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RIETAN: A SOFTWARE PACKAGE FOR THE RIETVELD ANALYSIS AND SIMULATION OF X-RAY AND NEUTRON DIFFRACTION PATTERNS

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A computer software package, RIETAN, has been developed for the application of the Rietveld method to angle-dispersive X-ray and neutron powder data. It incorporates large data bases storing information about space groups, atomic scattering factors, anomalous dispersion corrections, coherent scattering lengths, etc.; all space groups can be handled without additional programming. A profile shape function has been implemented which is the sum of a Gauss function and a Lorentz function with unequal peak heights and widths at one-half peak height. Three different algorithms for nonlinear least squares have been employed: Gauss-Newton, modified Marquardt, and conjugate direction methods. The method of least squares can be readily changed one after another in the course of refinement. These three methods are combined with an exterior penalty function method so that objective functions may be minimized under nonlinear equality and inequality constraints. One can not only plot the observed and calculated intensities after the refinement but also simulate diffraction patterns of pure substances and mixtures from user-supplied profile and structure parameters. A new version of RIETAN has been written to make it possible to analyze time-of-flight neutron data taken on a high-resolution powder diffractometer at KENS.

1. Introduction

The Rietveld method of structure refinement with powder diffraction patterns was originally devised for the analysis of fixed-wavelength (angle-dispersive) neutron data [1] [2] but now constitutes a major breakthrough for the usefulness of X-ray powder data [3]. This powerful method has greatly extended the amount of structural detail which can be obtained routinely from powder diffraction patterns. It 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. However, several problems limit the straightforward application of the method: restricted information contained in powder diffraction patterns, difficulty in correction of preferred orientation, inadequacy of profile shape functions so far used, flat and local minima, narrow convergence range, and inaccurate standard deviations [4].

A computer program, XPD, for the Rietveld analysis of X-ray powder data [5] has been extensively modified to overcome these difficulties to a considerable extent and to permit the refinement with neutron

powder data as well [6]. This new version, called RIETAN (RIETveld ANalysis), plus XPD are distributed to more than 60 research groups, domestic and foreign. It incorporates almost all convenient features of a standard program coded by Wiles and Young [7], for example, handling of anisotropic thermal parameters and the two wavelengths in the $K\alpha$ doublet, single-pass operation, multiphase capability, refinement of lattice and preferred-orientation parameters, and R factors in various shells. In the description that follows, emphasis is therefore placed on features that are not implemented in their program.

2. Hardware and OS Requirements

The RIETAN system has been designed for user convenience and for use by those who have access to any of standard large computers. It can be run on FACOM, HITAC, ACOS, VAX, and UNIX (4.2-BSD) machines without any modifications. The virtual storage necessary to process a standard job is less than 2.5 Mbytes. Laser-beam printers with densities larger than 300 dpi are desirable to obtain Rietveld refinement patterns (Fig. 1) with good quality.

In future, RIETAN will be run on personal computers (CPU: 80386 microprocessor) equipped with 80387 co-processors and operating under OS/2, Ver.

