Rietveld Analysis of Powder Patterns Obtained by TOF Neutron Diffraction Using Cold Neutron Sources

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(Received 11 March 1987; accepted 15 June 1987)

Abstract
A computer program has been developed for the Rietveld analysis of time-of-flight neutron diffraction data taken on a high-resolution powder diffractometer, HRP, at the pulsed spallation neutron source, KENS. A new profile shape function is implemented which is optimized for a solid-methane moderator at 20 K. The program has several convenient features such as single-pass operation, multiphase capability, automatic successive refinements and constrained minimization. The results of Rietveld refinements of Si and α-Al₂O₃ show that the profile shape function fits neutron diffraction patterns taken on the HRP very well, and that very precise crystal-structure parameters can be obtained with this program.

1. Introduction
The powder diffraction method is applied to the investigation of crystal structures when single crystals cannot be prepared at all or when the properties of interest of the single-crystal form differ from those of the polycrystalline form, for example in catalysts, sensors and bioceramics. High-resolution powder diffractometry is a very powerful tool for such purposes. High resolution is most easily achieved by using incident beams from (i) high-flux reactors, (ii) intense pulsed neutron sources, and (iii) synchrotron X-ray sources (Albinati & Willis, 1982). Not only the resolution but also the signal-to-noise ratio can be appreciably improved with these advanced diffraction methods because incident beams of excellent collimation and high intensity are available. Although large amounts of sample are needed in neutron diffraction, it has the advantage over X-ray diffraction that errors arising from preferred orientation are usually very small (Hewat, 1980). The availability in recent years of high-resolution neutron powder diffractometers has enabled highly accurate and rapid determination of crystal- and magnetic-structure parameters for polycrystalline materials.

A previous paper (Watanabe et al., 1987) reported a high-resolution time-of-flight (TOF) powder diffractometer, HRP, constructed at the pulsed spallation neutron facility (KENS) at the National Laboratory for High Energy Physics. The instrument utilizes narrow pulsed beams of thermal and epithermal neutrons from a solid-methane moderator at 20 K. A long flight-path length of ca 20 m, a back-scattering configuration (2θ = 170°), and high-efficiency multi-detectors are also adopted. As a result, a high resolution of \( \Delta d/d = 3 \times 10^{-3} \) has been realized at interplanar spacings \( d \) less than 1.5 Å with large counting rates and excellent signal-to-noise ratios. Moreover, the low repetition rate of the source pulse of 20 Hz greatly enlarges the range of \( d \) spacings accessible simultaneously.

The object of the present work is to obtain reliable structure parameters from TOF neutron powder diffraction patterns taken on the HRP by Rietveld analysis. The Rietveld method was originally devised for the analysis of angle-dispersive (fixed-wavelength) neutron data (Rietveld, 1969; Cheetham & Taylor, 1977) but has now provided a major breakthrough for the usefulness of X-ray powder data (Young, 1980). This powerful method has greatly extended the amount of structural detail which can be extracted routinely from powder diffraction patterns. It has also been applied very successfully to TOF neutron powder data taken on the high-resolution powder diffractometer at the pulsed spallation neutron source IPNS (Jorgensen & Rotella, 1982; Von Dreele, Jorgensen & Windsor, 1982).

One of the principal disadvantages of TOF neutron diffraction is that wavelength-dependent quantities such as absorption, incident intensity and efficiency of counters must be taken into account (Windsor, 1981)
since they are inherent in the energy-dispersive (fixed-scattering-angle) method. The advantage of TOF neutron diffraction over that of angle-dispersive geometry is the extension of \( d \) space towards the low-\( d \) region; reflections with \( d \) values as low as 0.4 Å can be observed without difficulty. In addition, the full width at half maximum of a diffraction peak decreases with decreasing interplanar spacing in TOF neutron diffraction. Since the density of peaks increases rapidly with decreasing \( d \) value, this feature is most favorable for structure refinement using powder diffraction. Collection of data to much lower \( d \) values increases the amount of information contained in diffraction patterns and enhances the accuracy of parameters refined by the Rietveld method.

