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RIETVELD ANALYSIS SYSTEM RIETAN
(TRANSLATION)

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Rietveld Analysis System RIETAN
(Translation)

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This is the manual of the RIETAN system (a Rietveld analysis program) which is originally written in Japanese by Fujio Izumi. The manual consists of two parts.

Part I is a general description of the fundamental concepts and methods of the RIETAN system. Part II is the user's manual of the RIETAN which mainly describes in detail how to create user's data sets, procedures of Rietveld analysis and how to read the results of analysis.

Keywords: Rietveld Analysis, RIETAN, X-ray Diffraction, Neutron
Diffraction

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リートベルト解析システム RIETAN

(翻訳)

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(1991年9月13日受理)

本書は泉富士夫によって日本語で著されたりートベルト解析プログラム RIETAN システムの使用説明書を英訳したものであり、I、II部から構成されている。

I部ではRIETANシステムの基本的な概念や方法についての一般的な解説が述べられており、II部では主としてRIETANシステムにおける使用者用データの作り方、解析作業手順、解析結果の読み方についての使用手引が詳述されている。

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Preface

This is the manual of the RIETAN system (a Rietveld analysis program) which is originally written in Japanese by Fujio Izumi. When the Japan-US cooperative program in neutron scattering research started, the RIETAN program was installed on a Data General computer at the Oak Ridge National Laboratory for the analysis of the neutron diffraction data obtained with WAND (Wide Angle Neutron Diffractometer) machine which was built for the cooperative program. Since then attendees in the research program have benefited from the RIETAN. As one of the cooperative activities, an English translation of the "user's manual" (Part II of this document) has been created by Y. Morii, H.R. Child and S. Funahashi. Their thanks is due to LANGUAGE SERVICE, Knoxville, Tennessee, for the primary translation from the Japanese.

The user's manual has been edited by F. Izumi for the completion of the translation. A general description of the RIETAN system (Part I of this document) is also provided by F. Izumi.

Rietveld Analysis System

RIETAN

Part I. A Software Package for the Rietveld Analysis and Simulation of X-Ray and Neutron Diffraction Patterns

Fujio Izumi

This document has been written on the basis of the following review article:

Izumi, F. (1989). *Rigaku J.* 6, No. 1, 10.

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Abstract

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 (Rietveld, 1969; Cheetham & Taylor, 1977) but now constitutes a major breakthrough for the usefulness of X-ray powder data (Albinati & Willis, 1982). 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 (Young, 1980).

A computer program, XPD, for the Rietveld analysis of X-ray powder data (Izumi, 1982) has been extensively modified to overcome these difficulties to a considerable extent and to permit the refinement with neutron powder data as well (Izumi, 1985). This new version, called RIETAN* (*RIET*veld *AN*alysis), plus XPD are distributed to more than 80 research groups, domestic and foreign. It incorporates almost all convenient features of a standard program coded by Wiles & Young (1981), 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 SUN machines without any modifications. The virtual storage necessary to process a standard job is less than 2.5 Mbytes. Laser-beam printers with dot densities larger than 300 dpi are desirable to obtain Rietveld refinement patterns 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. 1.1 or newer.

* This program, as well as a user's manual written in English, is available from the author upon request without charge or, where necessary, with cost reimbursement for reproduction and mailing.

Files storing X-ray intensity data written in a RIETAN format can be read directly by the program without any conversion of them. 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

RIETAN has been written in FORTRAN 77 in conformity with ANSI X3.9-1978 standards for portability, quite independently of the program developed by Rietveld (1969). 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 data sets 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. I (1969).
- 2) Corresponding descriptions in *International Tables*, Vol. A (1983).
- 3) Coefficients for analytic approximations of scattering factors and anomalous dispersion corrections listed in *International Tables*, Vol. IV (1974), coherent scattering lengths, incoherent scattering cross sections, and absorption cross sections (Sears, 1986), and atomic weights.

One merely enters names of constituent atoms and space group and setting numbers in conformity with *International Tables*, Vol. I (1969) or Vol. A (1983). After symmetry conditions have been input directly from data set 1) or 2), indices of possible reflections are generated from them with KDRREF subprograms written by Cooper, Rouse & Sayers (1977); no preparatory program is needed to generate unique reflection sets as in the original program of Rietveld (1969). If non-standard settings are required which are not described in *International Tables*, 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, h_s , $h \cdot t_s$ (Rollet, 1965), 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 , at a particular step, i , is modeled by a calculated intensity, $f(\theta_i; x_1, x_2, x_3, \dots) \equiv f_i(x)$:

$$f_i(x) = \sum_k s |F_k|^2 m_k P_k L(\theta_k) G(\Delta\theta_{ik}) + B(2\theta_i) \quad (1)$$

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), x = a set of variable parameters (x_1, x_2, x_3, \dots), 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, $B(2\theta_i)$ = 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 ($\beta_{11j}, \beta_{22j}, \beta_{33j}, \beta_{12j}, \beta_{13j}, \beta_{23j}$), where j is the site number. Either isotropic or anisotropic thermal motion can be arbitrarily assigned to each atom.

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

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

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 by using equations given by Shirane (1959). 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 (Sasa & Uda, 1976; Toraya & Marumo, 1981):

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

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, $h_p a^* + k_p b^* + l_p c^*$. 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 (1969) 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 (Hewat, 1980).

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, $a(\Delta\theta_{ik})$ (Rietveld, 1969):

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

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 (Rietveld, 1969), Lorentzian (Young, Mackie & Von Dreele, 1977), modified Lorentzian (Sonneveld & Visser, 1975), and intermediate Lorentzian (Khattak

& Cox, 1977). At present, better symmetric profile shape functions, *i.e.*, pseudo-Voigt (Wertheim, Butler, West & Buchanan, 1974) and Pearson VII functions (Hall, Jr., Veeraraghavan, Rubin & Winchell, 1977) are widely used in place of the above four functions (Young & Wiles, 1982).

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

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

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

$$H_k(L) = \frac{H_k(G)}{\delta}. \quad (9)$$

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 (Young & Wiles, 1982).

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 (Rietveld, 1969).

The difference between the conventional pseudo-Voigt function (Wertheim, Butler, West & Buchanan, 1974; Young & Wiles, 1982) 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 (1969) is used as $a(\Delta\theta_{ik})$:

$$a(\Delta\theta_{ik}) = 1 - \frac{A \cdot \text{sign}(\Delta\theta_{ik})(2\Delta\theta_{ik})^2}{\tan\theta_k} \quad (10)$$

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 & Hastings (1986) 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. Their profile shape function will be implemented in RIETAN in the near future.

9. Background corrections

Background corrections are evaluated as follows.

1) The background function, $B(2\theta_i)$, is used which is linear in six refinable parameters

$$b_0 - b_5:$$

$$B(2\theta_i) = \sum_{j=0}^5 b_j \left[\frac{2\theta_i - \theta_{\max} - \theta_{\min}}{\theta_{\max} - \theta_{\min}} \right]^j, \quad (11)$$

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

- 2) 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 $f_i(x)$.

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 (Rietveld, 1969); these elements are converted into lattice parameters upon printing of parameter values.

11. Constrained minimization procedures

11.1 Linear equality constraints

In RIETAN, 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 $f_i(x)$. 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 interatomic distances or bond angles fixed or equal (Pawley, 1980). True distances or angles are not exactly equal to expected ones. Therefore, the introduction of inequality constraints (Baerlocher, 1984) 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 (Zangwill, 1967). Rietveld analysis under nonlinear constraints is formally stated as

$$\text{Minimize: } S(\mathbf{x}) = \sum_i w_i [y_i - f_i(\mathbf{x})]^2 \quad (12)$$

subject to p linear and/or nonlinear inequality constraints

$$g_n(\mathbf{x}) \geq 0 \quad n = 1, 2, \dots, p \quad (13)$$

and q linear and/or nonlinear equality constraints

$$h_n(\mathbf{x}) = 0, \quad n = 1, 2, \dots, q \quad (14)$$

where w_i ($= 1/y_i$) is the weighting based on counting statistics.

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

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

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

The constraints are introduced into the program by means of a separately written function subprogram named CON, the purpose of which is to evaluate $H(g_n(x)) g_n(x)$ and $h_n(x)$ when provided with the 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 (Izumi, Mitomo & Bando, 1984). 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 (1984), and Howard & Snyder (1984). 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 (Young, 1980). 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 $f_i(x)$ with respect to x , whereas the conjugate direction method is based on a direct-search algorithm. Since the values of initial parameters in the input data set 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 data set 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, Δx , from the normal equation:

$$M\Delta x = N \quad (16)$$

with

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

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

In Eqs. (17) and (18), $g_n(x)$ and $h_n(x)$ are, respectively, abbreviated as g_n and h_n . The coefficient matrix M and the column matrixes Δx and 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 Δx is evaluated from $M^{-1}N$ 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, M , and back-solution for consistent systems of linear equations are performed. In cases where M is non-positive definite, the Marquardt method described in the next section should be used.

A new set of x , x' , is readily obtained by

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

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 $F(x, t^{(K)})$ does not decrease with x' , d is decreased, and 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 (Nakagawa & Oyanagi, 1982).

12.2 Modified Marquardt method

This method also uses Eqs. (17) and (18) but adds $\lambda \cdot \text{diag}(M)$ (λ : Marquardt parameter, diag : diagonal matrix) to M to stabilize the convergence to the minimum (Marquardt, 1963):

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

Then, Δx 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 (1971). Even if the coefficient matrix M is not positive definite, it can be made computationally positive definite by choosing the Marquardt parameter large enough. The modified Marquardt method is very effective for dealing with highly nonlinear model functions, $f_i(\mathbf{x})$, or problems in which starting values for parameters differ markedly from the true ones.

12.3 Conjugate direction method

The conjugate direction method (Powell, 1964) 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 (Himmelblau, 1972) 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 using 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 parameters in 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 (Young, 1980). RIETAN requires only a single 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 (1983). 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 (1964).

12.6 Reliability indices

Five kinds of reliability indices (R factors) are printed out as measures of the goodness of fit (Young, Prince & Sparks, 1982):

$$R_{wp} = \left\{ \frac{\sum_i w_i [y_i - f_i(x)]^2}{\sum_i w_i y_i^2} \right\}^{1/2}, \quad (21)$$

$$R_p = \frac{\sum_i |y_i - f_i(x)|}{\sum_i y_i}, \quad (22)$$

$$R_I = \frac{\sum_k |I_k(o') - I_k(c)|}{\sum_k I_k(o')}, \quad (23)$$

$$R_F = \frac{\sum_k |[I_k(o')]^{1/2} - [I_k(c)]^{1/2}|}{\sum_k [I_k(o')]^{1/2}}, \quad (24)$$

$$R_e = \left\{ \frac{N_p - N_r - N_c}{\sum_i w_i y_i^2} \right\}^{1/2}. \quad (25)$$

In Eqs. (23) and (24), $I_k(o')$ is the integrated intensity *evaluated* from summation of contributions of the k th peak to net observed intensities, $I_k(c)$ is the integrated intensity calculated from refined structural parameters, N_p is the number of data points, N_r is the number of refinable parameters, and N_c is the number of constraints. R_{wp} , R_p , and R_e are output in every iteration, whereas R_I and R_F after the refinement has been finished. R_e is the value of R_{wp} expected statistically. R_F corresponds to the R factor used in single-crystal X-ray analysis.

13. Graphic data processing

One can not only plot the observed and calculated intensities after refinement by the least-squares methods but also simulate powder diffraction patterns of pure substances and mixtures from user-supplied profile, lattice, and structure parameters. 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 data sets can be created which store (i) y_i , $f_i(x)$, and $2\theta_k$, (ii) final crystal-structure parameters and lattice parameters, their standard deviations, symmetry operations *etc.* and (iii) hkl , $F_{o'}$, and F_c . Single quotation marks in $F_{o'}$ are needed because it is estimated indirectly from summation of contributions of the peak to net observed intensities (Rietveld, 1969). The above three data sets respectively enable (i) drawing Rietveld refinement patterns, (ii) calculation of interatomic distances and bond angles with ORFFE (Busing, Martin & Levy, 1964), calculation of Madelung potentials by the Ewald method, and drawing crystal structure illustrations with ORTEP-II (Johnson, 1976), and (iii) Fourier and D syntheses with $F_{o'}$ and F_c data. Input data sets for ORTEP-II can be created very easily with 19 macro instructions by a preprocessor named PRETEP. Fourier and D syntheses, followed by drawing contour maps, are very useful for improving structural models in cases where most of the structure has been determined (Cheetham & Taylor, 1977). This group of programs including the data bases is called as a FAT-RIETAN system.

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. These intensity data were measured at a fixed scattering angle on a High-Resolution Powder diffractometer, HRP (Watanabe, Asano, Iwasa, Satoh, Murata, Karahashi, Tomiyoshi, Izumi & Inoue, 1987) 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 (Izumi, Asano, Murata & Watanabe, 1987). Recently, it has been applied successfully to the structure refinement of a series of high- T_c superconducting oxides (Izumi & Nakai, 1987).

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 Bragg-Brentano parafocusing geometry with the use of flat samples is unsuitable for collecting synchrotron intensity data because of marked preferred orientation caused by highly parallel X rays. The Debye-Scherrer geometry with rotation of quartz- or glass-capillaries containing samples (sometimes mixed with amorphous silica) is usually adopted to reduce the preferred-orientation effect as much as possible (Thompson, Cox & Hastings, 1986).

Honda, Goto & Kurahashi (1990) have recently collected synchrotron X-ray data by using a large-radius (28.65 cm) Weissenberg camera equipped with a Fuji Imaging Plate and succeeded in the *ab initio* structure determination of 5-aminovaleric acid. RIETAN was used to refine the structure parameters of this compound in the final stage of the structure analysis. The agreement between observed and calculated data was very good in spite of the facts that the peak shape was simply assumed to be symmetric Gaussian and that no preferred orientation was corrected.

Thus, RIETAN is now applicable to the refinement of crystal structures from powder data obtained by four different methods (Albinati & Willis, 1982):

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 (Maichle, Ihringer & Prandl, 1988). 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.

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Table 1 Parameters refined in Rietveld analysis

- *Global parameters*

Parameter to correct for the zero-point shift of a goniometer

- 1) Zero-point error: Z .

Parameters to calculate the background

- 2) Background parameters: $b_0, b_1, b_2, b_3, b_4, b_5$.

