**The Rietveld Method in Neutron and X-ray Powder Diffraction**

BY A. ALBINATI

Politecnico di Milano, Istituto di Chimica, 20133 Milano, Italy

AND B. T. M. WILLIS

Materials Physics Division, AERE Harwell, Oxon OX11 0RA, England

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**Abstract**

In the Rietveld method of analysing powder diffraction data, the crystal structure is refined by fitting the entire profile of the diffraction pattern to a calculated profile. There is no intermediate step of extracting structure factors. The method was applied first to diffraction patterns recorded with neutrons at a fixed wavelength. It has now been used successfully for the treatment of results from the four categories of experimental technique, with neutrons or X-rays as the primary radiation and with the scattered intensity measured at a fixed wavelength or at a fixed scattering angle. In this article we discuss the application of the Rietveld method to each of these techniques.

1. Introduction

The profile refinement method of analysing powder diffraction data, originally introduced by Rietveld (1967, 1969), has been widely used in the field of neutron diffraction. A review of this work, citing over 150 references, was published a few years ago (Cheetham & Taylor, 1977). Fewer papers have appeared so far on the application of the Rietveld method to X-ray diffraction, but it has been predicted (Young, 1980) that X-ray papers may soon outnumber those on neutron diffraction.

In this article we shall be concerned with a number of fundamental questions about the Rietveld method:

(i) What is the appropriate analytical form of the peak-shape function describing the variation with scattering angle, or with wavelength, of the intensity of a single reflection?

(ii) Is the customary formulation of the half-width function, which determines the \( \sin \theta / \lambda \) dependence of the width of a reflection, satisfactory?

(iii) Are the structural parameters derived by the Rietveld method reliable, and are the estimated standard deviations realistic?

In § 2 we summarize the basic scattering formulae for the various experimental techniques. The theory of the Rietveld method is outlined in § 3. The form of the peak-shape function is considered in § 4, and of the half-width function in § 5. § 6 describes some of the computer programs used for Rietveld refinement. § 7 discusses a few tests of the reliability of parameters derived by the Rietveld method.

A conference on ‘Diffraction Profile Analysis’, sponsored by the International Union of Crystallography, was held at Cracow, Poland, in August 1978. It was suggested then that the phrase ‘Rietveld Method’ should be used in preference to other phrases such as ‘Profile Analysis’ or ‘Pattern-Fitting Structure Refinement’. We shall follow this suggestion here, and hence avoid any confusion between the Rietveld method (which deals with the entire diffraction profile) and the analysis of the profiles of individual diffraction lines, as described, for example, by Wilson (1963).

2. Experimental techniques. Basic intensity formulae

The Rietveld method has been successfully applied to the analysis of powder diffraction data obtained by a variety of experimental techniques. In this section we shall describe briefly the experimental arrangement used for each technique, and quote the corresponding intensity formulae which are required in the theory of § 3. The techniques can be classified into four categories, according to whether neutrons or X-rays are used for the primary radiation, and whether the scattered radiation is measured at a fixed wavelength or at a fixed scattering angle.

(a) Neutron powder diffraction: fixed wavelength

In a typical experimental arrangement (see Fig 1), thermal neutrons from a nuclear reactor \((R)\) are monochromatized by a large single crystal \((M)\). The horizontal divergence \(z_1\) of the beam striking the monochromator is normally less than one degree of arc and is defined by the collimator between \(R\) and \(M\).
The monochromatic beam is scattered by the powder sample $S$ into a detector $D$ (or into a bank of detectors at different scattering angles). The neutron wavelength is usually chosen within the range 1.0–2.5 Å. A collimator between $M$ and $S$ defines the divergence $\alpha_2$ of the monochromatic beam, and one between $S$ and $D$ defines the divergence $\alpha_3$ of the scattered beam.

The detector records the intensity which is scattered by the sample at different values of the scattering angle $2\theta$. Fig. 2 is an example of a diffraction pattern (from deuterated hexamethylenetetramine). For samples of lower symmetry than cubic, the peaks would not be as well separated from one another as those in Fig. 2.

If we ignore the non-Bragg intensity, which is largely subtracted with the background, then the scattered intensity can be calculated as follows.

For a cylindrical sample, fully bathed in the neutron beam, the total number of neutrons diffracted into a length $L$ of the Debye–Scherrer ring is (Bacon, 1975)

$$N(2\theta) = \frac{\phi_0 \lambda^3 L V \rho' j_{hk1} N_f^2 F_{hk1}^2}{8 \pi R \rho \sin \theta \sin 2\theta} \delta(\theta - \theta_B).$$

$$f(2\theta) = \frac{2}{H} \left(\frac{\ln 2}{\pi}\right)^{1/2} \exp \left(-\frac{4 \ln 2}{H^2} (2\theta - 2\theta_B)^2\right).$$

where $\phi_0$ is the incident flux, $\lambda$ is the wavelength, $V$ is the specimen volume, $\rho'$ is the measured density, $j_{hk1}$ is the multiplicity of the $\{hk1\}$ family of planes, $N_f$ is the number of unit cells per unit volume, $F_{hk1}$ is the structure factor of the $\{hk1\}$ planes, $R$ is the specimen-to-detector distance, $\rho$ is the theoretical density, $2\theta$ is the scattering angle, and $\theta_B$ is the Bragg angle.