A computer software package, Rietan, developed by one of the authors (Izumi, 1985) has been used by more than 30 research groups for the Rietveld analysis and simulation of angle-dispersive powder data obtained with characteristic X-ray, synchrotron X-ray and neutron diffractometers. The Fortran 77 program of Rietan has now been modified extensively to make it possible to analyze TOF neutron diffraction data taken at a fixed scattering angle on the HRP. A function to model the observed intensity itself and a new profile shape function optimized for the cold neutron source at KENS have been implemented in it. This TOF neutron diffraction version retains all the advanced features of the angle-dispersive one such as single-pass operation, multiphase capability, and refinements under equality and inequality constraints. Therefore, it has the benefits of the common and user-friendly software for the Rietveld analysis of results from the above four categories of experimental technique.

2. Model function

The observed intensity, \( y_i(o) \), at a particular channel, \( i \), is modeled by a calculated intensity, \( y_i(c) \) (Von Dreele, Jorgensen & Windsor, 1982):

\[
y_i(c) = I_i e_i A_i \sum_k s |F_k|^2 m_k d_k^4 E_k P_k G(\Delta t_{ik}) + y_{ib}(c)
\]

(1)

where

\[
|F_k|^2 = |F_k(\text{nucl.})|^2 + |F_k(\text{magn.})|^2,
\]

(2)

\[
\Delta t_{ik} = t_i - t_k.
\]

(3)

In (1), (2) and (3), \( I_i \) = incident intensity, \( e_i \) = efficiency of counters, \( A_i \) = absorption factor, \( t_k \) = reflection number, \( s \) = scale factor, \( F_k \) = structure factor, \( m_k \) = multiplicity, \( d_k \) = interplanar spacing, \( E_k \) = correction factor for extinction, \( P_k \) = correction factor for preferred orientation, \( G(\Delta t_{ik}) \) = profile shape function, \( y_{ib}(c) \) = background, \( F_k(\text{nucl.}) \) = nuclear contribution to the structure factor, \( F_k(\text{magn.}) \) = magnetic contribution to the structure factor, \( t_i \) = TOF at the \( i \)th channel and \( t_k \) = TOF at the peak position. The summation must be carried out over all reflections contributing to the net intensity at the \( i \)th channel. The diffraction intensity is multiplied by the scale factor, \( s \), prior to the summation because Rietan can deal with mixtures of two or more phases; \( s \) has, of course, a constant value for all the reflections of a phase. Frame-overlap reflections need not be included in (1) because the repetition rate of KENS is sufficiently low.

The effective incident neutron intensity, \( I_i e_i \), for the HRP is determined from incoherent scattering from vanadium powder. Since it is not a smooth function of TOF owing to the presence of several aluminium windows located between the moderator and the sample, an analytical formula expressing the dependence of \( I_i e_i \) on TOF cannot be formulated. In addition, the incident intensity spectrum varies from run to run because it is appreciably influenced by experimental conditions of an LAM-40 quasielastic spectrometer placed upstream from the HRP as well as by the temperature of the solid-methane moderator. \( I_i e_i \) is, accordingly, calculated from the spectra from vanadium, the background (including incoherent scattering from a sample cell), and sample runs, all of which are normalized by the corresponding monitor counts:

\[
I_i e_i = \frac{C_m(s, t_i)}{A(V, t_i) M(V, t_i)} \left( \frac{C(V, t_i)}{C_m(V, t_i)} - \frac{C(b, t_i)}{C_m(b, t_i)} \right)
\]

(4)

where \( C_m(s, t_i) \) = monitor count for the sample at \( t_i \), \( A(V, t_i) \) = absorption factor for vanadium, \( M(V, t_i) \) = correction factor for multiple scattering by vanadium, \( C(V, t_i) \) = vanadium spectrum, \( C_m(V, t_i) \) = monitor count in the vanadium run, \( C(b, t_i) \) = background spectrum, \( C_m(b, t_i) \) = monitor count in the background run. \( M(V, t_i) \) is evaluated according to the procedure described by Blech & Averbach (1965). \( C_m(s, t_i) \), \( C(V, t_i) \), \( C_m(V, t_i) \), \( C(b, t_i) \), and \( C_m(b, t_i) \) are calculated from the intensity data smoothed by a nine-point quadratic algorithm.