- *Phase-dependent parameters*

Parameters to adjust integrated intensities

- 3) Scale factor: s .
- 4) Preferred-orientation parameters: p_1, p_2 .

Profile parameters

- 5) FWHM parameters: U, V, W .
- 6) Gaussian fraction: γ .
- 7) FWHM ratio: δ .
- 8) Asymmetry parameter: A .

Parameters to determine peak positions

- 9) Lattice parameters: $a, b, c, \alpha, \beta, \gamma$.

Crystal-structure parameters

- 10) Fractional coordinates: x_j, y_j, z_j .
- 11) Occupation factors: n_j .
- 12) Overall thermal parameter: Q .
- 13) Isotropic thermal parameters: B_j .
- 14) Anisotropic thermal parameters: $\beta_{11j}, \beta_{22j}, \beta_{33j}, \beta_{12j}, \beta_{13j}, \beta_{23j}$.

Magnetic-structure parameters

- 15) Magnetic moments in Bohr magneton: μ_j .
- 16) Angle between the spin direction and the unique axis*: Φ .
- 17) Angles between the spin direction and the three axes**: Φ_a, Φ_b, Φ_c .

* Tetragonal, hexagonal, and rhombohedral systems.

** Orthorhombic system.

Rietveld Analysis System

RIETAN

Part II. User's Manual

Fujio Izumi

This manual was translated from the Japanese by Y.Morii(JAERI), H.R.Child(ORNL) and S.Funahashi(JAERI) for the Japan-US cooperative program in neutron scattering research with an aid of LANGUAGE SERVICE, Knoxville, Tennessee, in the primary stage of the work and then edited extensively by F.Izumi(NIRIM).

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1. Introduction

The RIETAN (*RIET*veld *AN*alysis) system (Izumi, 1985; Izumi, 1989; Izumi, 1990b) is a software package which analyzes X-ray and neutron diffraction data measured with an angle-dispersive type diffractometer using the Rietveld method. Since development of this program began in 1980, it has been improved version by version, culminating in the functions of the present version. This system can be run easily with little change on a computer which has a main or virtual memory capacity of more than 2 Mbyte and furnishes a FORTRAN 77 upper level compiler.

In order to make Rietveld analysis widely available and increase the reliability of the software, the RIETAN system is now being provided without any charge, regardless of universities, national and public research institutions, and private corporations.

The RIETAN system is now in the public domain. It is *not* copyrighted; *any part of the program, database and this manual may be copied to be given to anyone without author's permission.*

This user's manual has been written on the assumption that the user has already read three review articles of RIETAN (Izumi, 1985; Izumi, 1989; Izumi, 1990b) and has fundamental knowledge of Rietveld Analysis. Before reading specific instructions for the use of RIETAN, the user is advised to read them. In particular, Izumi (1989) is essential because it describes all important equations used in RIETAN. Furthermore, the Rietveld method will be understood even better if other three reviews (Cheetham & Taylor, 1977; Albinati & Willis, 1982; Izumi, 1990a) are also read.

If the user, while using the RIETAN system, should find any bugs or any features which are difficult to understand or need to be improved, he is requested to inform the author. This kind of information will be invaluable for improving the program and

increasing its reliability.

The author requests that Izumi (1985), Izumi (1989) or Izumi (1990b) be cited if research results which have been obtained using this system are submitted to a scientific journal.

The author cannot be responsible for any results obtained using this system.

2. Summary of Data Sets

Ten sequential data sets (a)–(j) are recorded in EBCDIC codes with a density of 1600 or 6250 bpi on the magnetic tape distributed (standard label, volume serial number: RIETAN). In the case of 1600 bpi, file (j) may be deleted.

DCB of data sets (a), (d), (e), (f), (h), (i) and (j): RECFM = FB, LRECL = 80, BLKSIZE = 2080.

DCB of data sets (b) and (c): RECFM = FB, LRECL = 28, BLKSIZE = 2800.

DCB of data set (g): RECFM = VB, LRECL = 136, BLKSIZE = 1364.

In the above descriptions, DCB is the data control block, RECFM is the record format, LRECL is the record length, and BLKSIZE is the block size.

(a) RIETAN

A FORTRAN 77 program for Rietveld analysis and simulation of X-ray and neutron diffraction patterns (for FACOM, HITAC, ACOS, VAX and SUN computers).

(b) SPGRI

A data base containing various kinds of information about the space groups described in *International Tables*, Vol. I (1969).

(c) SPGRA

A data base containing various kinds of information about the space groups described in *International Tables*, Vol. A (1983).

(d) ASFDC

A data base of atomic scattering factors, correction terms for anomalous dispersion (*International Tables*, Vol. IV, 1974), coherent scattering lengths (Sears, 1986) and

so on.

(e) CASIALON

Input data for Ca α -sialon (Izumi, Mitomo & Bando, 1984).

(f) INTCA

Step-scanned X-ray powder diffraction data for Ca α -sialon

(g) OUTCA

Printer output of the case where the structure of Ca α -sialon is refined by the Rietveld method using data sets (e) and (f).

(h) ORFFE

A FORTRAN 77 program for calculation of interatomic distances and bond angles (Busing, Martin & Levy, 1964).

(i) PRETEP

A preprocessor for ORTEP-II (Johnson, 1976). A simple manual is included at the top of the source program as a form of comment lines.

(j) ORTEP

A FORTRAN 77 program, ORTEP-II (Johnson, 1976), to draw crystal structure models.

3. Changes in the Program by the User

3.1 Machine-Independent Modifications

Before using this program, the values of NB, NP, NA, NT, NR, NSF, NS, NAP, NCS, NPH and NGEN, which are written in PARAMETER statements in the main- and sub-programs, need to be changed to values that fit the problem the user is dealing with. These values can be changed immediately using a change-string command in full-screen editors as below:

```
CHANGE 'NP=2500' 'NP=3000' ALL (for FACOM and HITAC)
```

Of these constants, the values of NB and NS are the ones influencing the necessary memory capacity the most.

Parameter Content

- NB: upper limit of the number of diffraction peaks (in the case of X-ray diffraction, the sum of the numbers of $K\alpha_1$ and $K\alpha_2$ peaks).
- NP: upper limit of the number of step-scanned intensity data.
- NA: upper limit of (the number of real atoms + the number of imaginary atoms) (see line 6).
- NT: upper limit of the number of parameters.
- NR: upper limit of the number of variable parameters.
- NSF: upper limit of the number of variable structure-factor parameters (occupation factor, fractional coordinate, thermal parameter, magnetic moment, and angle between spin and a particular direction).
- NS: upper limit of the number of general equivalent positions excluding inverted and translated positions (≤ 48).
- NAP: upper limit of the number of atoms contained in an asymmetric unit.
- NCS: upper limit of the number of linear constraints.

NPH: upper limit of the number of phases.

NGEN: upper limit of the number of reflections which are temporarily created during the generation of diffraction ($\text{NGEN} > \text{NB}$).

When Rietveld analysis is carried out under nonlinear constraints ($\text{NC} > 0$ in Line 32 and Line 33), they are to be described in function subprogram CON (see Chapter 7).

3.2 Machine-Dependent Modifications

After comment lines in the program where `"*FACOM"`, `"*HITAC"`, `"*ACOS"`, `"*VAX"` or `"*SUN"` are written, statements are described specially for one of these computers. Most of them are calls for subroutines of CalComp-compatible graphic packages. If a different computer and/or a different graphic package is used, these lines must be rewritten. If the user wishes to know the statements that depend on the above types of computers, he should refer to the user's manuals of FORTRAN 77 and the CalComp packages.

In the case of VAX machines, patterns are plotted with an HP 7750A plotter and HP-ISPP subroutine packages. For SUN machines, CalComp subroutines create PostScript codes, which can be output to a laser-beam printer such as Apple Laser-Writer or a bitmapped display with the aid of a NeWS window system.

If you find it hard to adapt the CalComp subroutines to your computer, please write a short program to draw Rietveld-refinement and simulated patterns by yourself. Data necessary to draw them can be gotten from data set #20, which is created if NMODE in Line 2 is set at -1 or -3.

4. External Data Sets

4.1 List of External Data Sets

External data sets with the external unit identifiers 1, 11, 2, 3, 5, 10, 9, 16, 20 and 21 are used in RIETAN. These data sets must be connected to apparatus beforehand by a JCL or a command procedure if they are read or created during execution of RIETAN.

- 1: data base containing various kinds of information on space groups (coordinates of equivalent positions, Laue groups, presence or absence of the center of symmetry, *etc.*) described in *International Tables*, Vol. I (1969): SPGRI.
- 11: data base containing various kinds of information on space groups (coordinates of equivalent positions, Laue groups, presence or absence of the center of symmetry, *etc.*) described in *International Tables*, Vol. A (1983): SPGRA.
- 2: data base containing atomic scattering factors, correction terms for anomalous dispersion, coherent scattering lengths of the neutron, *etc.*: ASFDC.
- 3: data set containing intensity data measured with a θ - 2θ diffractometer using the step scan method.
- 5: input data set to be created by the user. Chapter 5 describes the input method in detail.
- 10: temporary data set containing three arrays.
- 9: data set storing structural parameters, lattice parameters, symmetry operations, a variance-covariance matrix, *etc.* (LRECL = 80). This can be used as an input data set for ORFFE (Busing, Martin & Levy, 1964) and ORTEP-II (Johnson, 1976), both of which are included in the distributed magnetic tape. The unit identifier of this file should be 9 for ORFFE and 5 for ORTEP-II.

- 16: graphic data set containing data which are used to a simulated powder diffraction pattern or Rietveld refinement patterns as output to the plotter or the graphic display.
- 20: data set storing data to draw Rietveld-refinement patterns (LRECL = 140).
- 21: data set storing data for Fourier and D syntheses (LRECL = 100).

4.2 Recording Format of Data Set #3

Data set #3 is read using the following list-directed READ statements:

```
READ(3,*) NTOTAL, THINIT, STEP
READ(3,*) (XINT(J), J=1, NTOTAL)
```

NTOTAL: number of intensity data.

THINIT: minimum of 2θ , $2\theta_{\min}$ /degree.

STEP: step width, 2θ /degree.

XINT: diffraction intensity.

In order to make input possible through the above statements, the data are recorded in the form of integers or real numbers, each separated from one another with a comma or a blank space or more. Naturally, more space is saved if integers are used. As many intensity data as desired can be placed in one line as long as they are within the record length. However, the step width must be equal across all the 2θ region; in other words, part of the intensity data cannot be deleted. If line-numbered (NUM) data sets are created, line numbers written in the 73rd to 80th columns of each line will be read as intensity data; therefore, *data sets with no line numbers (UNNUM) must be created.*

When the maximum count is less than 106, intensity data can be stored in an integer type array INT and written as follows using formatted sequential WRITE statements (unit identifier: NUNIT):

```
WRITE(NUNIT, '(15,2F10.3)') NTOTAL, THINIT, STEP
WRITE(NUNIT, '(1117)') (INT(I), I=1, NTOTAL)
```

If the subroutine shown below is called for instead of the WRITE statement in the second line, there will be only one blank space between data, so that the maximum amount of intensity data can be squeezed into one record with LRECL columns. However, LRECL must be 1024 or less.

```
SUBROUTINE PACK(INT, NTOTAL, LRECL, NUNIT)
*   PACK AND SAVE INTENSITY DATA
INTEGER INT(*), NTOTAL, LRECL, NUNIT
CHARACTER LINE*1024, FIG*7

IF (LRECL .GT. 1024) THEN
  WRITE(6, '(A)') ' TOO LONG RECORD LENGTH'
  STOP
END IF

OPEN(UNIT=NUNIT, STATUS='NEW', ACCESS='SEQUENTIAL')
REWIND(UNIT=NUNIT)
IDATA=1
1 CONTINUE
  LINE(:LRECL)=' '
  IP =1
2 CONTINUE
  WRITE(FIG, '(I7)') INT(IDATA)
```

```

DO 10 J=6,1,-1
    IF (FIG(J:J) .EQ. ' ') GO TO 3
10  CONTINUE
    3  IF (IP .GE. LRECL-5+J) GO TO 4
        LINE(IP:IP-J+6)=FIG(J+1:7)
        IP=IP-J+8
        IDATA=IDATA+1
        IF (IP .LE. LRECL .AND. IDATA .LE.
&  NTOTAL) GO TO 2
    4  WRITE(NUNIT,'(A)') LINE(:LRECL)
        IF (IDATA .LE. NTOTAL) GO TO 1
        CLOSE(UNIT=NUNIT)
END

```

4.3 Scratch Data Set #10

Data set #10 will be created during execution only when NRANGE = 1 in Line 3 (FORM='UNFORMATTED',ACCESS='SEQUENTIAL',STATUS='SCRATCH'), and will be deleted after the job is completed. However, the user had better define it with a JCL or a command procedure as a precaution.

5. Creation of External Data Set #5

5.1 General Remarks

Whenever (.....) appears after the heading of any line, that line needs to be input only if conditions in the parentheses are satisfied. For example, Line 4 contains the description (NBEAM = 1). Therefore, this line is necessary only when NBEAM is 1.

Data written after "⇒" will be input in free format by list-directed READ statements except for lines where only CHARACTER type data are entered. Thus, CHARACTER data input together with other types of data must be enclosed between apostrophes, and each piece of data must be separated from one another by a comma or a blank space or more. When data cannot be placed within one line, the remaining data can be placed on the next line.† REAL-type data can be entered in the form of INTEGER-type ones (for example, 2.0 as 2). Whenever data in any line need not be entered as input or when default values are used, the punctuation "," (first piece of data), ", ," (middle piece of data) and "/" (end of line) should be placed. If "/" is used, all data following "/" will be skipped. For example:

Lines 20 = "/": A(I) = 0.0; ID(I) = 0.

Line 33 = ",10, ,3/": NCYCLE = 10; NCONV = 3; NAUTO, CONV, NC, TK and FINC will take default values.

Unless specified otherwise, names of variables and arrays implicitly declare the types; that is, variables and arrays which have names beginning with I, J, K, L, M and N are integers. *All letters in the CHARACTER type data, such as element names and space*

† Data for each parameter (A, ID, STEP) must be put in only one line in Lines 20, only when NUPDT = 1 in Line 3.

group names, should be input as capital letters. When the plural form "Lines" is used in front of the line number, this indicates that input ranging over two or more lines is necessary or possible. "I = 1, 2," or "J = 1, 2," not enclosed by parentheses indicates that the values of arrays of subscripts I or J will be input from one or more lines 1, 2,"

If the user reads the descriptions below, referring to input and output data of Ca α -sialon, the input method may well be easier to understand.

