}$$

R -Structure factor

$$R_F = \frac{\sum_{hkl} |\sqrt{I(obs)_{hkl}} - \sqrt{I(calc)_{hkl}}|}{\sum_{hkl} \sqrt{I(obs)_{hkl}}}$$

The goodness of fit parameters χ^2 and S are better indicators of how close a fit to the observed profile as these take into account an expected R factor based on the number of data points and the number of refined parameters.

Goodness of fit
(GoF)

$$\chi^2 = \frac{\sum_i w_i (y(\text{obs})_i - y(\text{calc})_i)^2}{N - P} = \left(\frac{R_{wp}}{R_{ex}} \right)^2$$

$$S = \sqrt{\chi^2}$$

R -expected

$$R_{ex} = \sqrt{\frac{N - P}{\sum_i w_i y(\text{obs})_i^2}}$$

Finally the Durbin-Watson parameter d is useful for identifying serial correlations between y_i values. An ideal value is around 2.00. This is a good indicator of how the Bragg profile functions are fitting. In general it is always advisable to check the difference profile visually to see if a good fit has been obtained.

Durbin-Watson
statistic

$$d = \frac{\sum_{i=2}^N \left(\frac{y(obs)_i - y(calc)_i}{\sqrt{y(obs)_i}} - \frac{y(obs)_{i-1} - y(calc)_{i-1}}{\sqrt{y(obs)_{i-1}}} \right)^2}{\sum_{i=1}^N \left(\frac{y(obs)_i - y(calc)_i}{\sqrt{y(obs)_i}} \right)^2}$$

In general it is always advisable to check the difference profile visually to see if a good fit has been obtained.

Peak Shapes

A number of peak shapes have been used for modelling X-ray and neutron data.

The original Rietveld code was designed to analyse constant wavelength neutron data. Rietveld found that he could model the peaks in a neutron diffraction profile using a Gaussian function:

$$I_{i,k} = t S_k^2 j_k L_k \frac{2\sqrt{\ln(2)}}{H_k} \exp\left[\frac{-4\ln(2)}{H_k^2} (2\theta_i - 2\theta_k)^2 \right]$$

$I_{i,k}$ = intensity at point i due to reflection k

t = step width of the diffractometer

S_k^2 = sum of the nuclear and magnetic structure factors

j_k = the multiplicity of reflection k

L_k = the Lorentz factor

$2\theta_k$ = the Bragg angle for reflection k

$2\theta_i$ = the angle at point i

H_k = the full width at half maximum for reflection k

Incorporation of parameters describing vertical divergence of the neutron beam and different collimators gave a modified equation:

$$I_{i,k} = t S_k^2 j_k L_k \frac{2\sqrt{\ln(2)}}{H_k} \exp\left[\frac{-4\ln(2)}{H_k^2} (2\theta_i - 2\theta_k)^2\right] \left[1 - P(2\theta_i - 2\theta_k)^2 \frac{S}{\tan \theta_k}\right]$$

P = asymmetry parameter

S has values -1, 0, 1 and is the sign of $2\theta_i - 2\theta_k$

The variation of peak width across the profile is described by 3 parameters U , V and W .

$$H_k^2 = U \tan^2 \theta_k + V \tan \theta + W$$

A number of functions are used to model X-ray data. Typically the pseudo-Voigt function is used for laboratory X-ray data.

Normalised peak shape functions

Gaussian

$$I_{i,k} = \frac{2\sqrt{\ln(2)}}{H_k} \exp\left[\frac{-4\ln(2)}{H_k^2}(2\theta_i - 2\theta_k)^2\right]$$

Lorentzian

$$I_{i,k} = \frac{\sqrt{4}}{\pi H_k} \left[1 + \frac{4(\sqrt{2}-1)}{H_k^2}(2\theta_i - 2\theta_k)^2\right]^{-1}$$

Intermediate Lorentzian

$$I_{i,k} = \frac{\sqrt{\left(4\left(2^{\frac{3}{2}}-1\right)\right)}}{2\pi H_k} \left[1 + \frac{4\left(2^{\frac{2}{3}}-1\right)}{H_k^2}(2\theta_i - 2\theta_k)^2\right]^{-1.5}$$