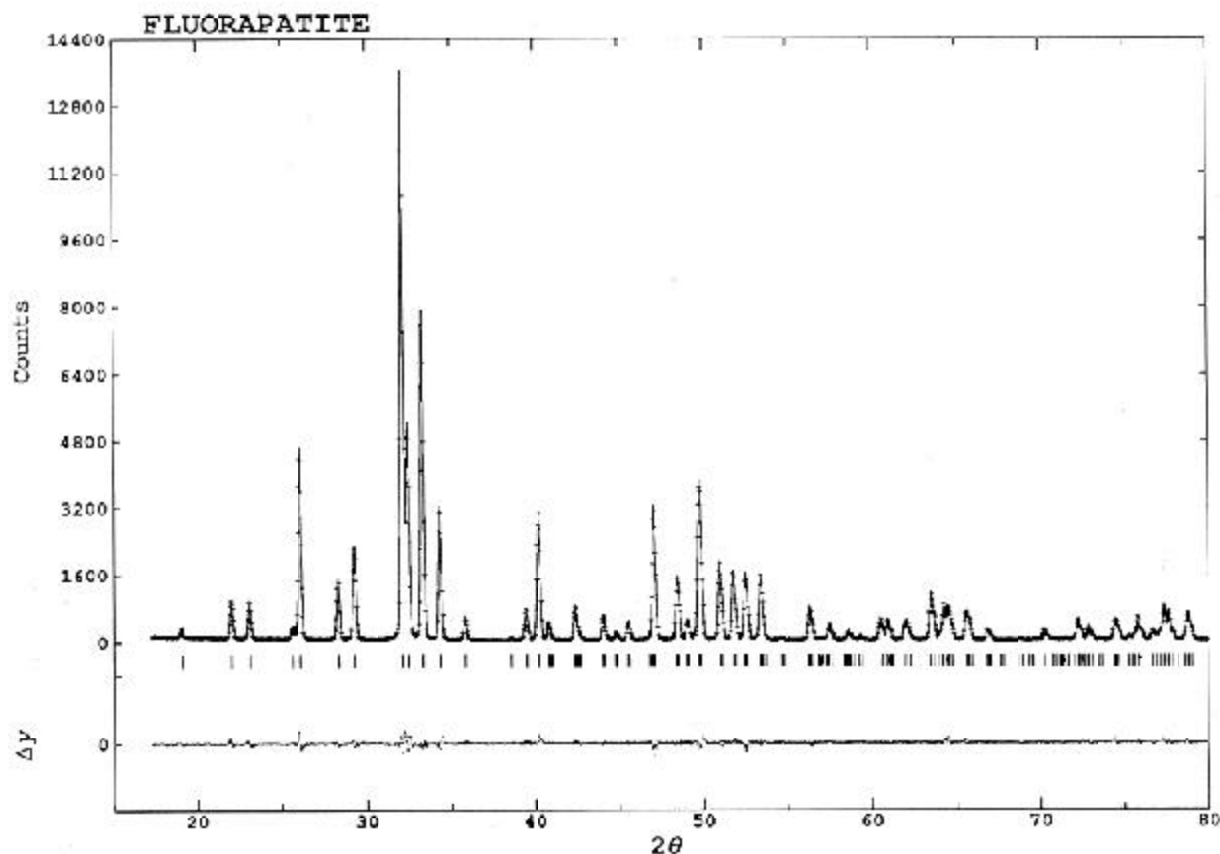


Fig. 1 X-Ray Rietveld refinement of fluorapatite (Cu K α). The solid line is the best-fit profile, and points superimposed on it are raw data. The differences between the observed and calculated intensities, $\Delta y = y_o - y_c$, are shown by points appearing at the bottom. Tick marks below the profile indicate the positions of all allowed K α_1 and K α_2 peaks.

1.1 or above. Disk files storing X-ray intensity data written in a RIETAN format can be read directly by the program without any conversion of the files. Although it takes longer times to obtain the final solution on the personal computers than on standard large ones, this OS/2 version must be fairly practical and easy to use owing to advanced features of the OS/2 operating system such as hierarchical file system, powerful full-screen editor, overlapping-type window system, and multi-task capability.

3. Programming Considerations

The RIETAN program has been written in FORTRAN 77 in conformity with ANSI X3.9-1978 standards for portability, quite independently of the program developed by Rietveld [1]. In order to facilitate reading the code and user-desired changes, the whole program is segmented into 1 main program and a little more than 100 subprograms, and many comment lines were sprinkled liberally throughout ca. 9000 lines of the program. FORTRAN 77 features which are not supported in FORTRAN IV are fully

utilized: block IF (block IF, ELSE, ELSE IF, and END IF statements), character type, character substring, list-directed READ statement, internal data set input/output statement, and PARAMETER statement.

The use of block IF makes it possible to reduce the number of GO TO statements to a great extent and facilitates understanding of the algorithms of the program. Except for lines in which only a character variable is input, all data are input in free format: data placed in a line are separated by a space or a comma; '/' is placed as the last character of the line if default values are assigned for the rest of data to be input. Maximum numbers of reflections, step-scanned intensity data, total parameters, refinable parameters, chemical species, etc. are declared in PARAMETER statements and used as declarator subscripts of many arrays. Accordingly, the dimensions of these arrays in the whole text can be changed very easily and without mistakes by using a text editor.

4. Data Bases

The following data stored in three sequential files are input during the execution of RIETAN.

- 1) Laue group numbers, presence/absence of centers of symmetry, Hermann-Mauguin space group symbols, symmetry conditions, and coordinates of general equivalent positions described for all the settings of 230 space groups in International Tables, Vol. 1 [8].
- 2) Corresponding descriptions in International Tables, Vol. A [9].
- 3) Coefficients for analytic approximations of scattering factors and anomalous dispersion corrections listed in International Tables, Vol. IV [10], coherent scattering lengths, incoherent scattering cross sections, and absorption cross sections [11], and atomic weights.

One merely enters names of constituent atoms and space group and setting numbers in conformity with *International Tables*, Vol. 1 [8] or Vol. A [9]. After symmetry conditions have been input directly from File 1) or 2), indices of possible reflections are generated from them with KDRREF subprograms written by Cooper, Rouse and Sayers [12]; no preparatory program is needed to generate unique reflection sets as in the original program of Rietveld [1]. If non-standard settings are required which are not described in *International Tables* [8][9], symmetry conditions may be specified directly in the input data. A further option is also provided to allow the suppression of specified reflection type; this facility is used when atoms are at special positions only. After all possible reflections have been generated, their multiplicities, interplanar spacings, diffraction angles, \mathbf{h}_s , $\mathbf{h} \cdot \mathbf{t}_s$ [13], etc. are calculated and then sorted on increasing scattering angle, 2θ .

As described above, this program calls for only a restricted amount of input data in free format owing to the presence of the data bases and use of list-directed READ statements. It is, therefore, especially suited for those who are not familiar with crystallography or FORMAT specification codes in FORTRAN.

5. Model Function

The observed intensity, $y_i(o)$, at a particular step, i , is modeled by a calculated intensity, $y_i(c)$:

$$y_i(c) = \sum_k s |F_k|^2 m_k P_k L(\theta_k) G(\Delta\theta_{ik}) + y_{ib}(c) \quad (1)$$

with

$$|F_k|^2 = |F_k(\text{cryst.})|^2 + |F_k(\text{magn.})|^2 \quad (2)$$

$$\Delta\theta_{ik} = \theta_i - \theta_k \quad (3)$$

In Eqs. (1), (2), and (3), k =reflection number, s = scale factor, F_k = structure factor, m_k = multiplicity, P_k = correction factor for preferred orientation, $L(\theta_k)$ = Lorentz and polarization factors, $G(\Delta\theta_{ik})$ = profile shape function, $y_{ib}(c)$ = background, $F_k(\text{cryst.})$ = crystal-structure factor, $F_k(\text{magn.})$ = magnetic-structure factor, θ_i = scattering angle at the i^{th} step, θ_k = Bragg angle. The summation in Eq. (1) must be carried out over all reflections contributing to the net intensity at the i^{th} step. 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.

6. Structure Factors

Several crystal-structure parameters are contained in $F_k(\text{cryst.})$: fractional coordinates (x_j , y_j , z_j), occupation factors (n_j), overall thermal parameters (Q), individual isotropic thermal parameters (B_j), and anisotropic thermal parameters (β_{11j} , β_{22j} , β_{33j} , β_{12j} , β_{13j} , β_{23j}), where j is the site number. Either isotropic or anisotropic thermal motion can be arbitrarily assigned to each atom.