In measurements of diffraction patterns with the HRP, a sample is usually contained in a cylindrical vanadium cell 5 mm in radius, \( r \). \( A(V, t_i) \) and \( A_i \) are, therefore, calculated from \( \mu r \) (\( \mu \) : linear absorption coefficient) by the interpolation of absorption factors listed in a table for cylinders (Rouse & Cooper, 1970). Absorption by the cell is neglected completely in (4) because the thickness of its wall is only 25 μm.

Several crystal-structure parameters are contained in the structure factor, \( F_k \): occupation factors, thermal parameters (overall, individual isotropic or anisotropic), and fractional coordinates. Either isotropic or anisotropic thermal vibration can be arbitrarily assigned to each atom. The present version can handle magnetic structures with collinear spin arrangements. The magnetic moment for each site and the angle between the spin direction and the unique axis of the
unit cell are directly refined by using equations derived by Shirane (1959). Implementation of magnetic scattering for non-collinear spin arrangements (Rietveld, 1969) is desirable; this will be undertaken in the near future.

Extinction is corrected with the following function containing a refinable ‘extinction’ parameter, g (Windsor & Sinclair, 1976; Von Dreele, Jorgensen & Windsor, 1982):

\[ E_k = 1 - g |F_k|^2 m_d d_k^a. \]  

Computational experience in Rietveld refinements revealed that application of the above correction factor lowered R factors to a considerable extent in most cases but that g sometimes became negative as a result of refinement. In the latter cases where extinction correction is physically meaningless, g was fixed at zero. It seems to us that uncorrected multiple scattering and self shielding (Windsor, 1981) are all absorbed into this simple correction factor.

Preferred orientation is corrected by using an empirical function containing two variable preferred-orientation parameters, \( p_1 \) and \( p_2 \) (Toraya & Marumo, 1981):

\[ P_k = p_1 + (1-p_1) \exp(-p_2\phi_2^2), \]  

where \( \phi_2 \) is the acute angle between the scattering vector of the kth reflection and the cleavage plane. However, we have not yet encountered cases in which preferred orientation must be corrected to improve R factors.

The TOF at the peak position is given by the relation (Rotella, 1982)

\[ t_k = c_0 + c_1 d_k + c_2 d_k^2, \]  

where \( c_0 \) is the zero-point error, \( c_1 \) is the diffractometer constant and \( c_2 \) is the refinable correction factor. The proportionality constant, \( c_1 \), depends on the flight path of the instrument and on the scattering angle at which intensity data were collected (Albinati & Willis, 1982). Once its value has been established by analysis of diffraction data of a standard sample, it may be fixed in subsequent Rietveld refinements. Lattice parameters are contained in \( d_k \) in (1) and (7); they can be refined simultaneously together with other structure and profile parameters.

The profile shape function, \( G(\Delta t) \), is an analytical expression which describes the shape of the diffraction peak. It is assumed to be the convolution of a moderator pulse shape with the peak width and shape due to the instrument and the particle size and strain of the sample. The profile shape function for the HRP will be described in detail in the next section.

The background in a diffraction pattern taken on the HRP resembles the incident neutron spectrum closely in wavelength dependence; it is likewise not a smooth function of TOF. In the present program, \( y_{ib}(c) \) is approximated by the product of \( I_i e_i \) and a polynomial linear in six background parameters \( b_0 - b_5 \):

\[ y_{ib}(c) = I_i e_i \sum_{j=0}^{5} b_j \left( \frac{2t_i - t_{\text{max}} - t_{\text{min}}}{t_{\text{max}} - t_{\text{min}}} \right)^j. \]  

In the above equation, \( t_{\text{max}} \) and \( t_{\text{min}} \) are, respectively, the maximum and minimum TOF in the diffraction pattern, and \( t_i \) is normalized between -1 and 1 to reduce the correlations between the background parameters.