The delta function in (1) implies that there is no diffracted intensity unless $\theta = \theta_B$. This situation occurs only for perfect collimation of the three beams in Fig. 1, i.e., for $\alpha_2 = \alpha_3 = \alpha_4 = 0$. Finite collimation (and finite strain, particle size, etc.) lead to a broadening in $2\theta$ of the Bragg peak. If the peak-shape function $f(2\theta)$ is Gaussian (see § 4), we can write

$$I(2\theta) = \frac{\phi_0 \lambda^3 L V \rho' j_{hk1} N_f^2 F_{hk1}^2}{8 \pi R \rho \sin \theta_B \sin 2\theta_B H} \exp \left\{ -\frac{4 \ln 2}{H^2} (2\theta - 2\theta_B)^2\right\}.$$  

where $H$ is the full-width at half-maximum (FWHM) of the peak and the normalizing constant ensures that the peak has unit area, independent of $H$.

To obtain the calculated diffracted intensity, $I(2\theta)$, the intensity in (1) must be convoluted with the broadening function in (2), giving

$$I(2\theta) = \frac{\phi_0 \lambda^3 L V \rho' j_{hk1} N_f^2 F_{hk1}^2}{8 \pi R \rho \sin \theta_B \sin 2\theta_B H} \times \exp \left\{ -\frac{4 \ln 2}{H^2} (2\theta - 2\theta_B)^2\right\}.$$  

With the notation of Rietveld (1969), (3) can be rewritten in the form

$$y_i = \frac{c j_k L_k F_k^2}{H_k} \exp \left\{ -\frac{4 \ln 2}{H_k^2} (2\theta_i - 2\theta_k)^2\right\}.$$  

where $y_i$ is the contribution of the Bragg reflection $k$ to the intensity measured at position $2\theta_i$, $c$ is a constant for a given sample and diffraction geometry, $L_k$ is the Lorentz factor, $2\theta_k$ is the calculated position of the Bragg peak, and $H_k$ is the FWHM of the peak.

(b) Neutron powder diffraction: fixed scattering angle

In the second possible experimental arrangement with neutrons, a pulsed source replaces the continuous source from a steady-state reactor. Pulsing can be accomplished on a reactor by a mechanical chopper (see, for example, Steichele & Arnold, 1973). Alternatively, the fission reaction itself can be pulsed, as is done in the IBR-2 reactor at Dubna, USSR. where the pulse length of 90 μs is comparable with the neutron slowing-down time for long wavelengths (~5 Å). Shorter pulses, suitable for diffraction work at wavelengths down to 0.2 Å, are attained with an electron linear accelerator by firing electrons into a uranium target, or with a proton synchrotron in which protons are aimed at a heavy metal target. Pulsed neutrons are produced in the first case by an electron Bremsstrahlung–photoneutron reaction, and in the
second case by the spallation process (spalling, or chipping, of the target nucleus). These bursts of fast neutrons must then be slowed down by collisions in a moderator to provide a pulsed beam. For further information on pulsed neutron sources, see Windsor (1981).

The neutron pulse contains a wide range of energies (wavelengths). By placing the detector at a fixed scattering angle (see Fig. 3), and by measuring the time-of-flight to the detector of the individual neutrons in a burst, the scattered intensity is determined as a function of wavelength. The time-of-flight $t$ is readily converted to wavelength $\lambda$ or to $d$ spacing with

$$t = \left( \frac{m_n}{h} \right) \lambda \text{ or } t = \left( \frac{2m_n \sin \theta_0}{h} \right) d,$$

where $m_n$ is the neutron mass, $h$ is Planck's constant, $l$ is the total flight path and $2\theta_0$ is the scattering angle.

Fig. 4 illustrates a portion of the diffraction pattern from Al$_2$O$_3$, as recorded at the ZING-P pulsed neutron source (Jorgensen & Rotella, 1982). The complete pattern covered a range of $d$ spacing which was four times the range shown in Fig. 4; at longer $d$ spacings the diffraction peaks are more widely separated, whereas at smaller $d$ spacings they are much closer together.

The form of the function describing the variation of the incident neutron flux with wavelength is different for radiations from a nuclear reactor and from a particle accelerator. For a reactor, the flux distribution is given by

$$\phi(\lambda) = \text{constant} \times T^{-3.2} \lambda^{-5} \exp \left[ -\frac{h^2}{2m_n k_B T \lambda^2} \right],$$

(5)

where $T$ is the effective neutron temperature and $k_B$ is Boltzmann's constant. Fig. 5 shows the flux spectrum for a temperature $T = 300$ K. The peak occurs between 1 and 1.5 Å and the flux is virtually zero below 0.5 Å. For a neutron source pulsed by an electron accelerator, the spectrum is given by the superposition of a Maxwellian distribution (with a characteristic temperature $T$) and a slowing-down spectrum representing the $1/E$ behaviour of the epithermal flux. The thermal and epithermal components are illustrated in Fig. 6, taken from Mildner, Boland, Sinclair, Windsor, Bunce & Clarke (1978). In contrast to the reactor source (Fig. 5), the intensity extends to very short wavelengths so that the diffraction data can be collected up to $\sin \theta/\lambda$ values approaching 3.0. The possibility of making measurements at such a high $\sin \theta/\lambda$ is a major advantage of accelerator sources.