The CHARACTER data of the coordinates of general equivalent points read in from the data base are converted into a set of rotation matrices and translation vectors. The program then 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; only these essential symmetry operations are used for the subsequent structure factor calculations. This procedure greatly reduces the times required for the calculation of structure factors and their derivatives especially when dealing with crystals with high symmetry. Furthermore, occupation factors can be input and refined directly without considering the site multiplicities arising because one or more symmetry elements act at the site.

The present version can handle magnetic structures with collinear spin arrangements. The magnetic moment, μ_j , of each site, the angle between the spin direction and the unique axis of the lattice (tetragonal, hexagonal, and rhombohedral), Φ , and the angles between the spin direction and three axes (orthorhombic), Φ_a , Φ_b , and Φ_c , are directly refined

* The polarization factor is unnecessary in neutron and synchrotron X-ray diffraction.

** $F_k(\text{magn.}) = 0$ in X-ray diffraction.

by using equations given by Shirane [14]. Implementation of magnetic scattering for non-collinear spin arrangements is roundly desired; this will be undertaken some day.

7. Preferred-Orientation Function

Preferred orientation is corrected by the following two-parameter function [15] [16]:

$$P_k = p_1 + (1 - p_1) \exp(-p_2 \phi_k) \quad (4)$$

with

- Flat-plate sample

$$\phi_k = \begin{cases} \psi_k & \text{(plate crystals)} \\ \pi/2 - \psi_k & \text{(needle crystals)} \end{cases}$$

- Cylindrical sample

$$\Phi_k = \begin{cases} \pi/2 - \psi_k & \text{(plate crystals)} \\ \psi_k & \text{(needle crystals)} \end{cases}$$

where ψ_k is the acute angle between the reciprocal vector for the k^{th} reflection and preferred-orientation vector, $h_p^2 + k_p^2 + l_p^2$. The direction of the preferred-orientation vector corresponds to that of a normal to the cleavage plane in the plate crystal, and to that of the extension axis in the needle-shaped crystal. Equation (4) includes the preferred-orientation function proposed by Rietveld [1] as a special case ($p_1 = 0$). One may be forced to fix p_1 at 0 or another constant value between 0 and 1 because the standard deviations of p_1 and p_2 often become extraordinarily large on refinement of both p_1 and p_2 .

Equation (4) is merely an empirical function, and neither p_1 nor p_2 has physical meaning. Neutron diffraction is highly recommended when dealing with very orientation-prone substances because it gives much smaller errors arising from preferred orientation than X-ray diffraction [17].

8. Profile Shape Function

The profile shape function to approximate the peak shape of each reflection can be represented by the product of a symmetric profile shape function, $g(\Delta\theta_{ik})$, and an asymmetric correction, $a(\Delta\theta_{ik})$ [1]:

$$G(\Delta\theta_{ik}) = g(\Delta\theta_{ik})a(\Delta\theta_{ik}) \quad (5)$$

This asymmetry correction is applied to intensity data in the low 2θ region.

8.1 Symmetric Profile Shape Function

Symmetric profile shape functions used earlier in Rietveld analysis for the X-ray case were Gaussian [1], Lorentzian [18], modified Lorentzian [19], and intermediate Lorentzian [20]. At present, better symmetric profile shape functions, i.e., pseudo-Voigt [21]

and Pearson VII functions [22], are widely used in place of the above four functions [23].

The present program adopts a modified pseudo-Voigt function, which is a linear combination of a Gauss function and a Lorentz function with unequal peak heights and full widths at half-maximum intensity (FWHM):

$$g(\Delta\theta_{ik}) = C \left\{ \gamma \exp \left[-4 \ln 2 \left(\frac{2\Delta\theta_{ik}}{H_k(G)} \right)^2 \right] + (1 - \gamma) \left[1 + 4 \left(\frac{2\Delta\theta_{ik}}{H_k(L)} \right)^2 \right]^{-1} \right\} \quad (6)$$

with

$$C = \left[\left(\frac{\pi}{4 \ln 2} \right)^{1/2} \gamma H_k(G) + \frac{\pi(1 - \gamma)H_k(L)}{2} \right]^{-1} \quad (7)$$

$$H_k(G) = [U(\tan \theta_k - c_s)^2 + V(\tan \theta_k - c_s) + W]^{1/2} \quad (8)$$

$$H_k(L) = H_k(G)/\delta \quad (9)$$

In the above equations, C = normalizing constant, γ = fraction of the Gaussian component, $H_k(G)$ = FWHM of the Gaussian component, $H_k(L)$ = FWHM of the Lorentzian component, δ = ratio of $H_k(G)$ to $H_k(L)$, $c_s = 0$ or 0.6 . Equation (8) represents the dependence of $H_k(G)$ on θ_k ; U , V , and W are referred to as FWHM parameters. When correlations among the FWHM parameters are very high, c_s should be set at 0.6 [23].

Equation (6) contains five refinable profile parameters: U , V , W , γ , and δ . With appropriate choices of γ , this profile shape function can vary from Gaussian ($\gamma = 1$) to Lorentzian ($\gamma = 0$). Neutron data are usually analyzed by fixing γ at 1 because the Gauss function fits neutron diffraction profiles very well [1].

The difference between the conventional pseudo-Voigt function [21] [23] and Eq. (6) is that δ is fixed at one in the former whereas δ is a variable parameter in the latter. The use of Eq. (6) leads to R factors a little lower than those obtained with the conventional pseudo-Voigt function. However, computational experience with refinements using Eq. (6) has shown that the correlation coefficient between γ and δ is usually very high; one may sometimes be obliged to fix δ at an appropriate value.

8.2 Asymmetric Correction

In the present version, an empirical equation described by Rietveld [1] is used as $a(\Delta\theta_{ik})$:

$$a(\Delta\theta_{ik}) = 1 - (\sin(\Delta\theta_{ik})(2\Delta\theta_{ik})^2) / \tan(\theta_k) \quad (10)$$

a is the asymmetry parameter to be refined. As θ_k is increased, $a(\Delta\theta_{ik})$ moves on toward 1.