### 3. Profile shape function

As described previously, the HRP at KENS utilizes neutrons from the solid-methane moderator at 20 K, covering a wide range of wavelengths. Peak shapes measured on the HRP depend primarily on the neutron wavelength; that is, epithermal and thermal neutrons afford nearly symmetric sharp peaks whereas cold neutrons give a long trailing tail to each broad peak. Profile shape functions designed for moderators at room temperature (Cole & Windsor, 1980; Von Dreele, Jorgensen & Windsor, 1982) can describe the present peak shape only in the thermal or the cold-neutron region; deviation between the observed and calculated intensities is marked in the transient region. Therefore, these two functions cannot be used, without any modifications, for the least-squares fitting of diffraction peaks over the entire TOF region. In previous work with a grooved moderator at 20 K (Asano, Umino, Onuki, Komatsubara, Izumi & Watanabe, 1986), a profile shape function proposed by Von Dreele, Jorgensen & Windsor (1982) was modified by the addition of two asymmetric Lorentz functions near the peak position and at the decaying tail. Rietveld refinements based on this function yielded fairly satisfactory results. However, it contains up to 29 variable profile parameters, and a simpler function is desirable.

The cold moderator at KENS was altered from the grooved type to a flat one in 1985 with the result that both the peak shape and the resolution in the diffraction patterns changed appreciably. Since then, a new profile shape function suitable for the Rietveld analysis of powder diffraction data taken on the HRP has been thoroughly reinvestigated.

Cole & Windsor (1980) represented the peak shape obtained with a moderator at room temperature by a function (hereinafter called the CW function) that consists of three separate regions: (i) a rising Gaussian with a standard deviation \( \sigma_1 \), (ii) a falling Gaussian with a standard deviation \( \sigma_2 \), and (iii) a decaying exponential with a decay constant \( \gamma \). The peak position, \( t_k \), of the kth reflection lies at the join of the two Gaussian functions with the same peak height. The falling Gaussian is joined continuously to the decaying exponential.
Ikeda & Carpenter (1985) have recently proposed a pulse-shape function covering a wide wavelength range by the sum of two components: slowing-down and storage terms. The mixing ratio of these two components is a function of wavelength, depending on the temperature and material of the moderator. On the basis of similar considerations, we devised a flexible profile shape function, \( G(\Delta t_{ik}) \), which is the sum of two CW functions, \( G_1(\Delta t_{ik}) \) and \( G_2(\Delta t_{ik}) \), in a \((1 - R): R\) ratio:

\[
G(\Delta t_{ik}) = A[(1 - R)G_1(\Delta t_{ik}) + RG_2(\Delta t_{ik})].
\] (9)

\( A \) is the normalization factor to set the integrated intensity to 1. Equation (9) includes the pure CW function for ambient-temperature moderators as a special case \((R = 0)\). \( G_1(\Delta t_{ik}) \) and \( G_2(\Delta t_{ik}) \) are given by

\[
t_i < t_k \quad G_1(\Delta t_{ik}) = G_2(\Delta t_{ik}) = \exp(-\Delta t_{ik}^2/2\sigma_1^2),
\] (10)

\[
t_k < t_i < t_k + \gamma_1 \sigma_2^2 \quad G_1(\Delta t_{ik}) = \exp(\gamma_1^2 \sigma_2^2/2 - \gamma_1 \Delta t_{ik}),
\] (11)

\[
t_i \geq t_k + \gamma_1 \sigma_2^2 \quad G_1(\Delta t_{ik}) = \exp(\gamma_1^2 \sigma_2^2/2 - \gamma_1 \Delta t_{ik}).
\] (12)

\[
t_k < t_i \leq t_k + \gamma_2 \sigma_2^2 \quad G_2(\Delta t_{ik}) = \exp(-\Delta t_{ik}^2/2\sigma_2^2),
\] (13)

\[
t_k < t_i \geq t_k + \gamma_2 \sigma_2^2 \quad G_2(\Delta t_{ik}) = \exp(\gamma_2^2 \sigma_2^2/2 - \gamma_2 \Delta t_{ik}).
\] (14)