The corrections for the spectral distribution of the incident beam, and for the variation with energy of the efficiency of the detector, can be made using the isotropic scattering from a standard vanadium sample as a measure of the total instrument function (Windsor & Sinclair, 1976). Von Dreele, Jorgensen & Windsor (1982) fit the apparent intensity distribution, as measured with vanadium, to the function

$$I(t) = A_0 + \frac{A_1}{t^5} \exp \left( -\frac{A_2}{t^2} \right) + A_3 \exp \left( -\frac{A_4 t^2}{t} \right)$$

$$+ A_5 \exp \left( -A_6 t^4 \right) + A_7 \exp \left( -A_8 t^4 \right),$$

(6)

where $t$ is the time-of-flight and $A_0, \ldots, A_8$ are treated as adjustable parameters.
In the time-of-flight method the diffracted intensity at constant $\theta$ from the \{hkl\} planes varies with the fourth power of the wavelength (Buras, 1963), or with $d_k^4$, where $d_k$ is the spacing for reflection $k$. The contribution of $k$ to the intensity $y_i$, recorded in the $i$th time channel is proportional, therefore, to

$$y_i = j_k d_k^4 \phi(\lambda_k) \sin \theta_k f(\lambda_k) F_k^2$$

(compare with (4) for a fixed-wavelength experiment). $f(\lambda_k)$ in (7) is the peak-shape function and the remaining quantities are as in (4). The analytical form of $f(\lambda_k)$ is discussed in § 4.

(c) X-ray powder diffraction: fixed wavelength

The first paper describing the application of the Rietveld method to the analysis of X-ray powder diffraction patterns was published by Malmros & Thomas (1977). These authors used a Guinier-Hägg focusing camera and an automatic microdensitometer to measure the film intensities. A powder camera with focusing geometry has a number of features which recommend it for recording intensities: (a) good resolution of the lines in the diffraction pattern; (b) complete removal of the $K\alpha_2$ component of the incident X-ray beam at the monochromator; (c) minimization of preferred-orientation effects, because the beam is transmitted through a thin rotating sample.

A sketch of the focusing arrangement used in the Guinier-Hägg camera is shown in Fig. 7. M is a bent-crystal monochromator lying along the circumference of the `monochromator focusing circle' with centre $O_1$. P is a thin powder sample which is positioned along the `sample focusing circle' with centre $O_2$. The diffraction pattern is recorded along the circular arc $FA$ and extends up to $2\theta \sim 90^\circ$.

Khattak & Cox (1977) have used the Rietveld method to analyse data recorded with an X-ray powder diffractometer. The complications introduced by overlap of the $\alpha_1\alpha_2$ doublet were avoided by mounting a pyrolitic graphite monochromator on the detector arm, and tuning the monochromator for Cu $K\beta$ radiation instead of the Cu $K\alpha$ doublet. The diffraction pattern in Fig. 8 was recorded with an X-ray diffractometer equipped with a diffracted-beam monochromator of curved graphite.

The expression for the intensity $y_i$ at a point $2\theta_i$ in the diffraction pattern is similar to that given in (4) for a neutron experiment at a constant wavelength. It is necessary, however, to add a polarization factor for crystal-monochromatized radiation and an absorption factor, both of which are $\theta$ dependent. (For neutrons there is no polarization factor for non-

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![Fig. 7. Principle of the Guinier-Hägg focusing camera.](image)

![Fig. 6. The measured spectrum (dots) and fitted spectrum (full line) for a polyethylene moderator at room temperature with the neutrons produced by an electron linear accelerator. (After mildner et al., 1978.)](image)

![Fig. 8. X-ray diffraction of fluorapatite, taken with Cu $K\alpha$ radiation. The tick marks show positions calculated for the Bragg reflections. (After Young, Mackie & Von Dreele, 1977.)](image)
magnetic samples, and the absorption factor is small and varies little with scattering angle.) Also, the shape of an individual reflection cannot be described by a simple Gaussian function, as in (2). The appropriate form of the peak-shape function is discussed in § 4.

(d) X-ray powder diffraction: fixed scattering angle

Another way of collecting X-ray diffraction data in a form suitable for analysis by the Rietveld method is to employ an energy-dispersive technique. In this method the full white spectrum (Bremsstrahlung radiation) from an X-ray tube or an electron synchrotron falls on the sample, and a solid-state detector, held at a fixed scattering angle and connected to a pulse-height analyser, performs an energy analysis of the diffracted beam (see Fig. 9).

There are a number of difficulties in using the energy-dispersive method:

(i) Commercial X-ray tubes have a limited spectral distribution, and the Bremsstrahlung is accompanied by characteristic X-ray emission lines.

(ii) With an X-ray tube there is uncertainty in calculating the polarization term in the expression for the scattered intensity. This is because the incident beam is neither completely polarized nor completely unpolarized, and the degree of polarization varies with the photon energy.

(ii) The corrections due to absorption and extinction are wavelength dependent.

The use of synchrotron radiation obviates difficulties (i) and (ii), as the white spectrum is wide and is devoid of characteristic lines, and the radiation is almost fully polarized at all energies. Synchrotron radiation also offers the advantages that data can be collected to much higher Bragg angles and so counting rates are much larger (Buras, Olsen & Gerward, 1976). Fig. 10 is an example of a diffraction pattern recorded with X-rays from the Daresbury synchrotron, NINA. The resolution is entirely determined by the intrinsic resolution of the lithium-drifted silicon detector, which is $\sim 180$ eV at 10 keV. Thus the resolution of the energy-dispersive technique (d) is rather poor compared with that obtainable with the other X-ray and neutron techniques (a)–(c).