8.3 Another Representation for the Dependence of FWHM on Scattering Angle

Thompson, Cox, and Hastings [24] reported that the pseudo-Voigt function can be represented by only $H_k(G)$ and $H_k(L)$ and that the variation of $H_k(G)$ and $H_k(L)$ with Bragg angle can be approximated closely by the functions $V \tan \theta_k$ and $X \cos \theta_k$ which respectively represent the contributions from instrumental resolution and particle size broadening. Thus, the profile shape function contains only two profile parameters: V and X . Their formulation is worth noting because it is soundly based on physical reality. The effectiveness of this function in Rietveld analysis will be tested in the near future.

9. Background Corrections

Background corrections are evaluated as follows.

(i) The background function, $y_{ib}(c)$, is used which is linear in six refinable parameters b_0 - b_5 :

$$y_{ib}(c) = \sum_{j=0}^5 b_j \left(\frac{2\theta_i - \theta_{\max} - \theta_{\min}}{\theta_{\max} - \theta_{\min}} \right)^j \quad (11)$$

where $2\theta_{\max}$ and $2\theta_{\min}$ are maximum and minimum diffraction angle, respectively.

(ii) Four pairs of smoothed values of operator-selected points in the pattern are fitted with a power-series polynomial of degree 3, and the value of this polynomial corresponding to the given value of $2\theta_i$ is calculated.

The use of Eq. (11) is preferable except for the case dealing with samples showing very simple diffraction patterns, because peaks overlap to a great extent in the high 2θ region. In Eq. (11), $2\theta_i$ is normalized between -1 and 1 to reduce the correlations between b_0 - b_5 .

10. Summary of Refinable Parameters

Table 1 shows variable parameters contained in $y_i(c)$.

Lattice parameters are contained in θ_k in Eq. (1). However, it is not lattice parameters but elements of the metric tensor for the reciprocal lattice (a^{*2} , b^{*2} , c^{*2} , $b^*c^*\cos\alpha^*$, $c^*a^*\cos\beta^*$, $a^*b^*\cos\gamma^*$) that are refined in the program [1]; these elements are converted into lattice parameters upon printing of parameter values.

Table 1 Parameters refined in Rietveld analysis.

<ul style="list-style-type: none"> Global parameters <p><i>Parameter to correct for the zero-point shift of a goniometer</i></p> <p>1) Zero-point error: Z</p> <p><i>Parameters to calculate the background</i></p> <p>2) Background parameters $b_0, b_1, b_2, b_3, b_4, b_5$</p> <ul style="list-style-type: none"> Phase-dependent parameters <p><i>Parameters to adjust integrated intensities</i></p> <p>3) Scale factor: s</p> <p>4) Preferred-orientation parameters: p_1, p_2</p> <p><i>Profile parameters</i></p> <p>5) FWHM parameters: U, V, W</p> <p>6) Gaussian fraction: γ</p> <p>7) FWHM ratio: δ</p> <p>8) Asymmetry parameter: A</p> <p><i>Parameters to determine peak positions</i></p> <p>9) Lattice parameters: $a, b, c, \alpha, \beta, \gamma$</p> <p><i>Crystal-structure parameters</i></p> <p>10) Fractional coordinates: x_j, y_j, z_j</p> <p>11) Occupation factors: n_j</p> <p>12) Overall thermal parameter: Q</p> <p>13) Isotropic thermal parameters: B_j</p> <p>14) Anisotropic thermal parameters: $\beta_{11j}, \beta_{22j}, \beta_{33j}, \beta_{12j}, \beta_{13j}, \beta_{23j}$</p> <p><i>Magnetic-structure parameters</i></p> <p>15) Magnetic moments in Bohr magneton: μ_j</p> <p>16) Angle between the spin direction and the unique axis*: Φ</p> <p>17) Angles between the spin direction and the three axes**: Φ_a, Φ_b, Φ_c</p>

* Tetragonal, hexagonal and rhombohedral systems

** Orthorhombic systems

11. Constrained Minimization Procedures

11.1 Linear Equality Constraints

In the RIETAN program, simple linear equality constraints are explicitly solved for selected variables, and those variables eliminated from the problem as independent variables. Linear constraints are input in just the same form as assignment statements in FORTRAN, e.g., ' $A(60) = A(9)$ ', ' $A(29) = 1.0 - A(24)$ ', and ' $A(41) = 0.95 - 0.5 * A(31)$ '. In these expressions, array A stores both variable and fixed parameters contained in $y_i(c)$. When dealing with mixtures of two or more phases, common profile parameters are usually assigned to each phase by introducing linear equality constraints.

11.2 Refinement Based on Information about the Crystal Structure

Powder diffraction patterns contain far poorer information than single-crystal intensity data mainly owing to the overlap of equivalent and neighboring reflections. Accordingly, *a priori* information on the crystal structure should be introduced into the program as constraints when reflections overlap very extensively or when a number of structure parameters have to be refined because many atoms are contained in an asymmetric unit. Most programs for Rietveld analysis are able to apply only equality constraints such as those required to keep certain bond lengths or bond angles fixed or equal [25]. True bond lengths or angles are not exactly equal to expected ones. Therefore, the introduction of inequality constraints [26] is preferred, permitting the imposition of ranges expected for interatomic distances and bond angles as well as thermal parameters as boundary conditions.