\( G_1(\Delta t_{ik}) \) and \( G_2(\Delta t_{ik}) \) have common standard deviations: \( \sigma_1 \) at \( t_i \leq t_k \) and \( \sigma_2 \) at \( t_i \geq t_k \), but they differ in decay constant: \( \gamma_1 \) for \( G_1(\Delta t_{ik}) \) and \( \gamma_2 \) for \( G_2(\Delta t_{ik}) \) \((\gamma_1 > \gamma_2)\). Then, the normalization

\[
\int_{-\infty}^{+\infty} G(\Delta t_{ik}) \, dt = 1
\]
gives rise to

\[
A^{-1} = (\pi/2)^{1/2} \sigma_1 + (\pi/2)^{1/2}(1 - R)\sigma_2 \text{erf}(\gamma_1 \sigma_2/\sqrt{2}) + [(1 - R)/\gamma_1] \exp(-\gamma_1^2 \sigma_2^2/2) + (\pi/2)^{1/2} R\sigma_2 \text{erf}(\gamma_2 \sigma_2/\sqrt{2}) + (R/\gamma_2) \exp(-\gamma_2^2 \sigma_2^2/2).
\] (15)

Fig. 1 shows \( G(\Delta t_{ik}) \), \( A(1 - R)G_1(\Delta t_{ik}) \) and \( ARG_2(\Delta t_{ik}) \) calculated from \( \sigma_1, \sigma_2, \gamma_1, \gamma_2, \) and \( R \) obtained by fitting (9) to the 311 peak for Si \((d_k = 1.637 \, \text{Å})\). It can be seen from Fig. 1 that the \( G_1 \) component is more symmetrical than the \( G_2 \) component, and that the trailing edge consists substantially of the latter.

However, suitable empirical functions to express the dependences of \( \sigma_1, \sigma_2, \gamma_1, \gamma_2, \) and \( R \) on \( d_k \) are required in Rietveld analysis. At first, stronger well resolved peaks of standard samples Si and \( \alpha-\text{Al}_2\text{O}_3 \) were fitted individually with the above five parameters along with two background parameters \( (b_0 \) and \( b_1) \). Next, the overall variation of the refined parameters with \( d_k \) was examined in detail. Of these five parameters, the decay constant of the long-lived exponential tail, \( \gamma_2 \), proved to be almost invariable regardless of \( d_k \), as is theoretically defensible (Carpenter, Robinson, Taylor & Picton, 1985). We have found that the following equations can adequately approximate the dependences of the other parameters on \( d_k \):

\[
\sigma_1 = \sigma_{11} + \sigma_{12} d_k,
\] (16)

\[
\sigma_2 = \sigma_{21} + \sigma_{22} d_k^{2.5},
\] (17)

\[
\gamma_1 = \gamma_{11} + \gamma_{12} \exp(-\gamma_{13} d_k^2),
\] (18)

\[
R = 1 - \exp(-(R_1 d_k^{d_k})).
\] (19)

Thus, the present profile shape function contains ten refinable profile parameters: \( \sigma_{11}, \sigma_{12}, \sigma_{21}, \sigma_{22}, \gamma_{11}, \gamma_{12}, \gamma_{13}, \gamma_{21}, R_1, \) and \( R_2 \). It is interesting to note that the second term in (18) is Gaussian and that (19) has the same form as Avrami's equation expressing conversion ratios in phase transformation.