5.2 Input Data

Line 1. Title

⇒ TITLE --- FORMAT (A80)

TITLE: title consisting of 80 letters or less.¹⁾

1) This is to be used as a heading for the printer output and the plotter output.

Line 2. Control Data No. 1

⇒ NBEAM, NMODE

Default values: NBEAM = 1; NMODE = 0.

NBEAM: = 0, neutron diffraction.¹⁾
 = 1, X-ray diffraction.

- = 2, synchrotron X-ray diffraction.²⁾
- NMODE: = 0, Rietveld analysis is performed.
- = -1, Rietveld analysis is performed, and data set #20 is created which stores data to draw Rietveld-refinement patterns.³⁾
- = 1, Rietveld analysis is performed, and Rietveld refinement patterns are drawn, *via* data set #16, on the graphic display or to the plotter.
- = 2, the 2θ 's, interplanar spacings, d , and diffraction intensities of possible reflections are calculated from the parameters the user has given.
- = 3, a powder diffraction pattern is simulated, *via* data set #16, on the plotter or the graphic display in addition to the calculation in the case of NMODE=2.
- = -3, a powder diffraction pattern is simulated, and data set #20 is created which store data to draw a simulated diffraction pattern.

- 1) Magnetic scattering can be handled only for collinear spin arrangements.
- 2) This feature has already been implemented, but is not described here.
- 3) Refer to Chapter 10 to obtain information about this data set.

Line 3. Control Data No. 2 (NMODE \neq 2)

- (a) In the case of NMODE = 0, 1

\Rightarrow NLESQ, NRANGE, NEXC, NUPDT, NPRINT, NFR, NDA

Default values: NLESQ = 2; NRANGE = 2; NEXC = 0; NUPDT = 0;

NPRINT = 1; NFR = 0; NDA = 0.

- (b) In the case of NMODE = 3

\Rightarrow NPRINT

Default value: NPRINT = 1.

- NLESQ: = 1, the conjugate direction method (Powell, 1964) is used as the least-squares method.
- = 2, the Marquardt method with Fletcher's modification (Fletcher, 1971) is used as the least-squares method.
- = 3, the Gauss-Newton method with a damping option (Nakagawa & Oyanagi, 1982) is used as the least-squares method.
- NRANGE: = 1, the background is fixed.¹⁾
- = 2, background parameters are refined.²⁾
- NEXC: = 0, parameters are refined using all the intensity data.
- = 1, parameters are refined by excluding part of the intensity data.³⁾
- NUPDT: = 1, variable parameters recorded in data set #5 (input at Lines 20) remain unchanged after the refinement.
- = 1, variable parameters recorded in data set #5 will be updated after the refinement.⁴⁾
- NPRINT: = 0, minimal output is required.
- = 1, standard output is required.⁵⁾
- = 2, most detailed output is required.⁶⁾
- NFR: = 0, no data set is created which store data for Fourier and D syntheses.
- = n , data set #21 is created which store data for Fourier and D syntheses for the n -th phase.
- NDA: = 0, no data set is created which store final structural parameters, lattice parameters, symmetry operations, a variance-covariance matrix, *etc.*
- = n , data set #9 is created which store final structural parameters for the n -th phase, lattice parameters, symmetry operations, a variance-covariance matrix, *etc.*⁷⁾

1) The background intensity at each diffraction point is calculated by means of the method described in Note 1 of Lines 27. The intensity data separated from the closest Bragg peak by more than $PC \times H_k$ are excluded, and then the parameters

are refined by a least-squares method. Here, PC is a constant specified in Line 30, and H_k , the FWHM of the k -th peak. Since this method cannot estimate background values very accurately in the high-angle regions where peaks are remarkably overlapped with each other, NRANGE = 2 should be selected except for the case where the number of peaks is extremely small.

- 2) All the intensity data, except for the regions specified in Lines 25, are used.
- 3) Regions where peaks due to impurities exist are excluded to prevent bad effects on the results of refinement.
- 4) If data set #5 is a member of a partition data set, the other members may be destroyed during parameter renewal. Thus, the user had better store the input data in a sequential data set.
- 5) The coordinates of equivalent positions, R factors and parameter values at each cycle and the reflection list after refinement are output.
- 6) Reflection lists before refinement, correlation matrix, observed and calculated diffraction intensities, and printer plots of refinement results are included in addition to the output for NPRINT = 1.
- 7) This data set is used for calculation of interatomic distances and bond angles with ORFFE (Busing, Martin & Levy, 1964) and drawing structural models with ORTEP-II (Johnson, 1976).

Line 4. Radiation Source (NBEAM = 1)

⇒ TNAME, R12, CTHM

Default values: TNAME = 'CU'; R12 = 0.497; CTHM = 0.8049.

TNAME: element name for characteristic X rays (CHARACTER*2).

R12: (intensity of the $K\alpha_2$ peak) / (intensity of the $K\alpha_1$ peak).

CTHM: coefficient contained in the polarization correction equation for the use of the monochrometer.²⁾

- 1) Choose from 'CR', 'FE', 'CU', 'MO' and 'AG'. *Lower case letters must not be entered.*
- 2) If the Bragg angle on the reflection plane of a monochrometer is α , then CTHM is equal to $\cos^2 2\alpha$. CTHM is set at 1.0 when the monochrometer is not used.

Line 5. Wavelength (NBEAM = 0, 2)

⇒ XLMD

Default value: XLMD = 1.08.

XLMD: wavelength of neutrons or synchrotron X rays, λ /angstrom.

Line 6. Number of Chemical Species

⇒ NREAL, NMIX

Default values: NREAL = 1; NMIX = 0.

NREAL: number of real chemical species.

NMIX: number of imaginary chemical species¹⁾ with an average scattering amplitude of two or more 'real' atoms, which are mixed in arbitrary proportions in the imaginary species.

- 1) When there are multiple kinds of atoms in one site whose occupation factors are constant, the number of structure-factor parameters can be reduced by assuming this kind of imaginary chemical species. Naturally, this convenient method cannot be used when the occupation factors of this site are refined. Let j be the component atom number; f_j , the atomic scattering factor; $f_j' + if_j''$, the correction term for anomalous dispersion; g_j , the occupation factor; and n , the number of atoms occupying the site, then the atomic form factor, $f(\text{imag})$, of the imaginary chemical species is:

$$f(\text{imag}) = \frac{\sum_{j=1}^n g_j (f_j^0 + \Delta f_j' + i\Delta f_j'')}{\sum_{j=1}^n g_j}.$$

FRCTN(J, I), the input in Lines 9, is $g_j / \sum_{j=1}^n g_j$ of the I-th chemical species. A similar equation can be formulated for coherent scattering lengths in neutron diffraction.

 Lines 7 and 8 are entered as input repeatedly, NREAL times (I = 1, 2, NREAL).

Lines 7. Names of Real Chemical Species

⇒ ANAME(I) --- FORMAT(A5)

ANAME: string representing a chemical species.¹⁾

- 1) Each chemical species is represented by capital letters, numbers, "+" and "-" (Table 1). However, names of neutral atoms must be entered in neutron diffraction. When the magnetic structure is analyzed on the basis of neutron diffraction data, "*" must be attached to the end of the name of an atom which has a magnetic moment (for example, "FE*", "MN*"). Refer to ASFDC to know names of chemical species.

Lines 8. Magnetic Form Factor Curve¹⁾ (when ANAME(I) contains "*")

⇒ (RLV(J, I), AMPMAG(J, I), J = 1, 2,

RLV: $\sin\theta/\lambda$.

AMPMAG: magnetic form factor, $f_j(\text{magn})$.

- 1) Any number of groups of data can be entered on one line. Input ranging over two or more lines is also permissible. However, the number of pairs has to be 20 or less, and "/" *must be entered right after the last data entry.*

Table 1 Chemical species stored in ASFDC. Species H(HF), H(SDS), C_{val}, Si_v and Si_{val} in *International Tables*, Vol. IV (1974a) are described as H, H.S, C.V, SI and SI.V, respectively.

At.No.	Element	Name of chemical species			
1	H	H	H.S	H-	D
2	He	HE			
3	Li	LI	LI+		
4	Be	BE	BE2+		
5	B	B			
6	C	C	C.V		
7	N	N			
8	O	O	O-		
9	F	F	F-		
10	Ne	NE			
11	Na	NA	NA+		
12	Mg	MG	MG2+		
13	Al	AL	AL3+		
14	Si	SI	SI.V	SI4+	
15	P	P			
16	S	S			
17	Cl	CL	CL-		
18	Ar	AR			
19	K	K	K+		
20	Ca	CA	CA2+		
21	Sc	SC	SC3+		
22	Ti	TI	TI2+	TI3+	TI4+
23	V	V	V2+	V3+	V5+
24	Cr	CR	CR2+	CR3+	
25	Mn	MN	MN2+	MN3+	MN4+
26	Fe	FE	FE2+	FE3+	
27	Co	CO	CO2+	CO3+	
28	Ni	NI	NI2+	NI3+	
29	Cu	CU	CU+	CU2+	
30	Zn	ZN	ZN2+		

At.No.	Element	Name of chemical species			
31	Ga	GA	GA3+		
32	Ge	GE	GE4+		
33	As	AS			
34	Se	SE			
35	Br	BR	BR-		
36	Kr	KR			
37	Rb	RB	RB+		
38	Sr	SR	SR2+		
39	Y	Y	Y3+		
40	Zr	ZR	ZR4+		
41	Nb	NB	NB3+	NB5+	
42	Mo	MO	MO3+	MO5+	MO6+
43	Tc	TC			
44	Ru	RU	RU3+	RU4+	
45	Rh	RH	RH3+	RH4+	
46	Pd	PD	PD2+	PD4+	
47	Ag	AG	AG+	AG2+	
48	Cd	CD	CD2+		
49	In	IN	IN3+		
50	Sn	SN	SN2+	SN4+	
51	Sb	SB	SB3+	SB5+	
52	Te	TE			
53	I	I	I-		
54	Xe	XE			
55	Cs	CS	CS+		
56	Ba	BA	BA2+		
57	La	LA	LA3+		
58	Ce	CE	CE3+	CE4+	
59	Pr	PR	PR3+	PR4+	
60	Nd	ND	ND3+		
61	Pm	PM	PM3+		
62	Sm	SM	SM3+		
63	Eu	EU	EU2+	EU3+	
64	Gd	GD	GD3+		

At.No.	Element	Name of chemical species			
65	Tb	TB	TB3+		
66	Dy	DY	DY3+		
67	Ho	HO	HO3+		
68	Er	ER	ER3+		
69	Tm	TM	TM3+		
70	Yb	YB	YB2+	YB3+	
71	Lu	LU	LU3+		
72	Hf	HF	HF4+		
73	Ta	TA	TA5+		
74	W	W	W6+		
75	Re	RE			
76	Os	OS	OS4+		
77	Ir	IR	IR3+	IR4+	
78	Pt	PT	PT2+	PT4+	
79	Au	AU	AU+	AU3+	
80	Hg	HG	HG+	HG2+	
81	Tl	TL	TL+	TL3+	
82	Pb	PB	PB2+	PB4+	
83	Bi	BI	BI3+	BI5+	
84	Po	PO			
85	At	AT			
86	Rn	RN			
87	Fr	FR			
88	Ra	RA	RA2+		
89	Ac	AC	AC3+		
90	Th	TH	TH4+		
91	Pa	PA			
92	U	U	U3+	U4+	U6+
93	Np	NP	NP3+	NP4+	NP6+
94	Pu	PU	PU3+	PU4+	PU6+
95	Am	AM			
96	Cm	CM			
97	Bk	BK			
98	Cf	CF			

Lines 9. Constituents (NMIX > 0)

⇒ ANAME(I), NOFRAC(I), (MFRAC(J, I), FRCTN(J, I), J = 1, NOFRAC(I))
 I = NREAL + 1, NREAL + 2,....., NREAL + NMIX

ANAME: name of an imaginary chemical species which occupies a certain site.

NOFRAC: number of atoms which occupy the site.

MFRAC: number representing the kind of each atom.¹⁾

FRCTN: mole fraction of MFRAC-th atom.

1) Corresponds to the order input in Lines 7.

Line 10. Number of Phases¹⁾

⇒ NPHASE

Default value: NPHASE = 1.

NPHASE: number of phases.

1) Although the RIETAN system can handle a mixture of multiple phases, the accuracy of refined parameters will then be reduced a great deal in comparison with the case of a single phase. The parameters for the phases with small contents cannot be determined very accurately, so that linear constraints should be given to the profile parameter (see Lines 22), or the structure-factor parameters should be fixed at the expected value to prevent convergence to an unreasonable solution.

 Lines 11 to 19 are entered repeatedly NPHASE times (I = 1, 2, NPHASE).

Lines 11. Information on Each Phase

⇒ PHNAME(I), VNS(I), LSPSYM(I), INDIV(I), (NOAT(J, I), J = 1, 2,)

PHNAME: phase name (CHARACTER*25).

VNS: volume name of *International Tables* ("I" or "A"), number for the space group (Table 2) and description number¹⁾ (CHARACTER*7).

LSPSYM: = 0, information about space groups is read from the data base of *International Tables*, Vol. I (1969) or Vol. A (1983), and reflections are generated in consideration of the extinction rule for general equivalent positions.²⁾

= 1, information about space groups is read from the data base described above. As regards types of reflections specified in Lines 12, only those reflections that satisfy conditions given in Lines 13 are produced.³⁾

= 2, a non-standard axes setting method not written in the data base described above is adopted. Those reflections that satisfy the symmetry conditions entered in Lines 16 are generated.

INDIV: = 0, overall isotropic thermal vibration is assumed, and isotropic or anisotropic thermal parameters are not entered for each site in Lines 20.⁴⁾

= 1, isotropic or anisotropic thermal parameters are entered for each site in Lines 20.

NOAT: numbers representing kinds of atoms in the asymmetric unit.⁵⁾

1) The volume name of *International Tables*, (Vol. I (1969) or Vol. A (1983)), the number given to each space group, the description number are written, and these three are connected with "-". For some space groups, two or more descriptions are available in *International Tables*. The following cases occur:

(a) Two choices of origin

Center of symmetry at the origin and not at the origin.