Modified Lorentzian

$$I_{i,k} = \frac{2\sqrt{\left(4(\sqrt{2}-1)\right)}}{\pi H_k} \left[1 + \frac{4(\sqrt{2}-1)}{H_k^2}(2\theta_i - 2\theta_k)^2\right]^{-2}$$

Pearson VII

$$I_{i,k} = \frac{2\sqrt{m}\Gamma\left(2^{\frac{1}{m}}-1\right)}{\pi\Gamma\left(m-\frac{1}{2}\right)H_k} \left[1 + \frac{4\left(2^{\frac{1}{m}}-1\right)}{H_k^2}(2\theta_i - 2\theta_k)^2\right]^{-m}$$

Voigt

$$I_{i,k} = \beta_g^{-1} \operatorname{Re} \left[\Omega \left[\frac{\sqrt{\pi}}{\beta} |2\theta_i - 2\theta_k| + i \frac{\beta_c^2}{\beta_g^2 \pi} \right] \right]$$

Pseudo Voigt

$$I_{i,k} = \eta \left[\frac{\sqrt{4}}{\pi H_k} \left[1 + \frac{4(\sqrt{2}-1)}{H_k^2}(2\theta_i - 2\theta_k)^2\right]^{-1} \right] + (1-\eta) \left[\frac{2\sqrt{\ln(2)}}{H_k} \exp\left[\frac{-4\ln(2)}{H_k^2}(2\theta_i - 2\theta_k)^2\right] \right]$$

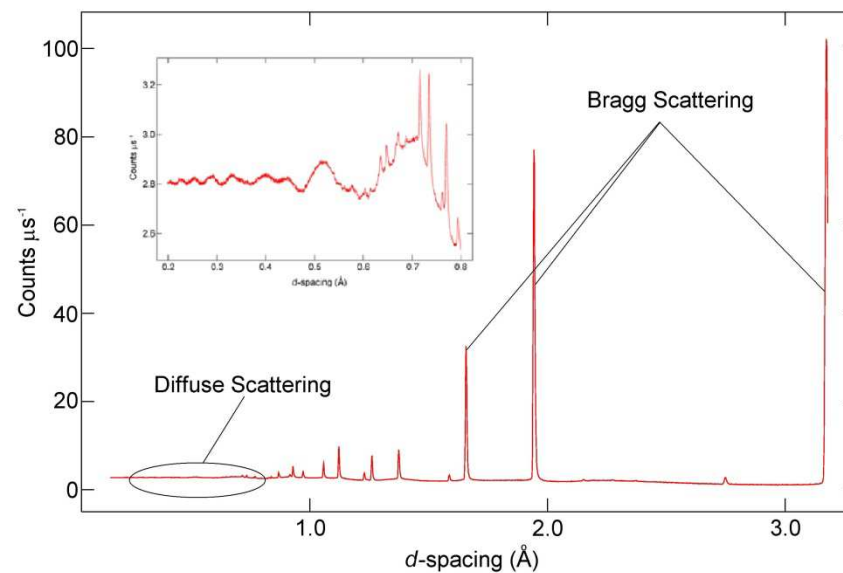
β_c and β_g are the integral breadths of Lorentzian and Gaussian components respectively; η is a mixing parameter; Ω is a complex error function and Re is the real part of the function.

Profile Background

The raw diffraction profile normally contains significant scattering in the background.

The background will contain components associated with the detector, diffraction geometry, amorphous components (diffuse scattering) etc.

Usually one is only interested in the Bragg peaks. Therefore a method of linearising the background is required.



Manual background subtraction

Although rarely used today, a manual background subtraction can be useful in cases where the background function cannot easily be modelled.

This normally involves the user taking points along the profile and performing a linear interpolation between the points.

The greater the number of points chosen the better the fit to the background. Like most manual methods the points chosen are very much subjective.

Background fitting

Background scattering is usually modelled using a low order polynomial function. The indices of the polynomial are usually refined as part of the refinement procedure. However increasing the order of the polynomial does not necessarily improve the fit and introduces extra variables into the refinement.