The value of \( \gamma_2 \) is believed to depend not on the particle size or strain of a sample but only on the neutron moderation process. Under such an assumption, Cole & Windsor (1980) have indicated that convolution of the constant-wavelength (CW) function with Gaussian sample broadening has the same form as the CW function. Since (9) is the sum of the two CW functions, convolution of (9) with sample broadening also has the same form as (9). Thus, the above profile shape function can be used without any modifications even if intrinsic broadening originating from the state of the sample is observed. Strictly speaking, strain broadening is Gaussian in shape whereas size broadening is Lorentzian; the assumption described above is only true for strain broadening in the sample. However, (9) is believed to be flexible enough to fit the diffraction peaks of samples showing size broadening.
4. Computer program for Rietveld analysis

The objective function to be minimized in our program is the weighted sum of squares

\[ S = \sum w_i [y_i(o) - y_i(c)]^2, \]

(20)

where \( w_i \) is the weight based on counting statistics, \( 1/y_i(o) \). Of course, \( y_i(o) \) consists of contributions from nearby diffraction peaks and the background. The observed intensities, \( \{y_1(o), y_2(o), y_3(o), \ldots\} \), are obtained with TOF as 'abscissa' in TOF neutron diffraction, whereas the absissa in angle-dispersive methods is the scattering angle \( 2\theta \).

Parameters to be refined are classified as follows:

(1) **Global parameters.** Zero-point error, \( c_0 \); diffractometer constant, \( c_1 \) (refined only in calibration runs); refinable correction factor, \( c_2 \); background parameters, \( b_0-b_5 \).

(2) **Phase-dependent parameters.** (a) Scale factor, \( s \). (b) Parameters used to correct integrated intensities: extinction parameter, \( g \); preferred-orientation parameters, \( p_1, p_2 \). (c) Profile parameters, \( \sigma_{11}, \sigma_{12}, \sigma_{21}, \sigma_{22}, \gamma_{11}, \gamma_{12}, \gamma_{13}, \gamma_{2}, R_1, R_2 \). (d) Lattice parameters, \( a, b, c, \alpha, \beta, \gamma \). (e) Structure-factor parameters (\( j \): site number): occupation factors, \( n_j \); fractional coordinates, \( x_j, y_j, z_j \); isotropic thermal parameters, \( B_j \); anisotropic thermal parameters, \( B_{11}, B_{22}, B_{33}, B_{12}, B_{13}, B_{23} \); magnetic moments in Bohr magneton, \( \mu_j \); angle between the spin direction and the unique axis, \( \psi \).

The **RIETAN** program (Izumi, 1985) for the Rietveld analysis of angle-dispersive X-ray and neutron diffraction patterns was adapted for the analysis of TOF neutron diffraction data taken on the HRP. **RIETAN** incorporates almost all the convenient features of programs developed from the original program written by Rietveld (1969). Therefore, the description that follows will emphasize features not implemented in these programs.

(1) **Data bases.** The **RIETAN** system incorporates large data bases stored in sequential files: (i) Laue-group number, presence of centers of symmetry, Hermann–Mauguin space-group symbols, symmetry conditions, coordinates of general equivalent positions for 230 space groups (International Tables for X-ray Crystallography, 1969; International Tables for Crystallography, 1983); (ii) coherent scattering lengths, absorption cross sections, incoherent scattering cross sections (Sears, 1984), and atomic weights. We merely enter space group and setting numbers in conformity with International Tables and names of constituent atoms.

(2) **Single-pass operation.** Generation of possible reflections and Rietveld analysis are combined into a single program so that they can be executed within a single job.

(3) **Multiphase capability.** **RIETAN** can deal with diffraction data of samples containing two or more phases. Profile parameters can be either refined independently or constrained in such a way that all the constituents have common profile parameters.

(4) **Use of essential symmetry operations.** The program automatically selects symmetry operations required for each site in an asymmetric unit by checking whether or not general equivalent positions calculated for the site overlap with each other. This procedure greatly reduces the times for the calculation of structure factors and their derivatives, especially when dealing with crystals with high symmetry. Furthermore, occupation factors, \( n_j \), can be input directly without considering the site multiplicity arising because two or more symmetry elements act at the site.

(5) **Least-squares methods.** Three different algorithms for nonlinear least squares have been employed: Gauss–Newton (Nakagawa & Oyanagi, 1982), modified Marquardt (Fletcher, 1971) and conjugate-direction (Powell, 1964) methods. All of them are designed to give stable convergence. The least-squares methods can be readily changed one after another in the course of refinement. The Gauss–Newton and modified Marquardt methods use derivatives of \( y_i(c) \) with respect to parameters. A damping factor in the former method and a Marquardt parameter, \( \lambda \), in the latter method are adjusted appropriately by the program. The conjugate-direction method is one of the most efficient algorithms to minimize objective functions without calculating derivatives. It is mainly used in the late stages of refinement to test the prospect of a local minimum being the global minimum or to escape from a local minimum by using sufficiently large step sizes of line search.