(b) Monoclinic space groups

Unique axes c and b . In Vol. A, additional descriptions are also given for eight space groups with centered lattices or glide planes.

(c) Trigonal space groups

Hexagonal and rhombohedral axes. When there is only one description, or when the first description is chosen, then the second "-" and the description number can be omitted.

In *International Tables*, Vol. I (1969), two descriptions exist in space groups bearing superscripts '*' in Table 2. In the monoclinic system, the first description is c -axis unique ($\gamma=90^\circ$), and the second description, b -axis unique ($\beta=90^\circ$). As regards a trigonal system with the rhombohedral lattice (R), the primitive cell (rhombohedral axes) is defined as the first description, and the rhombohedrally centered cell (hexagonal axes), the second description. As for the other space groups adopting two descriptions, two different methods of taking the origin are used.

In *International Tables*, Vol. A (1983), three or more descriptions are provided for eight monoclinic space groups with centered lattices or glide planes: Nos. 5, 7, 8, 9, 12, 13, 14 and 15. Make sure not to make an error in the description number.

Input Example

Volume I, space group P4/n, second description: 'I-85-2'.

Volume I, space group P6/mmm: 'I-191'.

Volume A, space group P2₁/c, sixth description: 'A-14-6'.

When LSPSYM = 2, VNS is used only for the purpose of examining the Laue group; therefore, either Volume I or A may be chosen. However, if it is a space group where there are two or more descriptions, the description of the same Laue group should be entered.

- 2) Extinction rules for general equivalent positions are contained in data sets #1 and #11.
- 3) Consider generation of possible reflections for Si as an example. Si belongs to the cubic system (space group: $Fd\bar{3}m$), and Si atoms occupy only the special position 8a (second description). The indices of possible reflections for this position must satisfy $h + k + l = 2n + 1$ or $4n$ (*International Tables*, Vol. I, 1969). If only the extinction rule for the general equivalent positions is taken into consideration, extra reflections which do not satisfy the above conditions will be generated.
- 4) In this case, the temperature factor is calculated from an overall isotropic thermal parameter.
- 5) They are equal to the order of the chemical species entered in Lines 7 and 9. For example, when Lines 7 are

AL

SI

O

(NREAL = 3), and Line 9 is

'SI,AL' 2 1 0.4 2 0.6

(NMIX = 1), 1 is appointed to AL, 2 to SI, 3 to O, 4 to 'SI,AL'. Inputs are repeated as many times as the number of atoms contained in the asymmetric unit, and "/" is placed at the end of the line.

When allocating an isotropic thermal parameter to this site, NOAT(J, I) > 0, and when allocating anisotropic thermal parameters to it, NOAT(J, I) < 0. Sites for which NOAT(J, I) is positive and negative may be mixed together.

Table 2 Numbers and symbols of 230 space groups.

No.	Symbol	No.	Symbol	No.	Symbol	No.	Symbol
1	P1	32	Pba2	63	Cmcm	94	P4 ₂ 2 ₁ 2
2	P $\bar{1}$	33	Pna2 ₁	64	Cmca	95	P4 ₃ 22
3*	P2	34	Pnn2	65	Cmmm	96	P4 ₃ 2 ₁ 2
4*	P2 ₁	35	Cmm2	66	Cccm	97	I422
5*	C2	36	Cmc2 ₁	67	Cmma	98	I4 ₁ 22
6*	Pm	37	Ccc2	68*	Ccca	99	P4mm
7*	Pc	38	Amm2	69	Fmmm	100	P4bm
8*	Cm	39	Abm2	70*	Fddd	101	P4 ₂ cm
9*	Cc	40	Ama2	71	Immm	102	P4 ₂ nm
10*	P2/m	41	Aba2	72	Ibam	103	P4cc
11*	P2 ₁ /m	42	Fmm2	73	Ibca	104	P4nc
12*	C2/m	43	Fdd2	74	Imma	105	P4 ₂ mc
13*	P2/c	44	Imm2	75	P4	106	P4 ₂ bc
14*	P2 ₁ /c	45	Iba2	76	P4 ₁	107	I4mm
15*	C2/c	46	Ima2	77	P4 ₂	108	I4cm
16	P222	47	Pnmm	78	P4 ₃	109	I4 ₁ md
17	P222 ₁	48*	Pnnn	79	I4	110	I4 ₁ cd
18	P2 ₁ 2 ₁ 2	49	Pccm	80	I4 ₁	111	P $\bar{4}$ 2m
19	P2 ₁ 2 ₁ 2 ₁	50*	Pban	81	P $\bar{4}$	112	P $\bar{4}$ 2c
20	C222 ₁	51	Pmma	82	I $\bar{4}$	113	P $\bar{4}$ 2 ₁ m
21	C222	52	Pnna	83	P4/m	114	P $\bar{4}$ 2 ₁ c
22	F222	53	Pmna	84	P4 ₂ /m	115	P $\bar{4}$ m2
23	I222	54	Pcca	85*	P4/n	116	P $\bar{4}$ c2
24	I2 ₁ 2 ₁ 2 ₁	55	Pbam	86*	P4 ₂ /n	117	P $\bar{4}$ b2
25	Pmm2	56	Pccn	87	I4/m	118	P $\bar{4}$ n2
26	Pmc2 ₁	57	Pbcm	88*	I4 ₁ /a	119	I $\bar{4}$ m2
27	Pcc2	58	Pnnm	89	P422	120	I $\bar{4}$ c2
28	Pma2	59*	Pmmn	90	P42 ₁ 2	121	I $\bar{4}$ 2m
29	Pca2 ₁	60	Pbcn	91	P4 ₁ 22	122	I $\bar{4}$ 2d
30	Pnc2	61	Pbca	92	P4 ₁ 2 ₁ 2	123	P4/mmm
31	Pmn2 ₁	62	Pnma	93	P4 ₂ 22	124	P4/mcc

No.	Symbol	No.	Symbol	No.	Symbol	No.	Symbol
125*	P4/nbm	156	P3m1	187	P6m2	218	P43n
126*	P4/nnc	157	P31m	188	P6c2	219	F43c
127	P4/mbm	158	P3c1	189	P62m	220	I43d
128	P4/mnc	159	P31c	190	P62c	221	Pm3m
129*	P4/nmm	160*	R3m	191	P6/mmm	222*	Pn3n
130*	P4/ncc	161*	R3c	192	P6/mcc	223	Pm3n
131	P4 ₂ /mmc	162	P31m	193	P6 ₃ /mcm	224*	Pn3m
132	P4 ₂ /mcm	163	P31c	194	P6 ₃ /mmc	225	Fm3m
133*	P4 ₂ /nbc	164	P3m1	195	P23	226	Fm3c
134*	P4 ₂ /nnm	165	P3c1	196	F23	227*	Fd3m
135	P4 ₂ /mbc	166*	R3m	197	I23	228*	Fd3c
136	P4 ₂ /mnm	167*	R3c	198	P2 ₁ 3	229	Im3m
137*	P4 ₂ /nmc	168	P6	199	I2 ₁ 3	230	Ia3d
138*	P4 ₂ /ncm	169	P6 ₁	200	Pm3		
139	I4/mmm	170	P6 ₅	201*	Pn3		
140	I4/mcm	171	P6 ₂	202	Fm3		
141*	I4 ₁ /amd	172	P6 ₄	203*	Fd3		
142*	I4 ₁ /acd	173	P6 ₃	204	Im3		
143	P3	174	P6	205	Pa3		
144	P3 ₁	175	P6/m	206	Ia3		
145	P3 ₂	176	P6 ₃ /m	207	P432		
146*	R3	177	P622	208	P4 ₂ 32		
147	P3	178	P6 ₁ 22	209	F432		
148*	R3	179	P6 ₅ 22	210	F4 ₁ 32		
149	P312	180	P6 ₂ 22	211	I432		
150	P321	181	P6 ₄ 22	212	P4 ₃ 32		
151	P3 ₁ 12	182	P6 ₃ 22	213	P4 ₁ 32		
152	P3 ₁ 21	183	P6mm	214	I4 ₁ 32		
153	P3 ₂ 12	184	P6cc	215	P43m		
154	P3 ₂ 21	185	P6 ₃ cm	216	F43m		
155*	R32	186	P6 ₃ mc	217	I43m		

Lines 12. Reflection Types (LSPSYM(I) = 1)

⇒ REFTYP(I) --- FORMAT(A3)

Default value: REFTYP(I) = 'HKL'.

REFTYP: type for possible reflections.¹⁾

- 1) One type is chosen from "HKL", "OKL", "HOL", "HK0", and "HHL". Among these types of reflections, only those that satisfy conditions entered in Lines 13 will be generated.

Lines 13. Reflection Conditions (LSPSYM(I) = 1)

⇒ LCON(J, I) J = 1, 2, --- FORMAT(A80)

LCON: conditional equation written for the indices of possible reflections.¹⁾

- 1) Conditional equations that can be related *via* logical product (AND) are arranged within one line. J is the reference number for a logical product set. A logical product set is expressed in the line by placing "," or ";" between conditional equations (three or less). An arbitrary number of blanks between equations can be placed. Lines are related *via* logical sum (OR) in the case where J is 2 or more.

For example, consider the case where which atoms occupy only the 4a position of the space group P4₁32 (No. 213). Conditions limiting possible reflections are (*International Tables*, Vol. I, 1969):

$hkl: h, k = 2n + 1$

or $h = 2n + 1, k = 4n$ and $l = 4n + 2$

or $h, k, l = 4n + 2$

or $h, k, l = 4n$.

Hence, the input at Lines 12 is

HKL

and inputs at Lines 13 and 14 are:

$H=2N+1, K=2N+1$

$H=2N+1, K=4N, L=4N+2$

$H=4N+2, K=4N+2, L=4N+2$

$H=4N, K=4N, L=4N$

ENDCON

Capital letters must be used for H, K, L and N.

Lines 14. End Reflection Condition(s) Label (LSPSYM(I) = 1)

⇒ Column 1 – Column 6: ENDCON

Lines 15. Presence or Absence of Center of Symmetry and the Name of the Space Group (LSPSYM(I) = 2)

⇒ NCENTR(I), SPGR(I)

NCENTR: = 0, the center of symmetry at the origin.
 = 1, the center of symmetry not at the origin.
 SPGR: name of the space group (CHARACTER*10).

Lines 16. Non-standard Symmetry Conditions (LSPSYM(I) = 2)

⇒ LINNSS(J, I) J = 1, 2, --- FORMAT(A40)

LINNSS: reflection type (Table 3) and symmetry condition of possible reflections¹⁾
 (Table 4).

- 1) They are entered as a string consisting of 40 letters or less, placing a colon between the reflection type and a reflection condition; for example, "HKL: H+K=2N" and "HOL: L=2N". An arbitrary number of blanks can be placed in the conditional equation. The seventh symmetry condition shows that h , k and l are all odd numbers or all even numbers (same as $h+k=2n$, $k+l=2n$ and $h+l=2n$). The 21st symmetry condition is applied to the rhombohedral lattice, but the user need not enter it.

Lines 17. End Non-standard Symmetry Condition(s) Label (LSPSYM(I) = 2)

⇒ Column 1 – Column 6: ENDNSS

Table 3 Reflection type

No.	Type
1	00L
2	OKO
3	OKL
4	HOO
5	HOL
6	HKO
7	HKL
8	OKK
9	HHO
10	HHL
11	HOH
12	HKK
13	HKH
14	HHH

Table 4 Symmetry conditions.

No.	Condition	No.	Condition
1	$H=2N$	15	$H-K+L=3N$
2	$K=2N$	16	$H=4N$
3	$L=2N$	17	$K=4N$
4	$K+L=2N$	18	$L=3N$
5	$H+L=2N$	19	$L=4N$
6	$H+K=2N$	20	$L=6N$
7	H,K,L ODD/EVEN	21	$ H \geq K \geq L $
8	$K+L=4N$	22	$2H+K=2N$
9	$H+L=4N$	23	$2H+K=4N$
10	$H+K=4N$	24	$H+2K=2N$
11	$2H+L=2N$	25	$H+2K=4N$
12	$2H+L=4N$	26	$H=2N, K=2N$
13	$H+K+L=2N$	27	$K=2N, L=2N$
14	$-H+K+L=3N$	28	$H=2N, L=2N$

Lines 18. Coordinates of General Equivalent Positions (LSPSYM(I) = 2)

\Rightarrow COORD(J, I) J = 1, 2 --- FORMAT(A20)

COORD: Coordinates of general equivalent positions.¹⁾

- 1) Coordinates of equivalent positions are entered on each line following the description method used in the data bases for the space groups SPGRI or SPGRA (x , y and z should be capital letters). Coordinates for inverted and translated positions must be omitted.

For example, the space group P21/c (No. 14) is entered as:

```
X,Y,Z
-X,-Y,-Z
-X,1/2+Y,1/2-Z
X,1/2-Y,1/2+Z
```

Lines 19. End Coordinate(s) Label (LSPSYM(I) = 2)

⇒ Column 1 – Column 8: ENDCOORD

Lines 20. Parameters and Refinement Conditions¹⁾

(a) When NMODE = 0, 1

⇒ A(I), ID(I)

(b) When NMODE < 1 and (NAUTO = 2 or NLESQ = 1) and ID(I) = 2

⇒ A(I), ID(I), STEP(I)

(c) When NMODE = 2, 3

⇒ A(I)

$I = 1, 2, \dots$

Default values²⁾: $A(I) = 0.0$; $ID(I) = 0$.

A: parameter, x , contained in the calculated intensity, $f_i(x)$.

ID: = 0, this parameter is fixed.

= 1, this parameter is refined.

= 2, this parameter is refined. Step(I) is entered.³⁾

= -1, this parameter is constrained by a linear equality constraint.⁴⁾

STEP: coefficient to determine the initial step interval of the direct search.