11.3 Nonlinear Constraints

Constrained nonlinear programming problems are solved by an exterior penalty function method [27]. Rietveld analysis under nonlinear constraints is formally stated as

$$\text{Minimize: } f(x) = \sum w_i [y_i(o) - y_i(c)]^2 \quad (12)$$

subject to p linear⁷ and/or nonlinear inequality constraints

$$g_n(x) \geq 0 \quad n = 1, 2, \dots, P \quad (13)$$

and q linear and/or nonlinear equality constraints

$$h_n(x) = 0 \quad n = 1, 2, \dots, Q \quad (14)$$

where x is the vector of variable parameters, and $w_i (= 1/y_i(o))$ is the weighting based on counting statistics.

The exterior penalty function method transforms a constrained optimization problem into a sequence of unconstrained optimizations for $K=0, 1, 2$, given by

$$\text{Minimize: } F(x, t^{(K)}) = f(x) +$$

```

      FUNCTION CON(J,A)
      * THIS FUNCTION RETURNS THE J-TH VIOLATED CONSTRAINTS. EACH
      * CONSTRAINT IS FORMULATED BY USING THE CURRENT VALUES OF
      * PARAMETERS (A). CELL CONSTANTS SHOULD NOT BE CONTAINED IN THESE
      * CONSTRAINTS.
      * FUNCTIONS DIS AND ANG SERVE TO OBTAIN THE VALUES
      * OF BOND DISTANCES AND ANGLES, RESPECTIVELY. FOR EXAMPLE,
      * BOUNDARY CONDITIONS DO EPS < D < DOEPS ARE EXPRESSED BY USING
      * STATEMENT FUNCTION G, WHERE D IS THE BOND DISTANCE BETWEEN THE
      * TWO ATOMS WHOSE FRACTIONAL COORDINATES ARE (X1,Y1,Z1) AND
      * (X2,Y2,Z2), AND DO IS THE EXPECTED BOND DISTANCE BETWEEN THEM.
      *
      * IN THE PRESENT ANALYSIS DEALING WITH AMMONIOLEUCITE, 12 (BT,AT)-O
      * DISTANCES ARE ASSUMED TO BE 1.65 +/- 0.05 ANGSTROM. IF THE BOND
      * DISTANCES ARE IN THIS RANGE, CON IS SET EQUAL TO ZERO.
      * CONSTRAINTS FOR BOND ANGLES CAN BE FORMULATED IN SIMILAR WAYS.

      REAL A(*)
      DATA DO,EPS/1.65,0.05/
      G(X1,Y1,Z1,X2,Y2,Z2)=MIN(0.0,EPS-ABS(DIS(X1,Y1,Z1,
      & X2,Y2,Z2,1)-DO))

      IF (J.EQ. 1) THEN
        CON=C(A(25),A(26),A(27),A(40),A(41),A(42))
      ELSE IF (J.EQ. 2) THEN
        CON=G(A(25),A(26),A(27),0.25-A(41),0.25+A(40),0.25-A(42))
      ELSE IF (J.EQ. 3) THEN
        CON=C(A(25),A(26),A(27),A(45),A(46),A(47))
      ELSE IF (J.EQ. 4) THEN
        CON=G(A(25),A(26),A(27),0.75-A(46),0.25+A(45),0.25+A(47))
      ELSE IF (J.EQ. 5) THEN
        CON=G(A(30),A(31),A(32),A(45),A(46),A(47))
      ELSE IF (J.EQ. 6) THEN
        CON=G(A(30),A(31),A(32),A(50),A(51),A(52))
      ELSE IF (J.EQ. 7) THEN
        CON=G(A(30),A(31),A(32),A(55),A(56),A(57))
      ELSE IF (J.EQ. 8) THEN
        CON=C(A(30),A(31),A(32),A(50),A(61),A(62))
      ELSE IF (J.EQ. 9) THEN
        CON=G(A(35),A(36),A(37),0.75+A(51)-1.0,0.75-A(50),
      & 0.75-A(52)-1.0)
      ELSE IF (J.EQ. 10) THEN
        CON=G(A(35),A(36),A(37),A(50),A(61),A(62))
      ELSE IF (J.EQ. 11) THEN
        CON=C(A(35),A(36),A(37),A(55),A(65),A(67))
      ELSE IF (J.EQ. 12) THEN
        CON=C(A(35),A(36),A(37),0.75-A(56)-1.0,0.25-A(65)+1.0,
      & 0.25-A(67))
      END IF
      END
  
```

Fig. 2 Function subprogram CON written for the introduction of 12 constraints in the Rietveld analysis of ammonioleucite.

$$t^{(K)} \left[\sum_{n=1}^p H(g_n(x)) g_n^2(x) + \sum_{n=1}^q h_n^2(x) \right] \quad (15)$$

where $t^{(K)}$ is a strictly increasing sequence of positive numbers, and H is the Heaviside operator such that $H(a) = 0$ for $a \geq 0$ and $H(a) = 1$ for $a < 0$. The second and third terms in Eq. (15) prevent the \mathbf{x} vector from getting too far away from the feasible region. A nonfeasible sequence of points generated by this algorithm may yield a feasible solution in the limit, i.e., $t^{(K)} = \infty$. Because Eq. (15) has a sum-of-squares form, conventional algorithms for nonlinear least-squares computations, which will be described in chapter 12, may be employed without any modifications.

The algorithm of the exterior penalty function method consists of the following four steps:

- 1) Set K at 0. Give the initial values of \mathbf{x} and $t^{(0)}$.
- 2) Refine a set of parameters \mathbf{x} which minimize $F(\mathbf{x}, T^{(K)})$.
- 3) If the second and third terms in Eq. (15) are reduced to nil, stop the calculation since the current values of \mathbf{x} are the solution.
- 4) Add 1 to K Increase $t^{(K)}$ and return to step 2).

As Fig. 2 shows, the constraints are introduced into the program by means of a separately written function subprogram named CON, the purpose of which is to evaluate $H(g_n(\mathbf{x}))g_n(\mathbf{x})$ and $h_n(\mathbf{x})$ when provided with the \mathbf{x} vector. Those partial derivatives of the functionals of constraints with respect to parameters which are used in least-squares calculations are approximated by centered differences not only to save preparation times to formulate analytical derivatives but also to avoid human errors.