Some common background functions include:

Simple Polynomial

$$y(\textit{back})_i = \sum_j B_j (2\theta_i - 90^\circ)^j$$

Chebyshev
Polynomial

$$y(\textit{back})_i = \sum_j B_j T'_{j-1}$$

$$T'_n = \sum_m C_m X^m$$

$$X = \frac{2(x_i - x_{\min})}{x_{\max} - x_{\min}} - 1$$

Cosine Fourier

$$y(\textit{back})_i = B_0 + \sum_j B_j \cos(P(j-1))$$

Background correction

In some cases sample containers and detector/instrument background are fairly constant. In these cases an background subtraction can be carried out on the empty sample holder and the background subtracted accordingly.

This of course does not take into account any variations due to the sample itself such as an amorphous component or thermal diffuse scattering.

Rietveld Software

There are a number of Rietveld refinement packages available see www.ccp14.ac.uk for full list.

These include:

REITAN (FAT-REITAN)

DBWS,

XRS-82

LHPM

QPDA

MPROF

REFINE (CCSL based)

TOPAS

JANA 2000

FullProf

GSAS (with ExpGui)

Most of the packages are based on Rietveld's original method involving two basic process.

1. A pre-refinement process involving calculation of the peak positions using unit cell, space group and zero point information. Using a peak width parameter to ensure that a peak's influence on the overall pattern is covered, the profile is chopped up into sections containing the peaks. The rest of the profile is background and this dealt as outlined previously.
2. The refinement process involving varying of refinement parameters using a least-squares method to minimise the difference between observed and calculated intensities of each point on the profile.

Starting model

As stated earlier the Rietveld method is a structure refinement technique. Therefore a structural model has to be input into the refinement in order to calculate structure factors.

The starting model may be found in a number of ways:

- (1) A known structure
- (2) A known isostructural analogue
- (3) A partially known structure
- (4) An educated guess
- (5) A structural distortion of a known structure
- (6) A structural model from *ab-initio* techniques

Refinement Parameters

Profile parameters

Background coefficients, zero-point correction, peak-shape parameters, scale factor

Structural model parameters

Unit cell dimensions, atomic coordinates, thermal parameters, absorption coefficients, preferred orientation parameters, fractional occupancies, phase fractions.