The spectral distribution of the incident beam and the energy dependence of the efficiency of the detector can be determined by measuring the diffraction pattern of a standard sample (e.g. silicon). Alternatively, with a storage ring as a synchrotron radiation source, it is possible to calculate the incident spectrum from the machine parameters (Buras, Gerward, Glazer, Hidaka & Staun Olsen, 1979).

3. Theory of the Rietveld method

(a) Original Rietveld formulation

The Rietveld method of analysing powder diffraction patterns was developed first for the case of neutron diffraction at a fixed wavelength (Rietveld, 1969).

The appropriate expression for the contribution of a single reflection $k$ to the intensity $y_i$ measured at a scattering angle $2\theta_i$ is given by (4) above, where $H_k$ is the full width of the reflection at half height. According to Caglioti, Paoletti & Ricci (1958) the dependence of $H_k$ on $\theta_k$ can be written in the simplified form

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

where $U, V, W$ are half-width parameters independent of $\theta_k$. We shall see later (§ 5) that (8) does indeed give an adequate representation of the variation of the FWHM with Bragg angle, although the Caglioti treatment ignores intrinsic sample broadening and so $U, V, W$ must be treated as adjustable variables in the refinement.

The tails of a Gaussian peak decrease rapidly with distance from the maximum, and the intensity at one and a half times the FWHM from the peak is only 0.2% of the intensity at the peak. Thus no large error is introduced by assuming that the peak extends over a range of $\pm 1.5 H_k$ and is cut off outside this range.

Because of the possibility of different Bragg peaks occurring at scattering angles which are within a few multiples of $H_k$ of one another, the intensity $y_i$ at a

![Fig. 9. Schematic lay-out of energy-dispersive technique. S sample, D solid-state detector, PA pre-amplifier, A amplifier, MCA multichannel analyser.](image)

![Fig. 10. Diffraction pattern of BaTiO$_3$, recorded with synchrotron radiation and at a fixed scattering angle of 24.75°. (After Glazer, Hidaka & Bordas, 1978.)](image)
point \( i \) in the diffraction pattern may have contributions from more than one Bragg reflection. The number of overlapping reflections at point \( i \) is readily determined from a knowledge of the peak positions \( 2\theta_i \) and corresponding widths \( H_k \), and (4) can then be employed to calculate \( y_i \) by summing over all such reflections. The Rietveld method owes a large measure of its success to its ability in analysing complex diffraction patterns with severe overlapping of Bragg peaks.

Least-squares refinement is achieved by minimizing the function

\[
M = \sum_i w_i [y_i(\text{obs}) - y_i(\text{calc})]^2,
\]

where the summation is over all points in the pattern. \( w_i \) is a weighting factor which is inversely proportional to the variance of the quantity in square brackets and \( c \) is an overall scale factor.

The least-squares parameters are of two kinds. The first group contains the usual structural parameters: \( T_0 \), overall isotropic temperature parameter; \( x_{lj} \), \( y_{lj} \), \( z_l \) fractional coordinates of the \( l \)th atom in the asymmetric unit; \( n_l \), occupation number of \( l \)th atom; \( B_l \), isotropic temperature factor of \( l \)th atom.

The second group represents 'profile parameters' which are not normally encountered in a least-squares refinement of single-crystal data. These include: \( U, V, W \) half-width parameters [see (8)]; \( 2\theta_0 \), zero position of detector; \( A, B, C, D, E, F \) unit-cell parameters where \( 1/d^2 = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk \).

Further parameters may be added, for special purposes, to both groups. For example, the first group may contain coefficients of the anisotropic temperature factors, and the second group parameters allowing for skewness of the reflections at extreme scattering angles (see § 4a) or for preferred orientation.

The maximum number of structural parameters which can be safely included in a powder refinement is largely determined by the quality (especially resolution) of the diffraction pattern. With neutron measurements at a fixed wavelength, this number might be between 50 and 100. Assuming isotropic thermal motion, there are four parameters for each atom in a general position, so that an upper limit to the complexity of the structure that can be examined is one with about 25 atoms in the asymmetric unit.

(b) The problem of correlated residuals

The observed intensity on the right-hand side of (9) is given by the difference between the total intensity \( Y_i \) at each position \( 2\theta_i \) and the background (non-Bragg) intensity \( B_i \):

\[
y_i(\text{obs}) = Y_i - B_i.
\]

Assuming Poisson counting statistics the weight \( w_i \) to be assigned to \( y_i(\text{obs}) \) is

\[
w_i = 1/\left[ \sigma_i^2(Y_i) + \sigma_i^2(B_i) \right].
\]

The variance \( \sigma_i^2(B_i) \) is usually arbitrarily set to zero, and as the variance of \( Y_i \) is equal to \( Y_i \), the weighting factor reduces to

\[
w_i = 1/ Y_i.
\]

This weighting factor is used in several computer programs for Rietveld refinement. However, it reflects only the statistical errors of counting for the observed intensities, and makes no allowance for errors in the calculated intensities in (9). If there are inadequacies in the structural model, or if the assumed peak shape differs from the true shape, then the calculated intensities will be in error. Moreover, for points on the profile which are close together the errors are likely to be in the same direction, and this correlation between residuals is greater the closer together are the profile points.

The existence of correlated residuals for an isolated Bragg peak is illustrated in Fig. 11. The full line represents the calculated peak as fitted by the Rietveld method and constrained by the structural model, whereas the broken line is simply a best fit of a Gaussian curve through the experimental points. By altering, for example, the overall temperature factor, points on the calculated peak will all move up (or down) together, leading to a positive correlation, or covariance, between pairs of residuals.