- 1) As discussed in Note 1 in Chapter 6, when $NUPDT = 1$, the input data for the I-th parameter — $A(I)$, $ID(I)$ and $STEP(I)$ — must be entered within one line. Even in the case where $NUPDT = 0$, the order of parameters will become ambiguous if the data extends to the next line; therefore, this should be avoided.
- 2) If the parameter in this line is not used in subsequent calculations, or if $A(I)$ and $ID(I)$ are both 0, "/" may be entered. An example is the profile parameters in the case $NMODE = 2$.
- 3) $STEP(I)$ is the coefficient used for determining the initial step interval of the direct search on the basis of $A(I)$ in refinement by the conjugate direction method. The initial step interval is $STEP(I) \times A(I)$. Except for the zero-point shift and the lattice constants, tedious input procedures can be omitted if a common step interval coefficient entered at Lines 32 or Lines 36 is used. It may be adequate to enter the values of about 0.1 for the $STEP(I)$ of the zero-point shift and about 0.001 for the $STEP(I)$ of the lattice constants. For convenience, $ID(I)$ is changed from 2 to 1 during execution. When $NUPDT = 1$, $ID(I)$ is changed to 1, and $STEP(I)$ is deleted in the renewed data set.
- 4) Refer to Lines 22.

Table 5 Summary of parameters. Parameters #1-#7 are parameters common to all phases, and the rest are parameters that depend on phases.¹⁾ Parameters #28-#39 are option inputs (see Note 1), of which parameters #35 and after are entered only when magnetic scattering is observed.

No.	Content of parameter	Symbol	Unit
1	Zero-point shift	Z	degree
2	Background parameter ²⁾	b_0	
3	Background parameter	b_1	
4	Background parameter	b_2	
5	Background parameter	b_3	
6	Background parameter	b_4	
7	Background parameter	b_5	
8	Scale factor ³⁾	s	
9	FWHM parameter	U	(degree) ²
10	FWHM parameter	V	(degree) ²
11	FWHM parameter	W	(degree) ²
12	Asymmetry parameter	A	
13	Fraction of Gauss component ⁴⁾	γ	
14	$H_k(\text{Gauss})/H_k(\text{Lorentz})$ ⁵⁾		
15	Preferred-orientation parameter ⁶⁾	p_1	
16	Preferred-orientation parameter	p_2	
17	Lattice constant ⁷⁾	a	angstrom
18	Lattice constant	b	angstrom
19	Lattice constant	c	angstrom
20	Lattice constant	α	degree
21	Lattice constant	β	degree

No.	Content of Parameter	Symbol	Unit
22	Lattice constant	γ	degree
23	Overall isotropic thermal parameter ⁸⁾	Q	(angstrom) ²
24	Occupation factor ⁹⁾	g_j	
25	Fractional coordinate ¹⁰⁾	x_j	
26	Fractional coordinate	y_j	
27	Fractional coordinate	z_j	
28	Isotropic thermal parameter	B_j	(angstrom) ²
29	Anisotropic thermal parameter	β_{11j}	
30	Anisotropic thermal parameter	β_{22j}	
31	Anisotropic thermal parameter	β_{33j}	
32	Anisotropic thermal parameter	β_{12j}	
33	Anisotropic thermal parameter	β_{13j}	
34	Anisotropic thermal parameter	β_{23j}	
35	Magnetic moment	μ_j	μ_B
36	Angle between the direction of spin and a particular direction of the crystal (tetragonal, hexagonal and rhombohedral) ¹¹⁾	ϕ	degree
37	Angle between the direction of spin and the a -axis (orthorhombic)	ϕ_a	degree
38	Angle between the direction of spin and the b -axis (orthorhombic)	ϕ_b	degree
39	Angle between the direction of spin and the c -axis (orthorhombic)	ϕ_c	degree

- 1) Following the global parameters for #1 through #7, parameters for #8 and on are entered as many times as the number of phases. Among them, the structure-factor parameters for #24 through #35 are repeatedly entered as many times as n_a number of atoms that exist in the asymmetric unit (subscript j in parameter symbols denote the site number). When an isotropic thermal parameter is assigned to the j -th site ($\text{NOAT}(J, I) > 0$ at Lines 11), parameter #28 is chosen, and when anisotropic thermal parameters are assigned ($\text{NOAT}(J, I) < 0$), parameters #29 through #34 are chosen. When an overall isotropic thermal parameter is used ($\text{INDIV}(I) = 0$ at Lines 11), the thermal parameters, #28 through #34, must not be entered.

Parameter #35 is entered only in neutron diffraction for atoms that have magnetic moments ("*" is placed after the names in Lines 7). In a phase which shows magnetic scattering and do not belong to the cubic system, data for #36 (tetragonal, hexagonal and rhombohedral systems) or #37 through #39 (orthorhombic system) need to be added after the structure-factor parameters for all the sites. When magnetic scattering is not observed, parameters #35 and after must not be entered.

- 2) Note that the values of $b_0 - b_5$ will change remarkably in response to changes in the values of $2\theta_{\max}$ and $2\theta_{\min}$.
- 3) To make algorithms simple, the intensity ratio, R12, between each pair of $K\alpha$ peaks is not absorbed in the scale factor, s , but in the multiplicity in X-ray diffraction. Therefore, only one scale factor is needed for each phase.

For complex lattices, the structure factor is not multiplied by a factor, c , listed below in RIETAN, with a result that c^2 is absorbed into s . Therefore, the true scale factor is equal to s/c^2 . Use this true scale factor for quantitative analysis of two or more mixtures (Hill & Howard, 1987).

Lattice type	P	A,B,C,I	F	R*
Centrosymmetric	2	4	8	6
Noncentrosymmetric	1	2	4	3

* R-Centered lattice described with hexagonal axes (triple cell).

- 4) *In the case where intensities drop sharply at the tail of each peak, as in neutron diffraction, $\gamma = 1$, and when the bottom has a very long tail, $\gamma = 0$. Otherwise, γ may diverge in the refinement process.*
- 5) If δ is 0, division by 0 occurs in the calculation of the normalization factor, and thus execution will stop there. *Enter a positive number other than 0 (1, for example) as δ .* When γ is fixed to be 0 or 1, it is necessary to refine parameters by fixing δ .
- 6) When p_1 and/or p_2 are refined, values other than 0.0 must be entered as A(I).
- 7) Refinable parameters for which ID(I)'s need to be set at 1 are as follows:

Cubic lattice: a .

Rhombohedral lattice: a and α .

Hexagonal lattice: a and c .

Tetragonal lattice: a and c .

Orthorhombic lattice: a , b and c .

Monoclinic lattice (unique axis c): a , b and c .

Monoclinic lattice (unique axis b): a , b and c .

Triclinic lattice: a , b , c , α , β and γ .

ID(I)'s of other lattice-constant parameters are all set at 0. A value of -1 must not be entered for ID(I) for b and c in the cubic lattice, b , c , β , and γ in the rhombohedral lattice and b in the hexagonal and tetragonal lattices; the system automatically takes into account constraints over those parameters.

Lattice constants are transformed to a^{*2} , b^{*2} , c^{*2} , $b^*c^* \cos\alpha^*$, $c^*a^* \cos\beta^*$ and $a^*b^* \cos\gamma^*$ during execution (Rietveld, 1969). It is the elements of the metric tensor rather than the lattice constants that are actually refined. However, the user need not be conscious of this internal treatment since these elements are changed back to the lattice constants, whose standard deviations are calculated with equations derived by Kelsey (1964).

- 8) Q must be fixed at 0 when an isotropic or anisotropic thermal parameters are used (INDIV(I) = 1 in Lines 11). Even if a value other than 0 is entered, it will be ignored.
- 9) Generally in programs to refine crystal structures, (occupation factor of a site) \times (number of equivalent positions for that site) / (number of general equivalent positions), rather than the occupation factor itself, is refined in order to simplify the algorithm (Takenaka, 1977). Since necessary and sufficient symmetry operations are selected in RIETAN, *occupation factors themselves can be entered as structure-factor parameters.*
- 10) This is dimensionless and takes values between 0 and 1 for atoms inside the unit cell. *Give only the first coordinate among the coordinates of equivalent positions for each site listed in International Tables, Vol. I (1969) or Vol. A (1983).* Translated positions in complex lattices need not be entered. For example, equivalent positions at the 4f site of the space group C222 (No. 21) are $(x, 0, 1/2)$, $(-x, 0, 1/2)$, $(x+1/2, 1/2, 1/2)$ and $(-x+1/2, 1/2, 1/2)$. Therefore, only $(x, 0, 1/2)$ needs to be entered as a representative of the above four equivalent positions.
- 11) The angle between the spin direction and the c -axis is entered for the tetragonal and hexagonal systems, and that between the spin direction and the [111] axis for the rhombohedral system. In the cubic system, $1 - \langle \cos^2\eta \rangle$ is $2/3$ independently of ϕ (Shirane, 1959), so that ϕ should not be entered.

Line 21. End Input Parameters Label

⇒ Column 1 – Column 4: ENDPARA

Lines 22. Linear Constraints¹⁾

(when there are one or more parameters for which $ID(I) = -1$).

⇒ LCON(I) I = 1, 2, 3, --- FORMAT(A80)

LCON: Linear constraints imposed among profile and structure-factor parameters.

- 1) Constraints linear with respect to parameters are input according to the following simple rules.
- (a) The total number of constraints is equal to the number of parameters set up as $ID(I) = -1$ in Lines 20. One constraint is the input in each line, but there is no special order among constraints.
 - (b) Linear constraints are described in the same way as in arithmetic assignment statements in FORTRAN using the parameter array name A and the parameter number (e.g., A(26)), "+", "*", the constant term and coefficients multiplied into parameters.
 - (c) Only a profile parameter (U, V, W, A, γ or δ) for which $ID(I)$ is set as -1 or a structure-factor parameter is placed on the left side of the expression. *Constraints cannot be imposed for the zero-point shift, background parameters, scale factor, preferred-orientation parameters or lattice constants.*
 - (d) Constant terms and coefficients are expressed by integers or decimal fractions. The use of exponential expressions using E is acceptable.

- (e) An arbitrary number of blanks can be inserted in a constraint expression.
- (f) As regards profile parameters, each parameter of the n -th phase ($n \geq 2$) can only be set as the same value as the corresponding parameter of the first phase.
- (g) When a structure-factor parameter is on the left side, only the other structure-factor parameters can be included on the right side.

The method for introducing constraints nonlinear with respect to parameters is described in detail in Chapter 6.

Input Example 1

Let the FWHM parameters (U , V and W) of the first phase be A(9), A(10) and A(11), respectively, and let those of the second phase be A(60), A(61) and A(62). To let U , V and W of the one phase be equal to the corresponding parameters of the other, let ID(60), ID(61) and ID(62) be -1 in Line 20, and in Lines 22,

$$A(60)=A(9)$$

$$A(61)=A(10)$$

$$A(62)=A(11).$$

Input Example 2

Let us suppose that there is an atom located at the coordinate (x , $-x$, z). Let the fractional coordinate of this atom be A(25), A(26) and A(27). Enter -1 as ID(26) in Lines 20. In Lines 22,

$$A(26)=-A(25)$$

is entered.

Input Example 3

If the sum of the occupation factor of Atom 1, A(24), and that of Atom 2, A(29), is 1, -1 is entered as ID(30) in Lines 20, and in Lines 22,

$$A(29) = 1.0 - A(24)$$

is entered.

Line 23. End Constraint(s) Label

(when there are 1 or more parameters for which ID(I) = -1).

⇒ Column 1 – Column 6: ENDLIN

Lines 24. Preferred Orientation¹⁾

⇒ NPROR(I), HP(I), KP(I), LP(I) I = 1, 2, NPHASE

Default values: NPROR(I) = 1, HP(I) = 0; KP(I) = 0; LP(I) = 1.

NPROR: = 0, preferred-orientation is not corrected.

= 1, plate crystal.

= 2, needle-shaped crystal.

HP,

KP,

LP: integers that indicate directions of preferred orientation expressed in reciprocal space, h_p , k_p and l_p .²⁾

- 1) This line should be entered for all the phases. In the case of NPROR = 0, HP, KP and LP are not used. Therefore, only '0/' may be needed as an input.
- 2) The direction of the preferred-orientation vector $h_p a^* + k_p b^* + l_p c^*$ corresponds to that of a normal to the plane of cleavage in the plate crystal, and to that of the extension axis in the needle-shaped crystal. Note that HP is an integer and does not follow implicit type declaration in FORTRAN.

Lines 25. Excluded 2θ Range¹⁾ (NMODE < 2 and NEXC = 1)

⇒ DEGEXC(1, I), DEGEXC(2, I) I = 1, 2,

DEGEXC(1, I): lower limit of the excluded range of 2θ/degree in the refinement.

DEGEXC(2, I): upper limit of the excluded range of 2θ/degree in the refinement.

- 1) When refinement is carried out excluding the 2θ ranges 45.0–46.2° and 87.5–88.9°, and the inputs because Lines 25 and 26 are as follows:

45.0 46.2

87.5 88.9

ENDRANGE

Line 26. End Excluded Range(s) Label (NMODE < 2 and NEXC = 1)

⇒ Column 1 – Column 8: ENDRANGE

Lines 27. Background Assignment¹⁾ (NMODE < 2 and NRANGE = 1)

⇒ (X(J), J = 1, 2,)

X: 2θ /degree of the measurement point to calculate the background value.

- 1) Two or more values of 2θ may be entered in each line. "/" *must be entered right after the last data entry to show the end of data input*. Smoothed values of the diffraction intensities at these 2θ 's are grouped to four neighboring data, and the coefficients of third-degree polynomial equations are determined from these data. Next, 2θ is substituted in this polynomial equation to give the background intensity at each diffraction point.

Line 29. Limits of 2θ ¹⁾ (NMODE > 2)

⇒ DEG1, DEG2

DEG1: minimum 2θ , $2\theta_{\min}$ /degree.

DEG2: maximum 2θ , $2\theta_{\max}$ /degree.

- 1) Diffraction intensities within these limits are calculated.

 When NMODE = 2, input is over here.

Line 30. Constants Related to the Peak Shape (NMODE \neq 2)

\Rightarrow PC, CSTB, RLIM

Default values: PC = 7.0; CSTB = 0.6; RLIM = 40.0.

PC: coefficient to determine the limits of 2θ for calculation of the profile shape of each peak.¹⁾

CSTB: constant, c_s , that takes the value of 0.0 or 0.6. If CSTB = 0.6, the correlation among U , V and W becomes smaller (Young & Wiles, 1982).

RLIM: only when 2θ is lower than this angle, the asymmetry of each diffraction peak is corrected with $a(\Delta\theta_{ik})$ (Rietveld, 1969).

1) Let the intensities of reflection k at diffraction angles separated from $2\theta_k$ by $PC \times H_k$ or more be 0. The FWHM increases with increasing 2θ . Therefore, the range of 2θ used to calculate the profile intensity of each diffraction peak will also be wider. When γ is close to 1 and therefore intensities drop rapidly at the tail of the peak, as in neutron diffraction, a PC value of ca. 1.5 is sufficient. On the other hand, a larger PC value is preferred when γ is almost 0 and therefore the peak has a long tail.