(6) **Automatic successive refinements.** We usually proceed in steps in Rietveld analysis, first refining only one or two parameters and then gradually letting more and more of the parameters be adjusted in the successive least-squares refinement cycles (Young, 1980). Our program requires only a single job to execute such successive refinements: that is, variable parameters in each cycle can be appointed when using the two methods of least squares with derivatives. Usually, linear parameters, i.e. the background param-
eters and the scale factor, are refined in the first cycle, profile parameters in the second cycle, lattice parameters in the third cycle, and subsequently all the parameters simultaneously. Thus far, almost all Rietveld refinements have been carried out routinely with this procedure.

(7) Constrained minimization. Most Rietveld refinement programs are able to apply only equality constraints such as those required to keep certain bond lengths or bond angles fixed or equal (Pawley, 1980). True bond lengths or angles are not exactly equal to expected ones. Therefore, the introduction of inequality or 'soft' constraints (Baerlocher, 1984) is preferable, permitting the imposition of ranges expected for interatomic distances and angles as well as thermal parameters as boundary conditions. In RIETAN, the three methods of least squares described above are combined with an exterior-penalty-function method (Zangwill, 1967) so that the sum of squares, S, can be minimized under equal and unequal constraints which may be nonlinear with respect to variable parameters.

5. Rietveld refinements of Si and \( \alpha \)-\( \text{Al}_2\text{O}_3 \) data
The structures of the standard samples, Si and \( \alpha \)-\( \text{Al}_2\text{O}_3 \), were refined with the present program without correction for preferred orientation. In both cases the gate width was 4 \( \mu \)s, and the refinements dealt with reflections that had \( d \) values larger than 0.5 A. A reflection was regarded as contributing to a profile up to the point for which the fraction of the peak height was 0.002. The intensity data in TOF regions where weak Bragg reflections from the vanadium cell appeared were excluded in the refinements. The diffractometer constant, \( c_1 \), of the HRP was determined to be 9887.8 \( \mu \)s A\(^{-1} \) by Rietveld analysis of the diffraction pattern of Si, whose lattice constant was set at \( a = 5.4307 \) A. In the subsequent refinement of \( \alpha \)-\( \text{Al}_2\text{O}_3 \) data, \( c_1 \) was fixed at the above value.

Tables 1 and 2 list the resulting main parameters and \( R \) factors defined by Young, Prince & Sparks (1982). Results obtained for \( \alpha \)-\( \text{Al}_2\text{O}_3 \) by the Rietveld analysis of angle-dispersive neutron and synchrotron X-ray data and by single-crystal X-ray analysis are also given in Table 2. Fig. 2 shows the profile fit and difference patterns for \( \alpha \)-\( \text{Al}_2\text{O}_3 \). The interplanar spacing, which was converted from \( t_i \), is plotted as abscissa and the intensity as ordinate. The solid lines are the calculated intensities, crosses overlaying them are observed intensities, and \( \Delta Y_i \) is the difference between observed and calculated intensities. The short vertical lines mark the peak positions of 238 possible Bragg reflections.

The agreement between the calculated and observed intensities was most satisfactory, and quite low \( R \) factors could be obtained in both cases. The goodness-of-fit index, \( \chi^2 = (R_{wp}/R_f)^2 \), for \( \alpha \)-\( \text{Al}_2\text{O}_3 \) was much lower in TOF and angle-dispersive neutron diffraction than in angle-dispersive X-ray diffraction. The isotropic thermal parameter of Si, 0.478(41) \( \text{Å}^2 \), is in good agreement with the literature value of 0.461 \( \text{Å}^2 \) (Glazer, Hidaka & Bordas, 1978). Table 2 shows that the final positional and isotropic thermal parameters for \( \alpha \)-\( \text{Al}_2\text{O}_3 \) also agreed very closely with the literature data. The introduction of anisotropic thermal parameters had little effect on the \( R \) factors.