The Rietveld analysis has been extended by Clarke & Rollett (1982) to take into account the problem of

Fig. 11. Diagram illustrating correlation between the residuals, \( y_i(\text{obs}) - y_i(\text{calc}) \), for pairs of points belonging to the same Bragg peak. The observed points are distributed randomly about the observed Gaussian, and the calculated Gaussian is derived from the Rietveld refinement. (After Sakata & Cooper, 1979.)
correlated residuals. They consider the correlation that occurs if points on the profile have contributions from the same Bragg peak. This means that if the peak extends, say, over two degrees and is sampled at intervals of 1/10 degree, there is no correlation between points more than 20 points apart, and the variance–covariance matrix of the observational equations has non-zero elements which are all close to the diagonal of the matrix. By using such ‘band-limited’ matrices in the least-squares refinement, Clarke & Rollett show that their computer program does not require much more machine time per cycle, nor much more storage, than the original Rietveld procedure with no correction for correlation.

(c) Criticisms of Cooper

In a number of papers (Sakata & Cooper, 1979; Cooper, Sakata & Rouse, 1980; Cooper, 1982) Cooper has criticized the Rietveld method, stating that the values obtained for the structural parameters are not exactly the same as those obtained by other refinement methods and that the standard deviations of the parameters are determined incorrectly. His principal objection to the method is that it fails to recognize that the two groups of least-squares parameters are determined by different features of the diffraction pattern. The structural parameters depend on the integrated intensities of the reflections and not on their shape or positions, whereas the profile parameters are governed by the peak shapes. The Rietveld analysis is satisfactory only if the goodness of fit is the same for the two groups of parameters.

To overcome this limitation Cooper recommends that the Rietveld method is replaced by a two-stage procedure, with the profile parameters refined in the first stage and the structural parameters in the second stage. A detailed discussion of Cooper's work is outside the scope of this article, as we are concerned only with the Rietveld method itself. However, we shall refer in § 7 to Cooper's results with the alternative two-stage approach, because they throw some light on the validity of the results from the Rietveld method.

4. The peak-shape function

The nature of the analytical expression which best describes the shape of the diffraction peak varies with the choice of experimental technique.

(a) Neutrons: fixed wavelength

For powder diffraction work with neutrons of a fixed wavelength, the peak shape depends on a number of factors, including the mosaic structure of the crystal monochromator, the geometry of the defining collimators and the crystallinity of the sample. The convolution of these factors produces a peak shape which is almost exactly Gaussian (Fig. 12). This is the justification for using a Gaussian function in (2).

At very low and at very high scattering angles, the diffraction peaks show asymmetry, which is mainly caused by the finite vertical divergence of the beam (Cooper & Sayer, 1975; Thomas, 1977). A good approximation to the asymmetric profile is obtained by multiplying the Gaussian function by (Rietveld, 1969)

$$1 - P(2\theta - 2\theta_B)^2 s \cot \theta_B,$$

where $P$ is the asymmetry parameter, $\theta_B$ the Bragg angle and $s = 1, 0 \text{ or } -1$ depending on $2\theta - 2\theta_B$ being positive, zero or negative. A Voigt function, which is a convolution of a Gaussian function and Cauchy function, can also be used to describe the shape of asymmetric diffraction peaks (Suortti, Ahtee & Unonius, 1979).

(b) Neutrons: fixed scattering angle

For time-of-flight neutron powder diffraction, with an electron accelerator, target and moderator as neutron source, it is possible to describe the peak shape in terms of three separate regions whose individual shapes are caused by different effects. At the leading edge of the pulse [region (i) in Fig. 13], the build up of the neutron pulse in the moderator is very rapid and so the major uncertainties in the time of flight arise from variations in the angle and distance, which are of Gaussian form. The first part of the trailing edge [region (ii)] also appears to be Gaussian but with a different constant from the leading edge. The long remaining part of the trailing edge [region (iii)] is a result of the slow decay of the thermalized...
neutron pulse, and is represented by an exponential function.

Each region in Fig. 13 is determined by two parameters (intensity and width), but there will be certain relations between these parameters, as demanded by the necessity for a smooth transition between adjacent regions. The principal parameters are $\sigma_1$ and $\sigma_2$, determining the widths of the Gaussian regions, and $\gamma$ the decay constant of the exponential region. Thus

(i) $t \leq t_0$, $I(t) = \exp\left[-(t - t_0)^2 / 2\sigma_1^2\right]$
(ii) $t_0 \leq t \leq t_1$, $I(t) = \exp\left[-(t - t_0)^2 / 2\sigma_2^2\right]$
(iii) $t \geq t_1$, $I(t) = \exp(\gamma^2\sigma_2^2 / 2) \exp\left[-\gamma(t - t_0)\right]$. (12)

A typical line shape is shown in Fig. 14, in which the experimental points are fitted to (12).