Line 31. Magnification Coefficient (NMODE = 3)

\Rightarrow FACFIG

Default value: FACFIG = 1.0

FACFIG: magnification coefficient to reduce figures¹⁾ (< 1.0).

- 1) The whole figure is reduced by this coefficient. When graphic output is photographed or made into a slide, a certain amount of reduction makes photographing easier.

 When NMODE = 3, the input is finished here.

Line 32. Control Data of the Conjugate Direction Method¹⁾ (NLESQ = 1)

⇒ MITER, STEP, ACC, NC, TK

Default values: MITER = 4; STEP = 0.03; ACC = 1.0E-4; NC = 0; TK = 0.0.

MITER: upper limit of the iteration number for minimization.

STEP: coefficient to calculate the initial step interval.²⁾

ACC: small positive number used for convergence judgment.

NC: number of nonlinear equality and inequality constraints.

TK: penalty parameter, $t^{(K)}$.

- 1) Constrained nonlinear programming problems are solved by an exterior penalty function method (Zangwill, 1967; Izumi, 1989). Rietveld analysis under nonlinear constraints is formally stated as

$$\text{Minimize: } S(\mathbf{x}) = \sum_i w_i [y_i - f_i(\mathbf{x})]^2$$

subject to p linear and/or nonlinear inequality constraints

$$g_n(\mathbf{x}) \geq 0 \quad n = 1, 2, \dots, p$$

and q linear and/or nonlinear equality constraints

$$h_n(\mathbf{x})=0 \quad n=1,2,\dots,q$$

where \mathbf{x} is a set of variable parameters, $w_i (=1/y_i)$ is the weighting based on counting statistics, y_i is the observed intensity, and $f_i(\mathbf{x})$ is the calculated intensity. The exterior penalty function method transforms a constrained optimization problem into a sequence of unconstrained optimizations for $K=0,1,2,\dots$ given by

$$\text{Minimize: } F(\mathbf{x}, t^{(K)}) = S(\mathbf{x}) + t^{(K)} \left[\sum_{n=1}^p H(g_n(\mathbf{x})) g_n^2(\mathbf{x}) + \sum_{n=1}^q h_n^2(\mathbf{x}) \right]$$

where the penalty parameter, $t^{(K)}$, 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 the above equation prevent the \mathbf{x} vector from getting too far away from the feasible region. Weight imposed on unsatisfied constraints, $t^{(K)}$. TK must have a value which makes the contribution of the second term in $F(\mathbf{x}, t^{(K)})$ sufficiently large. However, beware that errors in least-squares calculations become large if TK is too large. The value of TK is kept constant when the conjugate direction method is used.

- 2) A common coefficient used to calculate the initial steps of the direct search along A(I). The initial step is STEP \times A(I) except for the parameters entered as ID(I) = 2 in Lines 20. STEP may as well be from 0.01 to 0.04.

Line 33. Control Data of the Least-Squares Method with Derivatives¹⁾

(NLESQ = 2, 3)

⇒ NAUTO, NCYCL, CONV, NCONV, NC, TK, FINC

Default values: NAUTO = 0; NCYCL = 15; CONV = 1.0E-4; NCONV = 2; NC = 0;
TK = 0.0; FINC = 20.0.

NAUTO: = 0, variable parameters are refined simultaneously.

= 1, variable parameters are refined incrementally.

= 2, variable parameters are refined incrementally, and the correctness of the final solution is checked by the conjugate direction method (fully automatic refinement mode).

NCYCL: maximum number of iterations in nonlinear least-squares calculations.²⁾

CONV: small positive number to be used for convergence judgment.³⁾

NCONV: number of cycles to be used for convergence judgment.³⁾

NC: number of nonlinear equality and inequality constraints.

TK: penalty parameter.³⁾

FINC: factor by which the current TK is multiplied when TK is increased.³⁾

1) Modified Marquardt or Gauss-Newton method.

2) When NCYCL is 0, parameters are not refined, and only the coefficient matrix is calculated to obtain the estimated standard deviations of variable parameters.

3) When the convergence judgment formula $[S(\mathbf{x})^{(k-1)} - S(\mathbf{x})^{(k)}] / S(\mathbf{x})^{(k)}$ becomes CONV or less, repeating itself NCONV times, increase TK to $TK \times FINC$ and enter the next refinement stage, or finish refinement (NC = 0). In the above formula, $S(\mathbf{x})$ is the value of $F(\mathbf{x}, t^{(k)})$ function, and k is the cycle number.

Lines 34. Variable-Parameter Numbers (NLESQ \neq 1 and NAUTO > 0)

\Rightarrow (IPAR(J, I), J = 1, NPAR(I))¹⁾ I = 1, 2,

IPAR: reference numbers of parameters to be refined at the I-th cycle.²⁾

- 1) NPAR(I) denotes the reference numbers of parameters refined at the I-th cycle. NPAR(I) need not be entered, but "/" *must be input as the end marker of the line after the last reference number.*
- 2) It is well known that a solution tends to diverge if parameters are refined at once using initial values distant from the true solution. If parameters are refined incrementally in initial several cycles and if all the parameters are adjusted after some reduction in the sum of squared residuals, good convergence tends to occur (see Chapter 8).

Line 35. End of Reference Numbers for Variable Parameters Label

(NLESQ \neq 1 and NAUTO > 0)

\Rightarrow Column 1 – Column 6: ENDREF

Line 36. Control Data of the Conjugate Direction Method¹⁾

(NLESQ \neq 1 and NAUTO = 2)

\Rightarrow MITER, STEP, ACC

Default values: MITER = 4; STEP = 0.03; ACC = 1.0E-4.

MITER: upper limit of the iteration number for minimization.

STEP: coefficient to calculate the initial step interval in direct search.¹⁾

ACC: small positive number used for convergence judgment.

1) Refer to note 1 in Line 32.

Line 37. Scale of the Figure Drawn by the Printer¹⁾ (NPRINT = 2)

⇒ ISCALE, IDIF

Default values: ISCALE = 0; IDIF = 0.

ISCALE: counts²⁾ per letter³⁾ of observed and calculated diffraction patterns in a printer output.

IDIF: counts²⁾ per letter in a deviation curve.

- 1) Three patterns, that is, observed intensities (y_i), calculated intensities ($f_i(x)$), and deviations ($y_i - f_i(x)$) are drawn on printer paper (abscissa: count, ordinate: 2θ). Be prepared for an enormous length of list when there are a great deal of intensity data.
- 2) When ISCALE or IDIF is 0, the system determines an appropriate value.
- 3) Total number of letters on the abscissa = 120.

Line 38. Scales of Graphic Output (NMODE = 1)

⇒ FACFIG, INC

Default values: FACFIG = 1.0; INC = 0.

FACFIG: magnification factor for reducing a figure¹⁾ (< 1.0).

INC: increase per scale division of the ordinate in Rietveld refinement patterns²⁾ (unit: counts).

- 1) Refer to Note 1 for Line 31.
- 2) The maximum value of the ordinate is $9 \times \text{INC}$. When INC is 0 or less, the system will determine an appropriate INC value.

Lines 39. ORFFE Instructions (NDA > 0)

⇒ ORINS(I) I = 1, 2, --- FORMAT (A80)

ORINS: instructions of ORFFE.¹⁾

- 1) Any instructions compatible with ORFFE (Busing, Martin & Levy, 1964) can be input in these lines in just the same formats as in ORFFE and then copied in data set #9 for ORFFE, which is created if NDA > 0. For details in ORFFE instructions, refer to the manual of ORFFE.

Line 40. End of ORFFE Instructions Label (NDA > 0)

⇒ Column 1 – Column 5: ENDOR

6. Method for Rewriting Function Subprogram CON

Information on crystal structures is based on some measurements or facts, so that it can be regarded as a kind of indirect measurement. Hence, if this information is introduced into the program through the function subprogram CON, convergence to structural parameters illogical in view of crystal chemistry can be avoided. This subprogram is used to calculate the deviation from the j -th constraint, $\min(0, g_j(\mathbf{x}))$ or $h_j(\mathbf{x})$, from the present parameter values, \mathbf{x} . There are two dummy arguments: an integer-type variable J and a real-type array A.

REAL FUNCTION CON (J, A).

CON: deviation from the constraint.

J: constraint number, j .

A: one-dimensional array containing parameter values, \mathbf{x} (see Table 5).

Note that the value of CON is 0 when a satisfies an inequality constraint. Neither $g_j(\mathbf{x})$ nor $h_j(\mathbf{x})$ must contain lattice constants. The partial derivatives of $\min(0, g_j(\mathbf{x}))$ and $h_j(\mathbf{x})$ with respect to each parameter are computed by the difference approximation to avoid generation of bugs and also to reduce user's efforts.

6.1 Constraints for Interatomic Distances

Function subprograms DIS has been provided to calculate interatomic distances. If $g_j(\mathbf{x})$ and $h_j(\mathbf{x})$ are described using these functions, subprogram CON will be very simple.

REAL FUNCTION DIS (X1, Y1, Z1, X2, Y2, Z2, IP)

DIS: distance between Atom 1 and Atom 2, d_{12} /angstrom.

X1, Y1, Z1: fractional coordinate of Atom 1.

X2, Y2, Z2: fractional coordinate of Atom 2.

IP: phase number.

If the distance between two atoms whose fractional coordinates are (X1, Y1, Z1) and (X2, Y2, Z2) is D, and if D0 is the expected distance between the atoms, then the boundary condition $D0 - EPS < D < D0 + EPS$ can be expressed as a single statement function:

```
P (X1 , Y1 , Z1 , X2 , Y2 , Z2 ) = MIN ( 0 . 0 , EPS -
&ABS ( DIS ( X1 , Y1 , Z1 , X2 , Y2 , Z2 , I ) - D0 ) )
```

The following is the source list of CON when eight boundary constraints are set up (NC = 8) to put the (Si,Al)-(N,O) distance within the range of 1.75 ± 0.05 angstroms in an example — Rietveld analysis of Ca α -sialon — distributed to the user in the form of a magnetic tape. Detailed information about these eight bonds is listed in Table 3 of Izumi, Mitomo & Bando (1984).

```
REAL FUNCTION CON(J,A)
*   INEQUALITY CONSTRAINTS FOR CA ALPHA-SIALON
INTEGER J
REAL A(*)
*   (SI,AL)-(N,O) DISTANCE = 1.75 +/- 0.05 ANGSTROMS
DATA D0,EPS/1.75,0.05/
P(X1,Y1,Z1,X2,Y2,Z2)=MIN(0.0,EPS-
&ABS(DIS(X1,Y1,Z1,X2,Y2,Z2,I)-D0))
```



```

IF (J .EQ. 1) THEN
    CON=P(A(30),A(31),A(32),A(46),A(45),A(47)-0.5)
ELSE IF (J .EQ. 2) THEN
    CON=P(A(30),A(31),A(32),A(50),A(51),A(52))
ELSE IF (J .EQ. 3) THEN
    CON=P(A(30),A(31),A(32),A(50)-A(51),-A(51),
&      A(52)+0.5)
ELSE IF (J .EQ. 4) THEN
    CON=P(A(30),A(31),A(32),1.0-A(56),A(55)-A(56),
&      A(57))
ELSE IF (J .EQ. 5) THEN
    CON=P(A(35),A(36),A(37),A(40),A(41),A(42))
ELSE IF (J .EQ. 6) THEN
    CON=P(A(35),A(36),A(37),-A(51),A(50)-A(51),A(52))
ELSE IF (J .EQ. 7) THEN
    CON=P(A(35),A(36),A(37),A(55),A(56),A(57))
ELSE
    CON=P(A(35),A(36),A(37),A(56),A(55),A(57)-0.5)
END IF
END

```

The boundary conditions for $J = 1-8$ have been set up for the interatomic distances of the 8th to 15th bonds in Table 3 (Izumi, Mitomo & Bando, 1984), respectively.

6.2 Constraints for Bond Angles

Function subprograms ANG has been provided to calculate bond angles.

```
REAL FUNCTION ANG (X1, Y1, Z1, X2, Y2, Z2, X3, Y3, Z3, IP)
```

ANG: angle made by Atoms 1, 2 and 3 with Atom 2 at the vertex,
 ϕ_{123} /degree.

X1, Y1, Z1: fractional coordinate of Atom 1.

X2, Y2, Z2: fractional coordinate of Atom 2.

X3, Y3, Z3: fractional coordinate of Atom 3.

IP: phase number.

If the angle distance made by the three atoms is PHI, and PHI0 is the expected bond angle, then the boundary condition $\text{PHI0} - \text{EPS} < \text{PHI} < \text{PHI0} + \text{EPS}$ can be expressed as a single statement function:

```
P (X1 , Y1 , Z1 , X2 , Y2 , Z2 , X3 , Y3 , Z3 ) = MIN ( 0 . 0 , EPS -
&ABS ( ANG ( X1 , Y1 , Z1 , X2 , Y2 , Z2 , X3 , Y3 , Z3 , I ) - PHI0 ) )
```

When four O-P-O bond angles in $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ (Sudarsanan & Young, 1972) are confined in $109.47 \pm 2^\circ$, the source program of CON becomes as follows.

```
REAL FUNCTION CON(J,A)
*   INEQUALITY CONSTRAINTS FOR STRONTIUM
*   HYDROXIDE PHOSPHATE
INTEGER J
REAL A(*)
*   O-P-O ANGLE = 109.47 +/- 2 DEGREES
DATA PHI0, EPS / 109.47, 2.0 /
P (X1 , Y1 , Z1 , X2 , Y2 , Z2 ) = MIN ( 0 . 0 , EPS -
```

```

&ABS(ANG(X1,Y1,Z1,X2,Y2,Z2,X3,Y3,Z3,1)-PHI0))

  IF (J .EQ. 1) THEN
    CON=P(A(25),A(26),A(27),A(40),A(41),A(42),
&        A(30),A(31),A(32))
  ELSE IF (J .EQ. 2) THEN
    CON=P(A(25),A(26),A(27),A(40),A(41),A(42),
&        A(35),A(36),A(37))
  ELSE IF (J .EQ. 4) THEN
    CON=P(A(30),A(31),A(32),A(40),A(41),A(42),
&        A(35),A(36),A(37))
  ELSE
    CON=P(A(35),A(36),A(37),A(40),A(41),A(42),
&        A(35),A(36),0.5-A(37))
  END IF
END

```

As shown below, parameters #25-#42 in this function subprogram correspond to fractional coordinates of O(1), O(2), O(3) and P atoms (isotropic thermal parameters are assigned to all the sites).