Information required before you start

Unit cell dimensions, Z , space group, atomic coordinates, X-ray wavelength, approximate peak shape parameters (pseudo-Voigt for XRD).



```

Microsoft PowerPoint - [xrd-part2]
MS-DOS Prompt - EXPEDT
Auto
Is this the file you wish to use? (<?>,D,K,Q,R,Y) >y
Experiment title:
      NaMg(P03)3 PA-3
The last history record is :
      HSTRY 42 EXPEDT  U-MS-DOS 28-AUG-97 10:58:12 P P
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >1 a 1
Phase No. 1; Phase has      13 atoms; Title: NaMg(P03)3
SER TYPE      X          Y          Z          FRAC  NAME      UIISO    CODE    STSYM  MULT  FXU
 1 NA      .50000  .50000  .50000  1.00000  Na1      .01192  I XU   -3(111)  4 000
 2 NA      .00000  .00000  .00000  1.00000  Na2      .01192  I XU   -3(111)  4 000
 3 NA      .25311  .25311  .25311  1.00000  Na3      .01192  I XU    3(111)  8 000
 4 MG      .12573  .12573  .12573  1.00000  Mg1      .01192  I XU    3(111)  8 000
 5 MG      .38846  .38846  .38846  1.00000  Mg2      .01192  I XU    3(111)  8 000
 6 P       .02703  .26469  .48087  1.00000  P1       .03494  I XU     1      24 000
 7 P       .23490  .22214  .49349  1.00000  P2       .03494  I XU     1      24 000
 8 O       .47824  .26812  .10993  1.00000  O1       .01522  I XU     1      24 000
 9 O       .00255  .14274  .02989  1.00000  O2       .01522  I XU     1      24 000
10 O       .48295  .32219  .47231  1.00000  O3       .01522  I XU     1      24 000
11 O       .20507  .22430  .09195  1.00000  O4       .01522  I XU     1      24 000
12 O       .28230  .26526  .43019  1.00000  O5       .01522  I XU     1      24 000
13 O       .11881  .19610  .43622  1.00000  O6       .01522  I XU     1      24 000
Phase No. 1; Phase has      13 atoms; Title: NaMg(P03)3
Give atom editing command
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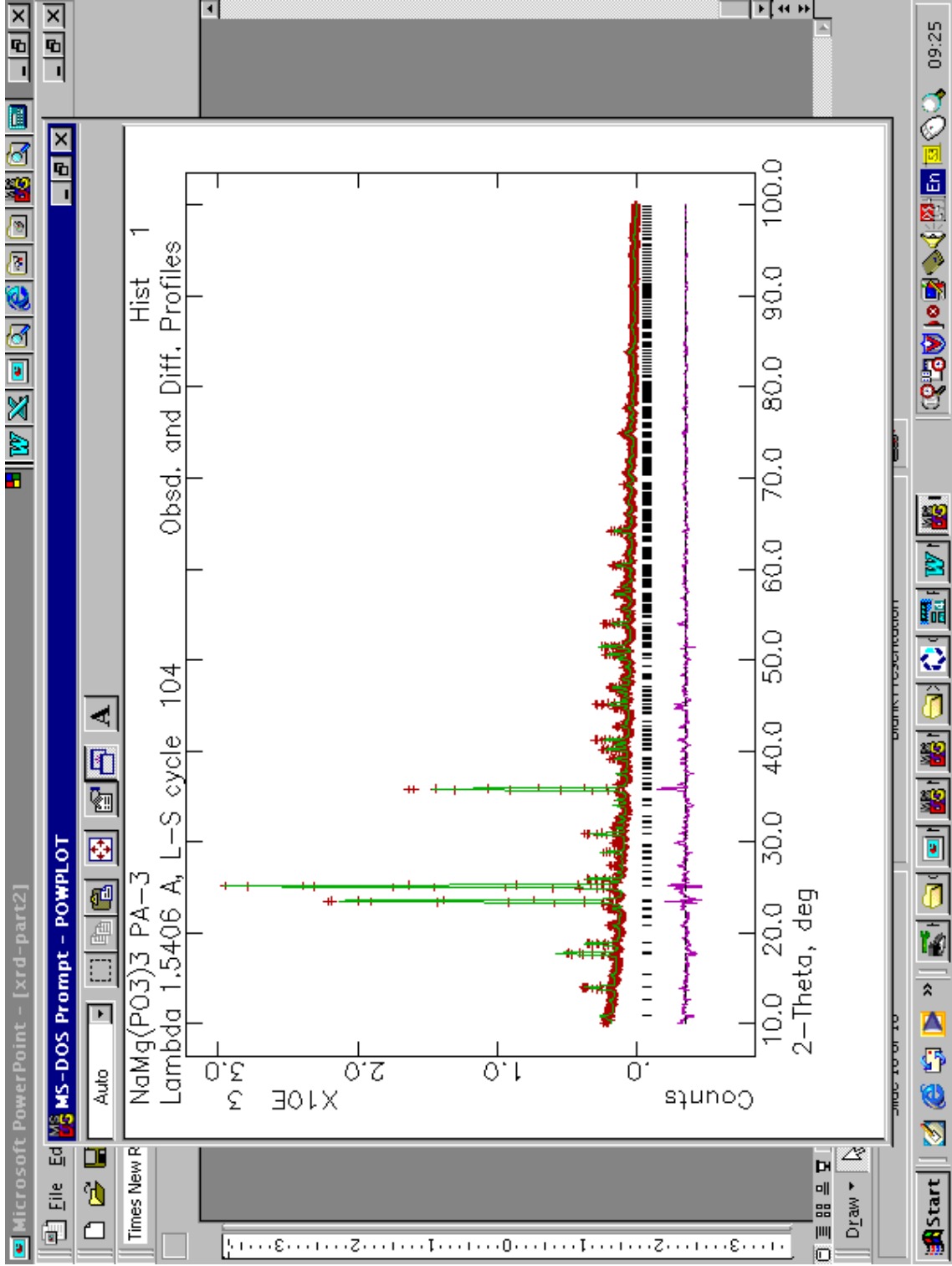
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Microsoft PowerPoint - [xrd-part2]
MS-DOS Prompt - EXPEDT
Auto
A
A, B, C, Alpha, Beta, Gamma      To be refined as allowed by symmetry
14.230130 14.230130 14.230130      90.0000  90.0000  90.0000  90.0000
Damping flag = 0
Enter lattice parameter editing command (<?>,$,C,D,F,K,L,P,U,X) >x
Enter overall parameter to be edited (<?>,A,B,C,D,E,F,H,L,O,P,S,X) >p
Change profile parameter values and refinement flags
Histogram no. 1 Bank no. 1 Lambda1,lambda2 = 1.54056 1.54430
Title: NaMg(P03)3 long scan
**** Histogram will be used in least-squares

Phase no. 1
Phase name: NaMg(P03)3
Aniso. broadening axis 0. 0. 1. Damp 0
Peak profile type no. 2 Number of coefficients: 18
Profile coefficients for Simpson's rule integration of pseudovoigt function
..J. Howard (1982). J. Appl. Cryst.,15,615-620.
..Thompson, D.E. Cox & J.B. Hastings (1987). J. Appl. Cryst.,20,79-83.
#1(GU) = 934.1 Y #2(GU) = -620.8 Y #3(GW) = 146.3 Y
#4(LX) = 4.158 Y #5(LY) = .000 N #6(trns) = .000 N
#7(asym) = .0000 N #8(shft) = .0000 N #9(GP) = .0 N
#10(stec) = .00 N #11(ptec) = .00 N #12(sfec) = .00 N