Carpenter et al. (1975) used different functions to describe the peak shape. They operated a time-of-flight powder diffractometer on a pulsed source, with neutrons produced by the spallation process in a target of lead. The time distribution of the resolution function was assumed to be of the form

$$I(t) = \frac{\alpha\beta}{2(\alpha + \beta)} [\exp(u) \text{erfc}(y) + \exp(v) \text{erfc}(z)],$$

(13)

where $\text{erfc}(y)$ is $1 - \text{erf}(y)$ and $\text{erf}(y)$ is the error function

$$\text{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y \exp(-x^2) \, dx$$

and

$$u = \frac{1}{2} \alpha(\alpha\sigma^2 + 2t)$$
$$v = \frac{1}{2} \beta(\beta\sigma^2 - 2t)$$

Equation (13) is derived by convoluting a Gaussian instrumental function (whose width is characterized by $\sigma$) with a rising exponential front edge

$$\exp(\alpha t), t \leq 0$$

and a falling exponential trailing edge

$$\exp(-\beta t), t \geq 0,$$

where $\alpha$ and $\beta$ are the rise- and decay-time constants.

With three adjustable coefficients, $\alpha$, $\beta$ and $\sigma$, (13) gives an excellent fit to the experimental line shape (Fig. 15).

If the neutron pulse is produced by chopping the beam from a steady-state reactor, the peak shape is approximately Gaussian (Worlton, Jorgensen, Beyerlein & Decker, 1976).

(c) X-rays: fixed wavelength

We have seen that Gaussian functions give a good fit to neutron powder-diffraction peaks recorded at constant wavelength. This is not the case for X-ray powder-diffraction peaks measured at fixed wave-
length, as the tails of the observed peaks fall off much less rapidly than a Gaussian.

A better fit to the peak shape is given by a Lorentzian (see Fig. 16):

$$f(2\theta) = \frac{1}{1 + C_k^L(2\theta - 2\theta_k)^2}, \quad (14)$$

where

$$C_k^L = 4/H_k^2$$

and $H_k$ is the FWHM in $2\theta$ of the reflection $k$. Parrish & Huang (1980) employ two or three Lorentzians to fit each $K\alpha_1$ and $K\alpha_2$ peak. However, although X-ray emission lines are Lorentzians, the instrumental resolution function (for a standard diffractometer arrangement or for a Guinier–Hägg camera) and the diffraction broadening function are not. Several authors have examined alternative functions in attempting to obtain closer agreement with the observed peak shape.

Malmros & Thomas (1977) employed a modified Lorentzian (ML function)

$$f(2\theta) = \frac{1}{[1 + C_k^{ML}(2\theta - 2\theta_k)^2]^2}, \quad (15)$$

with

$$C_k^{ML} = 4(\sqrt{2} - 1)/H_k^2$$

for interpreting powder patterns obtained with a Guinier–Hägg camera. A more detailed discussion of the peak-shape function in this type of camera is given by Ersson (1979). A different approach was adopted by Fichtner-Schmittler & Menz (1978), who divided each peak into two parts, for $\theta < \theta_k$ and $\theta > \theta_k$, with the parts characterized by Lorentzian functions of different widths.

For analysing data from a powder diffractometer by the Rietveld method, Khattak & Cox (1977) tried four simple functions to describe the peak shape. These were the Gaussian, Lorentzian, ML and the intermediate Lorentzian (IL). The best results were obtained with the IL function, which is defined by

$$f(2\theta) = \frac{1}{[1 + C_k^{IL}(2\theta - 2\theta_k)^2]^{1.5}}, \quad (16)$$

with

$$C_k^{IL} = 4(2^{1/3} - 1)/H_k^2.$$ 

None of the functions (14), (15), (16) is entirely satisfactory. The quality of fit obtained with X-rays is distinctly inferior to that obtained with a typical neutron diffraction pattern. The best weighted $R$ values for a standard sample such as silicon are twice the corresponding $R$ values with neutrons (Khattak & Cox, 1977). The full potential of the Rietveld method, as applied to the X-ray powder diffraction technique at fixed wavelength, will not be realized until improved peak-shape functions are found.

(d) X-rays: fixed scattering angle

The peaks formed in the energy-dispersive method are expected to be pure Gaussians (Glazer, Hidaka & Bordas, 1978). Thus the peak-shape function can be written [cf. (2)]:

$$f(E_i) = \frac{2}{H} \left( \frac{\ln 2}{\pi} \right)^{1/2} \exp \left[ - \frac{4 \ln 2}{H^2} (E_i - E_B)^2 \right], \quad (17)$$

where $E_i(= hc/\lambda)$ is the energy in channel $i$ and $E_B$ is the energy at the peak of the Bragg reflection.

Observed reflection profiles and those calculated with Gaussian functions fit extremely well (see Fig. 17). There is no need to incorporate an asymmetry parameter for extreme values of $\sin \theta/\lambda$. (cf. § 4a).
5. The peak-width function

All the expressions discussed in § 4 for the peak-shape function contain $H_k$, the FWHM of the peak. This width varies with scattering angle (or with wavelength in the fixed-2θ techniques) and its dependence on $\theta$ (or $\lambda$) must be parameterized in applying the Rietveld method.

For neutron diffraction at a fixed wavelength, Rietveld (1969) proposed (18) which was derived theoretically by Caglioti, Paoletti & Ricci (1958):

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

The refined values of $U$, $V$, $W$ are not the same as those calculated from theory: Fig. 18 shows the discrepancy between the observed and calculated peak widths for CeTaO$_4$. The focusing position of a two-axis diffractometer is close to $2\theta = 2\theta_M$ where $2\theta_M$ is the take-off angle of the monochromator, and this is the origin of the minima in Fig. 18. Equation (18) gives an adequate description of the dependence of the observed width on scattering angle, but $U$, $V$, $W$ are not constants for a particular instrument but vary from one sample to another.