The above method has been successfully applied to the refinement of the structure of yttrium-containing α -sialon [28]. In that work, X-ray powder data were supplemented with eight inequality constraints that restrict the (Si, Al)-(N, O) bond lengths within a reasonable range: 0.175 ± 0.005 nm.

12. Nonlinear Least-Squares Procedures

Almost all computer codes for Rietveld refinement employ the Gauss-Newton algorithm to find parameters which minimize the weighted sum-of-squares of the residuals apart from the progressive programs of Baerlocher [26], and Howard and Snyder [29]. However, when applied to Rietveld analysis without any improvements, this method suffers disadvantages that the range of convergence is not very great and that the refinements often converge to local minima [4]. Since none of the algorithms has

proved to be so superior that it can be classified as a universal panacea for nonlinear least-squares solutions, it is impolitic to persist in only one method of least squares.

Three different methods are available for nonlinear least-squares fitting: Gauss-Newton, modified Marquardt, and conjugate direction methods. All of them are designed to give stable convergence. The Gauss-Newton and Marquardt methods use derivatives of $y_i(c)$ with respect to \mathbf{x} , whereas the conjugate direction method is based on a direct-search algorithm. Since the values of initial parameters in the, input file can be replaced with those of final parameters after the refinement, it is very easy to change the method of least squares one after another and continue the calculation from the last point of the previous refinement.

In each of these methods, variable parameters in an input file can be updated after they have been refined. Thus, one can carry out Rietveld analysis again with parameter values obtained in the previous refinement.

12.1 Gauss-Newton Method

This algorithm calculates changes in parameters at each iterative step, $\Delta\mathbf{x}$, from the normal equation:

$$\mathbf{M}\Delta\mathbf{x} = \mathbf{N} \quad (16)$$

with

$$M_{jk} = \sum_i w_i \frac{\partial y_i(c)}{\partial x_j} \frac{\partial y_i(c)}{\partial x_k} + t^{(K)} \left[\sum_{n=1}^p H(g_n) \frac{\partial g_n}{\partial x_j} \frac{\partial g_n}{\partial x_k} + \sum_{n=1}^q H(h_n) \frac{\partial h_n}{\partial x_j} \frac{\partial h_n}{\partial x_k} \right] \quad (17)$$

$$N_j = \sum_i w_i [y_i(o) - y_i(c)] \frac{\partial y_i(c)}{\partial x_j} - t^{(K)} \left[\sum_{n=1}^p H(g_n) g_n \frac{\partial g_n}{\partial x_j} + \sum_{n=1}^q h_n \frac{\partial h_n}{\partial x_j} \right] \quad (18)$$

In Eqs. (17) and (18), $g_n(\mathbf{x})$ and $h_n(\mathbf{x})$ are, respectively, abbreviated as g_n and h_n . The coefficient matrix \mathbf{M} and the column matrixes $\Delta\mathbf{x}$ and \mathbf{N} are calculated in double precision owing to the large number of data points in Rietveld analysis and considerable numerical errors in the least-squares method with the normal equation.

Although $\Delta\mathbf{x}$ is evaluated from $\mathbf{M}^{-1}\mathbf{N}$ in most structure-refinement programs, there is little to recommend such a technique because of long computation time and low precision. In RIETAN, the Choleski decomposition of the symmetric, positive

definite matrix, \mathbf{M} , and back-solution for consistent systems of linear equations are performed. In cases where \mathbf{M} is non-positive definite, the Marquardt method described in the next section should be used.

A new set of \mathbf{x} , \mathbf{x}' , is readily obtained by

$$\mathbf{x}' = \mathbf{x} + d\Delta\mathbf{x} \quad (19)$$

with

$$d = 2^{-n} \quad n = 0, 1, 2, 3, 4$$

The initial value of the damping factor, d , is set at 1 ($n = 0$). If $F(\mathbf{x}, t^{(K)})$ does not decrease with \mathbf{x}' , d is decreased, and \mathbf{x}' is calculated again with Eq. (19). The value of d is automatically adjusted according to just the same rule adopted in a SALS program [30].

12.2 Modified Marquardt's Method

This method also uses Eqs. (17) and (18) but adds λ -diag(\mathbf{M}) (λ : Marquardt parameter, diag: diagonal matrix) to \mathbf{M} to stabilize the convergence to the minimum [31]:

$$(\mathbf{M} + \lambda - \text{diag}(\mathbf{M}))\Delta\mathbf{x} = \mathbf{N} \quad (20)$$

Then, $\Delta\mathbf{x}$ tends towards the steepest descents direction as λ becomes larger, while the Gauss-Newton solution is obtained when λ becomes negligible. The value of λ is adjusted during a series of iterations by the same technique as described by Fletcher [32]. Even if the coefficient matrix \mathbf{M} is not positive definite, it can be made computationally positive definite by choosing the Marquardt parameter large enough. Modified Marquardt's method is very effective for dealing with highly nonlinear model

functions, $y_i(c)$, or problems in which starting values for parameters differ markedly from the true ones.

12.3 Conjugate Direction Method

The conjugate direction method [33] is one of the most efficient algorithms to minimize objective functions without calculating derivatives. The minimum of $F(\mathbf{x}, t^{(K)})$ is located by successive unidimensional searches from an initial point along a set of conjugate directions generated by the procedure. A combination of the DSC and Powell algorithms [34] was selected as a unidimensional optimization routine.

Since the directions for minimization are determined solely from successive evaluations of the objective function, $F(\mathbf{x}, t^{(K)})$, this procedure is much slower than the two least-squares methods with derivatives but capable of solving ill-conditioned problems in which very high correlations exist between parameters. It is mainly used in the late stages of refinement to test the prospect of a local minimum being the global minimum or escape from a local minimum by using sufficiently large step sizes of line searches. On the other hand, the Gauss-Newton and Marquardt algorithms can check the convergence to the global minimum only by using different starting vectors.