#13(L11) = .000 N #14(L22) = .000 N #15(L33) = .000 N
#16(L12) = .000 N #17(L13) = .000 N #18(L23) = .000 N
Cut-off for peaks is 1.00 percent of the peak maximum
Profile editing options - (<?>,$,A,C,D,G,H,K,L,N,P,R,U,W,X) >

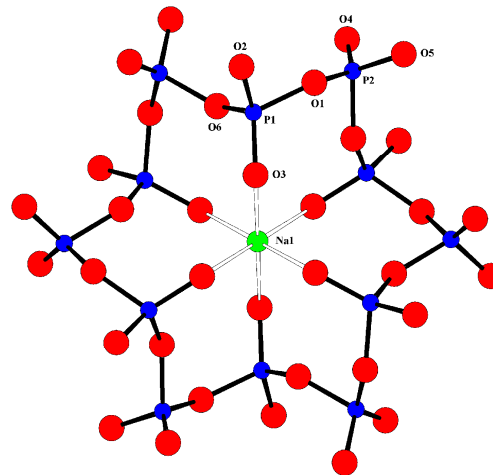
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NaMg(PO₃)₃ final refined parameters

Atom	Wyc.	x	y	z	U _{iso} (Å ²)
Na(1)	4b	0.5(-)	0.5(-)	0.5(-)	0.026(2)
Na(2)	4a	0.0(-)	0.0(-)	0.0(-)	0.026(2)
Na(3)	8c	0.2445(5)	0.2445(5)	0.2445(5)	0.026(2)
Mg(1)	8c	0.1269(7)	0.1269(7)	0.1269(7)	0.012(2)
Mg(2)	8c	0.3846(6)	0.3846(6)	0.3846(6)	0.012(2)
P(1)	24d	0.0247(4)	0.2386(4)	0.4850(4)	0.021(3)
P(2)	24d	0.2308(4)	0.2199(5)	0.4986(5)	0.038(3)
O(1)	24d	0.4832(5)	0.2676(7)	0.1151(5)	0.018(1)
O(2)	24d	0.0273(11)	0.1605(5)	0.0102(10)	0.018(1)
O(3)	24d	0.4729(8)	0.3386(7)	0.4681(9)	0.018(1)
O(4)	24d	0.2203(10)	0.2135(8)	0.0778(6)	0.018(1)
O(5)	24d	0.2843(9)	0.2591(9)	0.4186(7)	0.018(1)
O(6)	24d	0.1259(4)	0.1922(7)	0.4691(9)	0.018(1)



Refinement Strategy

It is particularly difficult to generalise refinement strategies since every refinement has its own particular problems. Nevertheless it is useful for the novice to sequence the refineable parameters. A typical structure refinement based on a single phase constant wavelength X-ray data set might proceed as follows.

- (1) Scale and background
- (2) Lattice parameters
- (3) Peak shape
- (4) Fractional coordinates
- (5) Isotropic thermal parameters
- (6) Fractional occupancies
- (7) Anisotropic thermal parameters
- (8) Preferred orientation extinction and absorption parameters

The initial refinement of scale and background parameters are very dependent on accurate unit cell parameters, zero point correction, peak shape parameters and starting model.

The key point is to make sure the refinement starts with accurate unit cell and zero point parameters. It is always good practice to refine the unit cell parameters and zero point correction from measured d -spacings prior to the Rietveld refinement.

It is not always evident from R-factors alone, that the initial refinement has failed to refine any Bragg peaks !

Fault finding chart for Rietveld Refinements

Fault	Reason	Action
Program crashes on initial powder preparation	(1) Bad Data. Data set corrupted, in wrong format or has gaps. (2) Data set range set incorrectly (3) Peak width too large or peak range too large (4) Too many reflections, reached array limit. (5) Data set too large	(1) Reformat or recollect data. (2) Reset data range correctly (3) Use narrower peak width and or peak width range (4) Cut down data set use exclude regions. (5) As for (4) also use larger bin width to reduce number of points in pattern
Program crashes on initial refinement with background and scale refining.	(6) Too many phases in multiphase refinement (7) Too many patterns in multi-pattern refinement (1) As above (2) Initial scale or background too far out (3) Background incorrect e.g. poor background function, wrong number of background coefficients.	(6) Reduce number of phases (7) Reduce number of patterns. (1) As above (2) Modify and repeat refinement. (3) Alter background type and or number of refineable parameters.