The above results have revealed that the sum of the two CW functions provides a very good description of the peak shape for the entire wavelength range, and that reliable structure parameters can be obtained by the present procedure for Rietveld analysis of TOF powder data taken on the HRP. The structures of metals, organic and inorganic compounds have been

### Table 1. Final parameters and \( R \) factors in Rietveld refinement of Si

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_0(\mu s) )</td>
<td>5.6(3)</td>
</tr>
<tr>
<td>( c_1(\mu s \text{Å}^{-1}) )</td>
<td>9887.8(4)</td>
</tr>
<tr>
<td>( \sigma_{\text{II}} )</td>
<td>2.1(2)</td>
</tr>
<tr>
<td>( \sigma_{12} )</td>
<td>19.7(2)</td>
</tr>
<tr>
<td>( \tau_{21} )</td>
<td>7.5(3)</td>
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<td>( \tau_{12} )</td>
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<td>( \tau_{11} )</td>
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</tr>
<tr>
<td>( \tau_{12} )</td>
<td>0.139(2)</td>
</tr>
<tr>
<td>( \tau_{13} )</td>
<td>0.426(8)</td>
</tr>
<tr>
<td>( \tau_{2} )</td>
<td>0.00840(4)</td>
</tr>
<tr>
<td>( R_I )</td>
<td>0.0114(6)</td>
</tr>
<tr>
<td>( R_2 )</td>
<td>5.58(7)</td>
</tr>
<tr>
<td>( R_{wp} )</td>
<td>0.075</td>
</tr>
<tr>
<td>( R_f )</td>
<td>0.069</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>1.16</td>
</tr>
</tbody>
</table>

### Table 2. Results of structure refinements for \( \alpha \)-\( \text{Al}_2\text{O}_3 \)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al} ): ( z )</td>
<td>0.3523(1)</td>
<td>0.3522(18)</td>
<td>0.3518(1)</td>
<td>0.35219(1)</td>
</tr>
<tr>
<td>( \text{Al} ): ( B(\text{Å}^2) )</td>
<td>0.22(2)</td>
<td>0.22(2)</td>
<td>0.26(1)</td>
<td>0.26(1)</td>
</tr>
<tr>
<td>( \text{O} ): ( x )</td>
<td>0.3065(1)</td>
<td>0.30636(9)</td>
<td>0.3086(6)</td>
<td>0.30633(5)</td>
</tr>
<tr>
<td>( \text{O} ): ( B(\text{Å}^2) )</td>
<td>0.27(1)</td>
<td>0.23(1)</td>
<td>0.74(7)</td>
<td>0.28(1)</td>
</tr>
<tr>
<td>( a(\text{Å}) )</td>
<td>4.7585(3)</td>
<td>4.7640(1)</td>
<td>4.7586(1)</td>
<td>4.75999(3)</td>
</tr>
<tr>
<td>( c(\text{Å}) )</td>
<td>12.9914(5)</td>
<td>13.0091(3)</td>
<td>12.9897(1)</td>
<td>12.994817(7)</td>
</tr>
<tr>
<td>( R_I )</td>
<td>0.018</td>
<td>0.018</td>
<td>0.065</td>
<td>0.069</td>
</tr>
<tr>
<td>( R_{wp} )</td>
<td>0.071</td>
<td>0.071</td>
<td>0.220</td>
<td>0.220</td>
</tr>
<tr>
<td>( R_f )</td>
<td>0.066</td>
<td>0.060</td>
<td>0.144</td>
<td>0.144</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>1.17</td>
<td>1.40</td>
<td>3.33</td>
<td>3.33</td>
</tr>
</tbody>
</table>
refined with the current version of *RIETAN* described above. The results of these structure refinements will be reported elsewhere.

We wish to thank other members of the HRP experimental group for help with the collection of intensity data.

**References**