Turning to neutron time-of-flight measurements, we recall that the peak shape can be described by (12), containing three basic parameters $\sigma_1$, $\sigma_2$ and $\gamma$. However, each parameter varies with neutron wavelength and hence from one peak to another. Suitable empirical functions expressing the wavelength dependence of the three shape parameters have been derived by Cole & Windsor (1980). Von Dreele (1979) uses (13) to describe the peak shape, and again there are three shape parameters, $\alpha$, $\beta$, and $\sigma$. He represents the wavelength dependence of these parameters by the expressions

$$\begin{align*}
\alpha &= \alpha_0 + \lambda^{-1} \alpha_1, \\
\beta &= \beta_0 + \lambda^{-4} \beta_1, \\
\sigma &= \sigma_0 + \lambda \sigma_1
\end{align*}$$  

where the coefficients on the right-hand side are independent of $\lambda$. Equation (18) was used successfully by Malmros & Thomas (1977) in their work on Guinier–Hägg photographs. At a certain $\theta$ value, the chromatic dispersion of the specimen exactly compensates that of the monochromator, and Fichtner-Schmittler & Menz (1978) show that above this focusing position $H_k$ is a linear function of $\tan \theta_k$, requiring only two parameters to specify it:

$$H_k = a + b \tan \theta_k.$$  

A two-parameter function was also adopted by Khattak & Cox (1977) for X-ray powder diffraction data. For the $2\theta$ range 24–100°, the expression (18) with $U = 0$,

$$H_k = (V \tan \theta_k + W)^{1/2},$$

gave an adequate account of the variation of peak width with scattering angle.

Finally, in the X-ray energy-dispersive method, the peak width varies with the energy or inversely with the wavelength. The FWHM can be expressed as

$$H_k = A/\lambda + B,$$

where $A$ and $B$ are constants to be determined in the Rietveld refinement (Glazer, Hidaka & Bordas, 1978).
6. Computer programs for Rietveld refinement

In this section we shall make a few general comments on some of the computer programs which have been used for Rietveld refinement.

The original program of Rietveld (1969) is in two parts. The first part determines those reflections which can contribute to the intensity \( I_\text{calc} \), in accordance with some of the computer programs which have been discussed in § 3(a). This part also corrects the observed intensities \( I_\text{obs} \) for the background, which is estimated by interpolation of the background level in regions between the Bragg peaks. The second part of the program contains the main least-squares routine with the structural parameters and the profile parameters as variables.

Before starting the Rietveld analysis, it is necessary to know which reflections can contribute to the diffraction pattern, their positions in the pattern, and their multiplicities. This information is readily obtained with a computer program such as KDREF (Rouse, Sayers & Cooper, 1977; Rouse & Cooper, 1978). The program generates a set of unique reflections within a specified range of \( d \) values, for a particular space group and for a given set of unit-cell dimensions. Its output is a list of these unique reflections, with their Miller indices, \( d \) spacings and multiplicities.

Pawley, Mackenzie & Dietrich (1977) describe a refinement program EDINP [based on the well-known ORFLS program of Busing, Martin & Levy (1962)], which allows the introduction of constraints between parameters, such as those associated with fixed bond lengths or with rigid-body thermal motion. It is also possible to introduce constraints in the program described by Immirzi (1978).

Von Dreele (1979) has written a program for the refinement of time-of-flight neutron data. The calculated intensity in the \( i \)th time channel consists of a background intensity and a sum of contributions from all reflections \( k \) sufficiently close to give a significant contribution to the \( i \)th channel. The test of significance is that the flight-time for the \( k \)th reflection \( t_k \) differs from the flight time for the \( i \)th channel \( t_i \) by no more than \( 3\sigma_k \):

\[
|t_k - t_i| \leq 3\sigma_k,
\]

where \( \sigma_k \) is the FWHM of the \( k \)th reflection. The diffraction peak is described by an asymmetric function of the form given in (13).

For the Rietveld refinement of Guinier–Hägg powder diffraction patterns, Malmros & Thomas (1977) employed the peak-shape function (15), multiplied by (11), to account for the asymmetry of the peaks. They avoided the necessity, as did Khattak & Cox (1977), of accommodating the program for two wavelengths by adopting an experimental arrangement with only one wavelength impinging on the specimen. Khattak & Cox found that the tails of the X-ray peaks fall off much more gradually than Gaussian peaks, and so the refinement was carried out over a range of \( \pm 1.5H_k \) on each side of the peak maximum rather than the \( \pm 1.5H_k \) range appropriate to the analysis of neutron data at fixed wavelength. The computer program of Wiles & Young (1981) copes explicitly with the two wavelengths of the X-ray \( K\alpha \) doublet.

Sometimes more than one diffraction pattern occurs in the observed intensity profile. This could arise, for instance, in high-temperature studies where scattering occurs from the sample container or from the furnace element. Impurities may be deliberately added to reduce preferred orientation. The simultaneous refinement of two or more phases is a feature which has been incorporated in a number of programs (Werner, Salome, Malmros & Thomas, 1979; Worlton, Jorgensen, Beyerlein & Decker, 1976).

7. Some tests of the Rietveld method

The Rietveld method appears to lead to the determination of structural parameters with quite high precision, even from poorly resolved powder diffraction data. This raises the important question: Are the calculated structural parameters reliable and the error estimates realistic?