O(1): $x=A(25)$, $y=A(26)$, $z=A(27)$.

O(2): $x=A(30)$, $y=A(31)$, $z=A(32)$.

O(3): $x=A(35)$, $y=A(36)$, $z=A(37)$.

P: $x=A(40)$, $y=A(41)$, $z=A(42)$.

6.3 Constraints for Thermal Parameters

When Rietveld analysis is being carried out, the isotropic thermal parameter B_j sometimes becomes negative. Since such a value is physically meaningless, the inequality constraint $B_j > 0$ should be introduced. Consider the case where the number of phases is two and atoms occupy at two sites in each phase. Then, reference numbers of four isotropic thermal parameters are 28, 33, 54 and 59. Let NC be 4 in Line 32 or Line 33 and rewrite the subprogram CON as follows:

```

REAL FUNCTION CON(J,A)
*   INEQUALITY CONSTRAINTS FOR ISOTROPIC THERMAL
*   PARAMETERS
INTEGER J
REAL A(*)
P(I)=MIN(0.0,A(I))

IF (J .EQ. 1) THEN
    CON=P(28)
ELSE IF (J .EQ. 2) THEN
    CON=P(33)
ELSE IF (J .EQ. 3) THEN
    CON=P(54)
ELSE
    CON=P(59)
END IF
END

```

7. Method for Creating the Double-Precision Version Load Module

Only normal equations and sums of many values are calculated in double precision in RIETAN. Least-squares methods which use normal equations are low in computational precision (Nakagawa & Oyanagi, 1982). Therefore, when the numbers of intensity data and/or parameters are large, this kind of partial double precision calculation may result in difficulty in reducing sums of squared residuals or a non-positive definite coefficient matrix. In the latter case, the message "THE COEFFICIENT MATRIX IS NOT POSITIVE DEFINITE." is output, and calculation is terminated. In this case, it is strongly recommended to use the automatic precision expansion function as a compiler option and to specify only the REAL type and the COMPLEX type as objects for precision expansion. Specify AUTODBL as a compiler option and choose DBLPAD4 as a parameter in the case of FACOM. However, since the plotter output subroutines, such as PSP (FACOM) and GPSL (HITAC), are especially for single-precision variables, the double-precision version load module cannot be used when NMODE = 1, 3. Therefore, the single-precision version must be used when a figure is output.

8. Refinement Strategy

The powder diffraction pattern gives only information which is much inferior to that given by the single crystal method both in quality and quantity. Furthermore, in the Rietveld method, the profile parameters, lattice constants and background parameters must also be refined in addition to the scale factor and structure-factor parameters which are refined in the single crystal method. As a result, the solution may fall into a false minimum or may diverge in Rietveld analysis unless the initial values of parameters are considerably close to the true ones (Young, 1980).

8.1 Procedures for Rietveld analysis

Although there are several kinds of techniques to achieve stable convergence, the correct solution will be reached, in most cases, by analysis through the following procedures, unless the number of parameters is extremely large or the material to be dealt with shows a very complex diffraction pattern.

- (a) Roughly infer the atomic configuration through information about crystal chemistry, search for an isomorphous compound or a compound with a similar structure, or direct observation of the crystal-structure image by high-resolution transmission electron microscopy. Then, simulate a powder diffraction pattern on the basis of the structural model (NMODE = 3).
- (b) Unless the theoretical diffraction pattern plotted in step (a) is similar to the pattern actually measured, the analysis thereafter will most probably fail. Thus, return to step (a) and assemble another structural model.
- (c) After accurately measuring peak positions, $2\theta_k$, using a pattern-decomposition program (Sonneveld & Visser, 1975) and so forth, refine lattice constants by a least-squares method.

- (d) After FWHM's in the full 2θ range have been measured, rough values of the FWHM parameters, U , V and W are obtained by a least-squares method. Unless broadening of diffraction lines depending on samples is very marked, values obtained with standard materials, such as Si, can be used.
- (e) Execute Rietveld analysis. Parameters obtained in steps (c) and (d) are used as initial values for the lattice constants and FWHM parameters, respectively. γ is fixed at 1 in neutron diffraction, the initial value of γ is 0.5, and that of δ is 1 in X-ray diffraction. The initial value of A is 0. By letting NLESQ be 2 or 3, NAUTO be 1 and LISO(I) be 1, parameters are refined incrementally in the following order:

- (1) scale factor and background parameters which are linear parameters,
- (2) profile parameters,
- (3) lattice constants,
- (4) preferred-orientation parameter (p_2) and scale factor
- (5) structure-factor parameters,
- (6) all parameters.

When the number of atoms in the asymmetric unit is large, first refine parameters using an overall thermal parameter, and then refine them again by assigning an isotropic thermal parameter to each atom or each type of atom.

- (f) When R_I does not go down to 10% or below, carry out refinement with NLESQ being 1 to check if the solution is not trapped at a false minimum.
- (g) When anisotropic thermal vibration is assumed for the j -th atom, obtain the initial values of the anisotropic thermal parameters, β_{ij} , from the printer output, and then change to LISO(I) = 2 to carry out refinement including β_{ij} . However, linear constraints imposed between β_{ij} 's must be considered when there are atoms located at special positions (Peterse & Palm, 1966).
- (h) Calculate interatomic distances and bond angles from the final fractional coordinates and check if the obtained values are within reasonable ranges in view of crystal chemistry. If abnormal values appear, impose constraints on the

interatomic distances or bond angles, and perform refinement again, by the least-squares method using derivatives. In this case, all the parameters can be refined at the same time.

8.2 Hints toward Smooth Refinement

As regards the least-squares method, it is adequate to use the modified Marquardt method or the Gauss-Newton method as described in step (e). Since the conjugate direction method is very slow in convergence, it should be used only when convergence cannot be attained in any way with the above methods with derivatives or when one checks whether or not the obtained solution has fallen into a false minimum.

Although RIETAN can handle a mixture of two or more phases, the chemical composition and crystal structure of each phase need to be roughly known in this case. Since the overlap of peaks is yet increased in a mixture, profile parameters per phase often cannot be refined. In this case, it is inevitable to approximate that all phases have the same profile parameters.

When there is a completely unknown impurity in a mixture, execute Rietveld analysis, letting $NMODE = 1$, and get Rietveld-refinement patterns on an XY plotter or a graphic display. There is a great possibility that peaks due to impurities are contained in ranges having large differences between y_i and $f_i(x)$. Then, assign excluded 2θ regions in Line 25, and examine how the R -factors decrease.

A negative preferred-orientation parameter, p_2 indicate that correction of preferred orientation in the present refinement is physically meaningless. In such a case, change the preferred-orientation vector or fix the preferred-orientation parameters at $p_1 = p_2 = 0$. If $p_1 < 0$ and $p_2 > 0$, fix p_1 at 0 and refine only p_2 . When a positive p_2 value results, such correction, which corresponds to the one proposed by Rietveld (1969), can be regarded as appropriate. In cases where standard deviations of p_1 and p_2 become extraordinarily large, p_1 should be fixed at 0.

9. Reading Printer Output

9.1 Output during Execution of RIETAN

The following does not include the output data that are mere repetitions of input data, nor those whose contents are readily understood at a glance.

A1, B1,, A4, B4, C: nine coefficients contained in the equation to approximate atomic scattering factors (*International Tables*, Vol. IV, 1974).

DELTF1: real part of the correction term for anomalous dispersion, $\Delta f'$ (*International Tables*, Vol. IV, 1974).

DELTF2: imaginary part of the correction term for anomalous dispersion, $\Delta f''$ (*International Tables*, Vol. IV, 1974).

SCATTERING LENGTH: coherent scattering length, b/fm (Sears, 1986).

EQUIVALENT POSITIONS USED FOR THE CALCULATION OF STRUCTURE

FACTORS: atomic names at each site, FACTOR, NEQ and coordinates of equivalent positions are listed. Since the coordinates at inverted positions (when the center of symmetry is at the origin) and translated positions (in the case of centered space groups) are not used in structure-factor calculation, they are omitted.

FACTOR: output is obtained only when the center of symmetry is at the origin. Atoms with FACTOR = 2 do not overlap at the original position even if it is inverted around the origin, while atoms with FACTOR = 1 overlap after inversion.

NEQ: number of equivalent positions for each site in a unit cell. This is listed in the part Number of positions in *International Tables*, Vol. I (1969). Let the lattice multiplicity (primitive cell: 1; body- and face-centered cells: 2; rhombohedrally centered cell: 3; all-face centered cell: 4) be m_c , and if the number of equivalent

positions printed for each site is n_{pr} , then when the center of symmetry is not at the origin

$$NEQ = m_c \times n_{pr},$$

and when the center of symmetry is at the origin

$$NEQ = FACTOR \times m_c \times n_{pr}$$

(Takenaka, 1977). If NEQ is multiplied by the occupation factor, the number of atoms in a unit cell that occupy positions equivalent to the site can be calculated.

N: number of atoms in the unit cell.

AT.WT.: atomic weight. For imaginary atoms, imaginary atomic weight in which weights based on the contents of constituents are imposed.

6.02214E23: Avogadro number.

WT.: weight of atoms contained in the unit cell.

D: density/g cm⁻³.

BETA11, BETA22, BETA33, BETA12, BETA13, BETA23: anisotropic thermal parameters multiplied by 10⁶ when the temperature factor is represented as

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

U11, U22, U33, U12, U13, U23: anisotropic thermal parameters in 10⁶ × (angstrom)² when the temperature factor is represented as

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

BEQ: isotropic thermal parameter in (angstrom)². For sites assigned anisotropic thermal parameters, equivalent isotropic thermal parameters are printed.

STEP: step interval of 2θ/degree.

NSTEP: number of observed points (number of steps). Observed points in the excluded regions are excluded.

CUT-OFF: value between "=" and "* FWHM" represents PC.

SYMMETRY CONDITIONS: when there is no special extinction rule in reflection hkl , the output is "NO LATTICE ABSENCES". Below that, follow the conditional equations established among indices of possible reflections for various types of reflections. For example,

$K=2N$; OKO ;
 HKH ;

indicate that reflections of the $Ok0$ and hkh types appear only when k is an even number.

PHASE: phase number.

CODE: always 1 in neutron diffraction; 1 for $K\alpha_1$ peaks and 2 for $K\alpha_2$ peaks in X-ray diffraction.

IOBS: observed value of the relative integrated intensity when the observed integrated intensity of the maximum intensity peak is 105.

ICAL: calculated value of the relative integrated intensity when the observed integrated intensity of the maximum intensity peak is 105.

|F(NUCL)|: absolute value of the crystal-structure factor.

|F(MAGN)|: absolute value of the magnetic-structure factor.

POF: preferred-orientation function.

FWHM: full-width at half-maximum of a diffraction peak, H_k /degree. Note it is not H_k (Gauss).

LF: Lorentz factor. It includes polarizing factor in X-ray diffraction (except synchrotron X-ray diffraction).

M: multiplicity.

T(0), T(1),: penalty parameter at each refinement stage, $t^{(K)}$.

AOF: augmented objective function, $F(x, t^{(K)})$.

OF: sum of the squares of residuals, $S(x)$.

PF: $TK \times$ (penalty term).

LAMBDA: Marquardt parameter, λ .

DAMP: damping factor, d .

NFNEV: number of calculations of the sums of squared residuals in this cycle (least-squares method using derivatives).

NFUNCT: number of calculations of sums of squared residuals in this cycle (conjugate direction method).

$$\text{R.WP: } R_{wp} = \left\{ \frac{\sum_i w_i [y_i - f_i(x)]^2}{\sum_i w_i y_i^2} \right\}^{1/2},$$

$$\text{R.P: } R_p = \frac{\sum_i |y_i - f_i(x)|}{\sum_i y_i},$$

$$\text{R.E: } R_e = \left\{ \frac{N_p - N_r - N_c}{\sum_i w_i y_i^2} \right\}^{1/2},$$

where w_i is the weight for the i -th step, y_i is the observed intensity at the i -th step, $f_i(x)$ is the calculated intensity, N_p is the number of intensity data, N_r is the number of parameters to be refined, and N_c is the number of constraints. Background is included in both y_i and $f_i(x)$.

A(OLD): value of the parameter before refinement.

DELTA.A: amount of correction of the parameter in this cycle.

A(REFINED): value of the parameter after refinement.

$$\text{R.I: } R_I = \frac{\sum_k |I_k(o') - I_k(c)|}{\sum_k I_k(o')},$$

$$\text{R.F: } R_F = \frac{\sum_k |[I_k(o')]^{1/2} - [I_k(c)]^{1/2}|}{\sum_k [I_k(o')]^{1/2}},$$

where k is the reflection number, $I_k(o')$ is the observed integrated intensity calculated indirectly from y_i and $f_i(x)$ according to the procedure proposed by Rietveld (1969), and $I_k(c)$ is the calculated integrated intensity.

SIGMA: estimated standard deviation, σ , of the refined parameter. The standard deviations of structural parameters are calculated according to the method proposed by Scott (1983).

CORRELATION MATRIX: correlation matrix, δ . Values in the top row and the left-most column are parameter numbers. The value of each matrix element (correlation coefficient), δ_{ij} , is a measure of the correlation between A(I) and A(J). If the absolute value is 100, the coefficient matrix is singular, so the normal equation cannot be solved. Generally, in a parameter whose correlation with other parameters is large, its value oscillates in the process of refinement, and thus becomes large. On the other hand, the parameter value can be determined with high precision if $|\delta_{ij}|$ is small.

In the printer plot, "+" in "-+-" is y_i , "0" is $f_i(x)$, and "*" is $y_i - f_i(x)$. When "-+-" and "0" are at the same position, "0" will be a chosen output. Both y_i and $f_i(x)$ become 0 at the left edge of the printer paper, so does $y_i - f_i(x)$ around the center of the paper.

9.2 Main Error Messages

CONTROL PARAMETER OUT OF RANGE

There are nonpermissible values in the control data that have been entered in Line 2 or Line 3.

IONIC SPECIES SHOULD NOT BE INPUT IN NEUTRON DIFFRACTION.