12.4 Incremental Refinements

One usually proceeds 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 [4]. RIETAN requires only a single

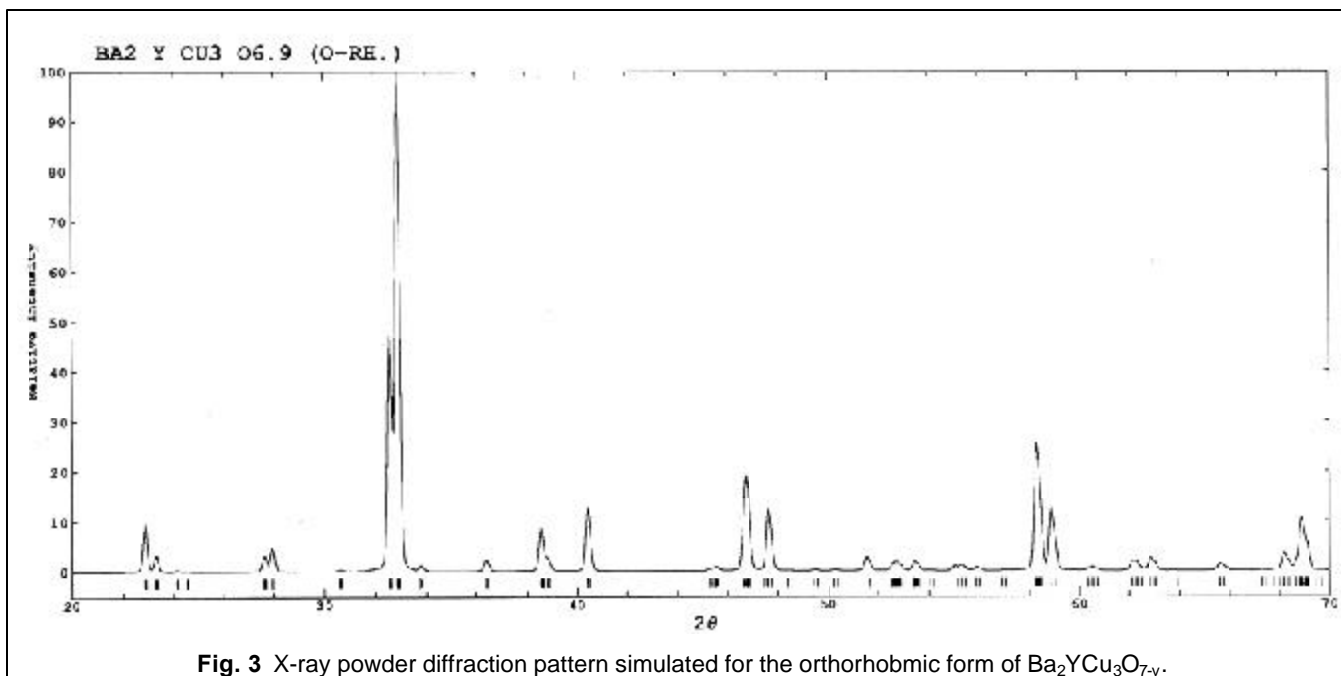


Fig. 3 X-ray powder diffraction pattern simulated for the orthorhombic form of $\text{Ba}_2\text{YCu}_3\text{O}_{7-y}$.

job to execute such incremental refinements; that is, variable parameters in each cycle can be appointed when using the methods of least squares with derivatives. Troublesome repetition of batch jobs is, therefore, unnecessary in most Rietveld refinements. Usually, linear parameters, that is, the background parameters 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.

Automatic refinements are also possible in which the parameters obtained by the successive refinements described above are further adjusted by the conjugate direction method to ensure that there are no lower minima in the vicinity of the one found by the initial refinement.

12.5 Standard Deviations

The standard deviations of parameters are calculated from diagonal elements in the inverse of the coefficient matrix M according to the procedure proposed by Scott [35]. M is neither inverted in each iteration in the two methods using derivatives nor calculated in Powell's method. For this reason, the standard deviations are calculated by selecting the Gauss-Newton method and specifying the number of iterations as zero after the refinement has finished.

The standard deviations of lattice parameters are calculated from those of the elements of the metric tensor (cf chapter 10) with formulae given by Kelsey [36].

13. Graphic Data Processing

One can not only plot the observed and calculated intensities after refinement by the least-squares methods (Fig. 1) but also simulate powder diffraction patterns of pure substances and mixtures from user-supplied profile, lattice, and structure parameters (Fig. 3). These figures are drawn using an incremental plotter, a laser beam printer, or a graphic display in interactive mode. Theoretical diffraction patterns serve for various semi-qualitative analyses such as examination of the validity of structural models, order-disorder distribution, degree of preferred orientation, characterization of polytype structures, and estimate of occupation factors in solid solutions. Since CalComp-compatible graphic subroutine packages are used for portability, RIETAN must be run on other computers without difficulty.