A comparison of the results obtained from powder diffraction and single-crystal diffraction experiments on forsterite, \( \text{Mg}_2\text{SiO}_4 \), has been given by Lager, Ross, Rotella & Jorgensen (1981). The powder data were obtained using the neutron time-of-flight technique and refined by the Rietveld method; the single-crystal data were recorded with both X-rays and neutrons, and each set separately refined from independent structure factors. Forty seven variables were derived in the powder analysis, including anisotropic temperature factors for all atoms (space group \( \text{Pbnm}, Z = 4 \)).

Table 1 summarizes the results for the positional parameters. The Rietveld estimates are in excellent agreement with the single-crystal values and exhibit comparable uncertainties.

For the molecular crystal \( \alpha \)-resorcinol, the positional parameters derived from a constrained refinement of powder intensities with the EDINP program (§ 6) were in good agreement with single-crystal values (Bacon, Lisher & Pawley, 1979).

To determine reasonable thermal parameters by the Rietveld method, it is essential to have well-resolved peaks, or groups of peaks, separated by clear background. There is a strong correlation between thermal parameters and the background, so that the standard deviations of the thermal parameters will be under-estimated if the background is not included in the refinement. By substituting (10) into (9) it is clear that the background can be readily incorporated in the refinement model: see Prince (1981).
Table 1. Comparison of atomic coordinates for Mg$_2$SiO$_4$ derived by the Rietveld method from neutron powder diffraction with those from single-crystal diffraction (after Lager et al., 1981)

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(2)</td>
<td>0.9915 (1)</td>
<td>0.2774 (1)</td>
<td>0.25</td>
</tr>
<tr>
<td>Mg(1)</td>
<td>0.9914 (3)</td>
<td>0.2773 (2)</td>
<td>0.25</td>
</tr>
<tr>
<td>Si</td>
<td>0.4263 (1)</td>
<td>0.0932 (2)</td>
<td>0.25</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.7658 (1)</td>
<td>0.0917 (1)</td>
<td>0.25</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.2118 (1)</td>
<td>0.4472 (1)</td>
<td>0.25</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.2774 (1)</td>
<td>0.1631 (1)</td>
<td>0.0331 (1)</td>
</tr>
</tbody>
</table>

Table 2. Comparison of thermal parameters for Mg$_2$SiO$_4$ derived by the Rietveld method from neutron powder diffraction with those from single-crystal diffraction (after Lager et al., 1981)

Thermal parameters ($\times 10^5$) are of the form

$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

$X = $ parameters from X-ray single-crystal data. $N = $ parameters from neutron single-crystal data. $R = $ parameters from Rietveld refinement of neutron powder data.

<table>
<thead>
<tr>
<th></th>
<th>$\beta_{11}$</th>
<th>$\beta_{22}$</th>
<th>$\beta_{33}$</th>
<th>$\beta_{12}$</th>
<th>$\beta_{13}$</th>
<th>$\beta_{23}$</th>
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<tr>
<td>Mg(1)</td>
<td>394 (6)</td>
<td>132 (2)</td>
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<td>483 (7)</td>
<td>88 (2)</td>
<td>314 (4)</td>
<td>2 (2)</td>
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</tr>
<tr>
<td>Si</td>
<td>241 (5)</td>
<td>78 (1)</td>
<td>208 (3)</td>
<td>4 (1)</td>
<td></td>
<td></td>
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<tr>
<td>O(1)</td>
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<td>117 (9)</td>
<td>302 (6)</td>
<td>4 (4)</td>
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<tr>
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<td>411 (10)</td>
<td>77 (2)</td>
<td>324 (6)</td>
<td>-3 (4)</td>
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<td></td>
</tr>
<tr>
<td>O(3)</td>
<td>430 (7)</td>
<td>116 (2)</td>
<td>269 (4)</td>
<td>5 (3)</td>
<td>-20 (4)</td>
<td>50 (2)</td>
</tr>
</tbody>
</table>

8. Conclusions

Diffraction studies of powder samples, with X-rays or with neutrons, present a number of advantages compared with single-crystal work. It is easier to obtain a...
powder specimen than a single crystal: for neutron diffraction, in particular, it may be impossible to grow a suitably large crystal. In a single-crystal study, extra time is spent in aligning the crystal and in checking for twinning. Systematic errors arising from extinction are more serious for single crystals than for powders.

On the other hand, the determination of the space group, which is the starting point of any structural analysis, usually requires a single-crystal study, as does the solution of the phase problem by any of the standard procedures. The powder method can only be used to solve relatively simple structures (see Berg & Warner, 1977) or to refine the structure when its main features are already known.

The important contribution made by Rietveld was to recognize that structures could be refined from powder data, even where there was severe overlapping of diffraction peaks. The essential idea was to forget about the individual Bragg reflections and to refine the pattern as a whole in the way described in § 3. By this means refinement could be extended to reasonably complex structures.

Several authors have pointed out that the original formulation of the Rietveld method is not entirely satisfactory. The goodness-of-fit of the structural parameters may be quite different from the goodness-of-fit of the profile parameters, and yet the conventional Rietveld analysis implies that they are the same (Cooper, 1982). Residuals associated with observations at different points on the same Bragg peak are correlated with one another, but this correlation is usually ignored (Clarke & Rollett, 1982). There seems to be no simple modification of the Rietveld procedure for overcoming these problems. It is comforting to note, therefore, that the atomic coordinates are in good agreement with single-crystal values for each case in which this test has been made.

We are deeply grateful to a number of people who have sent us information on the Rietveld method in advance of publication. Especial thanks are due to Dr R. B. Von Dreele for an account of his work on the analysis of neutron time-of-flight data.

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References