Initial refinement successful but no Bragg peaks fitted.	(4) Too many parameters refining (1) Scale factor not refining (2) peak positions do not correspond to Bragg peaks (3) Peak shape incorrect.	(4) Switch off unwanted parameters. (1) Switch on scale factor (2) Unit cell and or zero point incorrect, refine separately directly from measured d-spacings and re-enter. (3) Select correct peak shape. If peak width too narrow or too broad- modify.
Refinement crashes on introduction of lattice parameters or zero-point	(1) Poor data (2) Wrong space group symmetry, crystal system. (3) Poor starting model	(1) recollect data (2) Examine data carefully for split or absent peaks change lattice parameters/ space group accordingly. (3) Use better starting model. Fix lattice and zero point and refine positional parameters of heavy atoms to improve model.

Fault	Reason	Action
Refinement diverges or crashes on introduction peak shape parameters	(1) As above (2) Peak shape incorrect	(1) As above (2) Change peak shape, use better starting parameters, refine peak shape parameters sequentially.
Refinement crashes or diverges on introduction of fractional coordinates	(1) Poor starting model (2) Wrong space group or crystal system (3) Wrong enantiomorph in non-centrosymmetric structure (4) Scattering dominated by heavy atom	(1) Improve starting model or introduce fractional coordinates sequentially. (2) Use alternative space group/crystal system. (3) transform coordinates to other enantiomorph. (4) Use neutron data.
Divergence of positional parameters for certain atoms only	(1) as above	(1) as above
Thermal parameters diverge, or are negative or too large	(1) as above (2) Absorption correction required (3) Fractional occupancies incorrect (4) Preferred orientation or extinction correction required (5) weak second phase present (6) Positional disorder, split positions.	(1) as above (2) Apply and or refine absorption correction (3) modify/refine fractional occupancies (4) Apply/refine preferred orientation or extinction correction as required. (5) check difference plot carefully for unassigned reflections and refine 2nd phase (6) Refine anisotropic parameters to see in which direction the positional disorder occurs. Split positions accordingly or move from special to general positions.
Poor difference plot	(1) Background poor (2) Peak shape poor (3) Model incorrect (4) Preferred orientation, extinction or absorption correction required. (5) Lattice parameters and or zero point out.	(1) Change background type / order of polynomial etc. (2) Modify/refine peak shape, rerun powder preparation program. (3) Look for missing atoms, alter model accordingly. (4) Apply required correction and refine. (5) Rerun powder preparation program.
Refinement converges on false minimum.	(1) Convergence criteria too low.	(1) increase convergence criteria.