14. Connection with Other Programs

After the refinement has been finished, three files can be created which store (i) $y_i(o)$, $y_i(c)$, and $2\theta_k$, (ii) final crystal-structure parameters, their standard deviations, final lattice parameters, symmetry operations etc., and (iii) hkl , F_o , and F_c . Single quotation

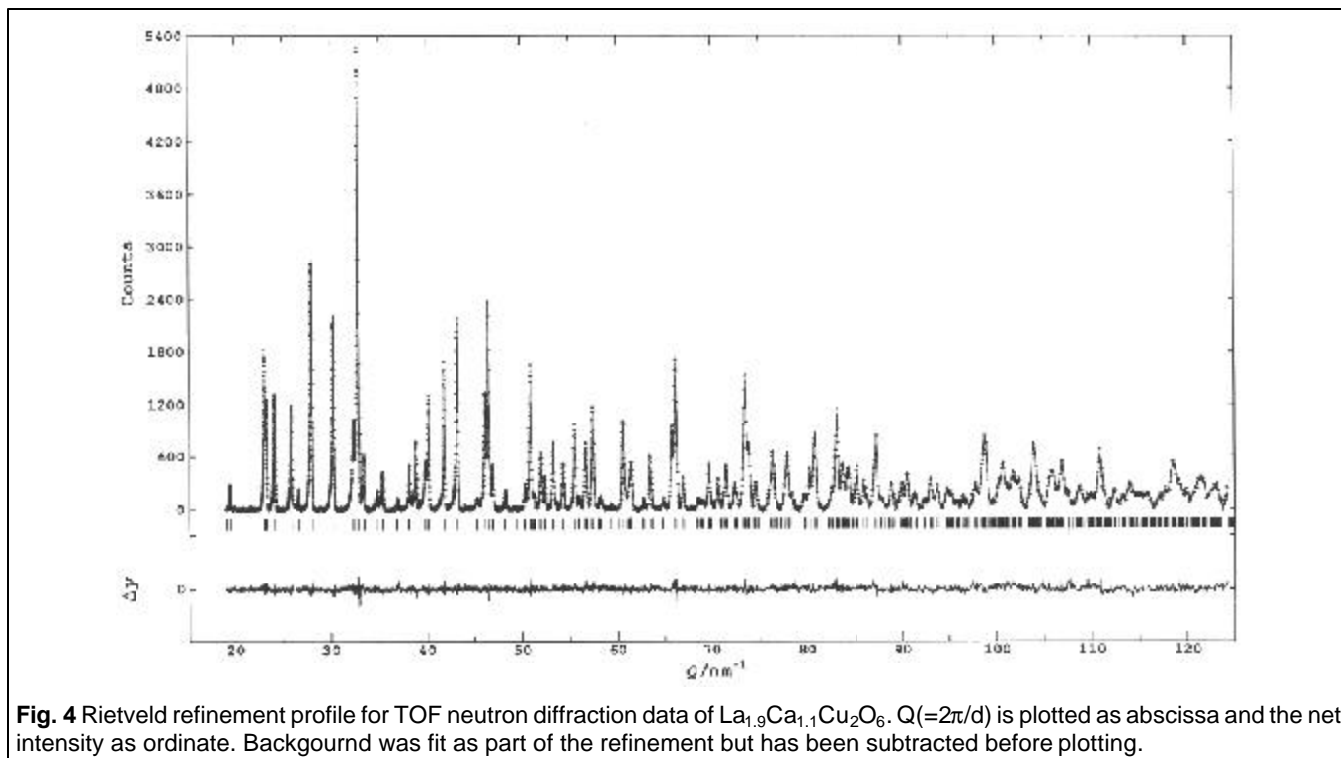


Fig. 4 Rietveld refinement profile for TOF neutron diffraction data of $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_6$. $Q(=2\pi/d)$ is plotted as abscissa and the net intensity as ordinate. Background was fit as part of the refinement but has been subtracted before plotting.

marks in F_o are needed because it is estimated indirectly from summation of contributions of the peak to net observed intensities [1]. The above three files respectively enable (i) drawing Rietveld refinement patterns (Fig. 1), (ii) calculation of interatomic distances and bond angles with an ORFFE program [37], calculation of Madelung energies by Ewald's method, and drawing crystal structure illustrations with an ORTEP 11 program [38], and (iii) Fourier and D syntheses with F_o and F_c data. Fourier and D syntheses, followed by drawing contour maps, are very useful for improving incomplete structural models.

15. Further Developments of RIETAN

The Rietveld method has been successively applied to time-of-flight (TOF) neutron powder diffraction data with an adaptation of the above program (Fig. 4). These intensity data were measured at a fixed scattering angle on a High-Resolution Powder diffractometer, HRP [39], at the pulsed neutron source (KENS) at the National Laboratory for High Energy Physics (KEK). This TOF neutron diffraction version retains all the features of the angle-dispersive one. A new profile shape function optimized for a cold neutron source (solid methane at 20 K) at KENS was implemented in it. Details on this version have been reported elsewhere [40]. Recently, it has been applied successfully to the structure refinement of a series of high- T_c superconducting oxides [41].

The program written for the fixed-wavelength case has been modified so as to enable the Rietveld analysis of synchrotron X-ray data obtained from a new dedicated powder diffractometer set up at the Photon Factory at KEK. The flat-plate geometry is unsuitable for collecting intensity data because of marked preferred orientation caused by highly parallel X rays. The Debye-Scherrer geometry with rotation of glass capillaries containing samples (some-times mixed with amorphous silica) is usually adopted to reduce the preferred-orientation effect as much as possible [24].

Thus, RIETAN is now applicable to the refinement of crystal structures from powder data obtained by four different methods [3]:

Fixed-wavelength methods with	characteristic X-ray source
	synchrotron X-ray source
	reactor neutron source

Fixed-angle method with pulsed neutron source

One can enjoy the benefits of the common and user-friendly software for the Rietveld analysis of results from the four categories of experimental technique.

Some time later, the two versions of RIETAN will be integrated into one program so that structure parameters can be refined simultaneously with the use of both X-ray and neutron diffraction data [42]. The different diffraction methods allow the collection of several, in many respects complementary, data sets from one kind of sample. Therefore, Rietveld refinements with the combined intensity data will be very helpful to obtain detailed information about the structure parameters of whole kinds of atoms.

Acknowledgment

The author wishes to thank Dr. A. Yamamoto for helpful advice on computing methods in crystallography. X-Ray powder diffraction data used to plot Fig. 2 were kindly provided by Professor R. A. Young.

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