Although names of neutral chemical species must be entered in Lines 7 in neutron diffraction, a cation or anion name has been entered.

ATOMIC NUMBER OUT OF RANGE

The number that represents the kind of atom (NOAT) entered in Line 11 is wrong.

THE NUMBER OF PARAMETERS IS NOT CONSISTENT WITH THE NUMBER OF ATOMS IN ASYMMETRIC UNIT(S).

The number of parameters entered in Lines 20 does not correspond to the number of parameters calculated from the number of atoms in the asymmetric unit(s).

MISSING 'ENDLINE' LINE

Either the line that indicates the end of linear constraints (Line 23) has not been entered, or the number of parameters where $ID(I) = -1$ in Line 20 does not correspond with the number of linear constraints.

FWHM CANNOT BE CALCULATED FROM U, V, AND W.

There is a reflection in which $H_k^2(\text{Gauss})$ became negative. $H_k^2(\text{Gauss})$ is calculated from U , V and W the user entered: $H_k^2(\text{Gauss}) = U(\tan\theta_k - c_s)^2 + V(\tan\theta_k - c_s) + W$. Accordingly, U , V , and W should be changed so that $H_k^2(\text{Gauss})$ is positive in all the range of 2θ .

A CONSTANT PARAMETER WAS REGARDED AS A VARIABLE ONE.

The reference number of a parameter to which $ID(I) = 0$ or -1 has been assigned in Lines 20 has been entered in Lines 34. Remove the entered number from Lines 34.

THE COEFFICIENT MATRIX IS NOT POSITIVE DEFINITE.

The coefficient matrix in a normal equation is not positive definite. There is a good possibility that the structure model and/or the input data is critically wrong. Let $NPRINT = 2$, output equivalent coordinates and reflection lists, and check them thoroughly. Furthermore, investigate if there are any initial values of parameters that far from the true values, if parameters to be fixed have been refined, and if the intensity data are read normally.

TOO LARGE MARQUARDT PARAMETER

In refinement of parameters by the modified Marquardt method, the Marquardt parameter, λ , has become larger than 104. The following two situations can be considered in such a case:

- (a) immediately before convergence, the sum of squared residuals sometimes stops decreasing any more, and λ increases rapidly. Because this phenomenon is mostly due to digit drop in calculation, convergence is regarded as having been attained.
- (b) the correct solution cannot be obtained owing to a problem in computational precision. In the case of (b), refinement should be carried out using the double-precision version load module as described in Chapter 7.

10. Content of Data Set #20

When NMODE is set at -1 or -3 at Line 2, data set #20 (LRECL = 140) is created which stores data to draw Rietveld refinement patterns (NMODE = -1) or simulate diffraction patterns (NMODE = -3). These data can be input by calling the following subroutines after setting the unit identifier, NUNIT.

10.1 Reading the Results of Rietveld Analysis

```

SUBROUTINE RDRSLT(NUNIT, TITLE, NDATA, NBLOCK,
&TWOH, YOBS, YCAL, BG, NTOTAL, PEAK, NREFL)
*   READ THE RESULTS OF RIETVELD REFINEMENT
      INTEGER NUNIT, NDATA(*), NBLOCK, NTOTAL, NREFL
      REAL TWOH(*), YOBS(*), YCAL(*), BG(*), PEAK(*)
      CHARACTER*80 TITLE

      OPEN(UNIT=NUNIT, STATUS='OLD', ACCESS='SEQUENTIAL')
      REWIND(UNIT=NUNIT)
      READ(NUNIT, '(A)') TITLE
      READ(NUNIT, *) NBLOCK, STEP, NREFL

      NTOTAL=1
      DO 20 I=1, NBLOCK
*   READ INTENSITY DATA IN EACH BLOCK
          READ(NUNIT, *) NDATA(I), START
          READ(NUNIT, *) (YOBS(J), YCAL(J), BG(J),
& J=NTOTAL, NTOTAL+NDATA(I)-1)
          DO 10 J=NTOTAL, NTOTAL+NDATA(I)-1

```



```

*           CALCULATE TWO-THETA VALUES
           TWOTH(J) = START + ( J - NTOTAL ) * STEP
10        CONTINUE
           NTOTAL = NTOTAL + NDATA( I )
20        CONTINUE
           NTOTAL = NTOTAL - 1

*           READ PEAK POSITIONS
           READ( NUNIT, * ) ( PEAK( I ), I = 1, NREFL )
           CLOSE( UNIT = NUNIT )
           END

```

Contents of dummy arguments

NUNIT: unit identifier (input).

TITLE: title.

NDATA: number of intensity data for each block.

NBLOCK: number of blocks for intensity data.

TWOTH: $2\theta/\text{degree}$.

YOBS: observed intensities, y_i ($i = 1, 2, \dots, \text{NTOTAL}$).

YCAL: calculated intensities, $f_i(x)$ ($i = 1, 2, \dots, \text{NTOTAL}$).

BG: background.

NTOTAL: total number of intensity data.

PEAK: 2θ values at peak positions, $2\theta_k$ ($k = 1, 2, \dots, \text{NREFL}$).

NREFL: total number of peaks.

When $\text{NBLOCK} \geq 2$, intensity data between two blocks have been skipped. NBLOCK is equal to 1 when all the intensity data have been used for Rietveld refinement.

10.2 Reading the Results of Simulation

```

SUBROUTINE RDSIM(NUNIT, TITLE, TWOTH,
&YCAL, BG, NTOTAL, PEAK, NREFL)
*   READ THE RESULTS OF SIMULATION
    INTEGER NUNIT, NTOTAL, NREFL
    REAL TWOTH(*), YCAL(*), BG(*), PEAK(*)
    CHARACTER*80 TITLE

    OPEN(UNIT=NUNIT, STATUS='OLD', ACCESS='SEQUENTIAL')
    REWIND(UNIT=NUNIT)
    READ(NUNIT, '(A)') TITLE
    READ(NUNIT, *) NOTOTAL, START, STEP, NREFL

*   READ INTENSITY DATA
    READ(NUNIT, *) (YCAL(J), J=1, NTOTAL)

*   CALCULATE TWO-THETA VALUES
    DO 10 J=1, NTOTAL
        TWOTH(J) = START + (J-1) * STEP
10 CONTINUE

*   READ PEAK POSITIONS
    READ(NUNIT, *) (PEAK(I), I=1, NREFL)
    CLOSE(UNIT=NUNIT)
END

```

Contents of dummy arguments are common to SUBROUTINE RDRSLT, but array YCAL is normalized in such a way as the intensity of the strongest reflection is adjusted to 100000.

11. Content of Data Set #21

This data set is used for Fourier and D syntheses based on the results of Rietveld analysis. Call the following subroutine to get data contained in it after setting the value of NUNIT.

```

SUBROUTINE RDFOUR(NUNIT,P,R,T,H,K,L,RLV,
&FC,FO,COSP,SINP,DELTA,NSYM,NREFL)
*   READ F(C) AND F(O) DATA FOR FOURIER SYNTHESIS
*   NB: MAXIMUM NUMBER OF REFLECTIONS
PARAMETER (NB=1500)
INTEGER NUNIT,R(3,3,48),H(*),K(*),L(*),NSYM,NREFL
REAL P(6),T(3,48),RLV(*),FC(*),FO(*),
&COSP(*),SINP(*),DELTA(*)

OPEN(UNIT=NUNIT,STATUS='OLD',ACCESS='SEQUENTIAL')
REWIND(UNIT=NUNIT)
READ(NUNIT,*) (P(I),I=1,6)
READ(NUNIT,*) NSYM
DO 10 I=1,NSYM
    READ(NUNIT,*) ((R(J,K,I),K=1,3),T(J,I),J=1,3)
10 CONTINUE

DO 20 I=1,NB
    READ(NUNIT,*,END=9) H(I),K(I),L(I),RLV(I),
& FC(I),FO(I),COSP(I),SINP(I),DELTA(I)
20 CONTINUE
9 NREFL=I-1
CLOSE(UNIT=NUNIT)

```

END

Contents of dummy arguments

- NUNIT: unit identifier (input).
- P: lattice constants (unit: angstrom or degree).
- R: rotation matrixes.
- T: translation vectors.
- H,
K,
L: diffraction indices, hkl .
- RLV: $\sin\theta/\lambda$.
- FC: $|F_c|$.
- FO: $|F_o'|$. $|F_o|$ estimated according to a method described by Rietveld (1969).
- COSP: $\cos(\phi)$ (ϕ : phase).
- SINP: $\sin(\phi)$.
- DELTA: $|F_o'| - |F_c|$.
- NSYM: number of symmetry operations.
- NREFL: number of reflections.

12. Content of the Data Base

Since the three sequential data sets SPGRI, SPGRA and ASFDC that are contained in the RIETAN system are text data sets written in certain formats, they can be used for crystallographic calculations other than Rietveld analysis. Their content is made available below. The reader is encouraged to use them with other programs.

12.1 SPGRI and SPGRA

Various kinds of information described in the *International Tables*, Vol. I (1969) and Vol. A (1983) are recorded in the form of fixed columns in the order of space group numbers. Let the following subroutine call after getting the values of NSPGR, NSET and NUNIT.

```

SUBROUTINE RDSPGR(NSPGR,NSET,NUNIT,LAUEG,
&NCENTR,NSYM,SPGR,ICOND,COORD,IERR)
*   READ INFORMATION ABOUT THE NSET'TH DESCRIPTION OF
*   NSPGR'TH SPACE GROUP
  INTEGER NSPGR,NSET,NUNIT,LAUEG,NCENTR,NSYM,
&ICOND(14),IERR
  CHARACTER SPGR*10,COORD(*)*20

  IERR=0
  OPEN(UNIT=NUNIT,STATUS='OLD',ACCESS='SEQUENTIAL')
  REWIND(UNIT=NUNIT)
1  CONTINUE
    READ(NUNIT,'(5I3,3X,A10)',IOSTAT=IOCOND)
&   I SPGR,NSET,LAUEG,NCENTR,NSYM,SPGR

```

```

IF (IOCOND .LT. 0) THEN
  IERR=1
  GO TO 9
ELSE IF (NSPGR .EQ. ISPGR .AND.
& NSET .EQ. ISET) THEN
  READ(NUNIT, '(14I2)') (ICOND(I), I=1, 14)
  READ(NUNIT, '(A20)') (COORD(I), I=1, NSYM)
  GO TO 9
END IF
GO TO 1
9 CLOSE (UNIT=NUNIT)
END

```

Contents of dummy arguments

- NSPGR: space group number (input).
- NSET: description number (input).
- NUNIT: unit identifier (input).
- LAUEG: = 1, triclinic system ($\bar{1}$).
- = 2, monoclinic system, unique axis a ($2/m$).
- = 3, monoclinic system, unique axis b ($2/m$).
- = 4, monoclinic system, unique axis c ($2/m$).
- = 5, orthorhombic system (mmm).
- = 6, tetragonal system ($4/m$).
- = 7, tetragonal system ($4/mmm$).
- = 8, trigonal system, rhombohedral lattice ($\bar{3}$).
- = 9, trigonal system, hexagonal lattice ($\bar{3}$).
- =10, trigonal system, rhombohedral lattice ($\bar{3}m$).
- =11, trigonal system, hexagonal lattice ($\bar{3}m$).

- =12, hexagonal system (6/m).
 - =13, hexagonal system (6/mmm).
 - =14, cubic system (m3).
 - =15, cubic system (m3m).
- NCENTR: = 0, center of symmetry not at the origin.
 = 1, center of symmetry at the origin.
- NSYM: number of general equivalent positions (excluding inverted and translated positions).
- SPGR: Hermann-Mauguin space group symbol.
- ICOND: symmetry conditions (Table 4) for 14 kinds of reflection types (Table 3).
- COORD: coordinates of general equivalent positions
- IERR: = 0, data has been input successfully.
 = 1, data for the NSPGR and NSET input by the user are absent.

The values of ICOND can be different between SPGRI and SPGRA even though the ways the origin and three axes are set up are the same. In the case of SPGRI, practically the same symmetry conditions are always designated also for the subsets (for example, the symmetry conditions for $hk0$ are also written for $h00$ and $0k0$), while those for subsets are sometimes omitted in the case of SPGRA. In both data sets, ICOND(I) gives the lattice type (Table 6).

Table 6. Correspondence between ICOND(7) and the lattice type.

ICOND(7)	Condition	Centering symbol
0	None	P
4	$k + 1 = 2n$	A
5	$h + 1 = 2n$	B
6	$h + k = 2n$	C
7	h, k, l odd/even	F
13	$h + k + 1 = 2n$	I
14	$-h + k + 1 = 3n$	R (rhombohedrally centered, obverse setting, hexagonal axes)
15	$h - k + 1 = 3n$	R (rhombohedrally centered, reverse setting, hexagonal axes)
21	$ h \geq k \geq l $	R (rhombohedral axes)

12.2 ASFDC

Numerical data, such as atomic scattering factors, correction terms for anomalous dispersion and coherent scattering lengths for almost all neutral atoms and important ions, are recorded in this data set. Let the following subroutine call after getting the values of NAME and NUNIT. Values of ATWT, B, SA and SI are recorded only for neutral atoms.

```

SUBROUTINE RDATOM(NAME, NUNIT, ATWT, ABC, B, DF,
&SA, SI, IERR)
*   READ DATA FOR A SPECIES
      INTEGER NUNIT, IERR

```



```

REAL ATWT,ABC(9),B,DF(2,5),SA,SI
CHARACTER*5 NAME,TNAME

IERR=0
OPEN(UNIT=NUNIT,STATUS='OLD',ACCESS='SEQUENTIAL')
REWIND(UNIT=NUNIT)
1 CONTINUE
  READ(NUNIT,'(A5,4X,F10.0)',IOSTAT=IOCOND)
& TNAME,ATWT
  IF (IOCOND .LT. 0) THEN
    IERR=1
    GO TO 9
  ELSE IF (NAME .EQ. TNAME) THEN
    IF (INDEX(NAME,'+') .EQ. 0 .AND.
& INDEX(NAME,'-') .EQ. 0) THEN
*      NEUTRAL ATOM
        READ(NUNIT,*) (ABC(I),I=1,9),B
        READ(NUNIT,*) ((DF(I,J),I=1,2),J=1,5),SA,SI
      ELSE
*      CATION OR ANION
        READ(NUNIT,*) (ABC(I),I=1,9)
        READ(NUNIT,*) ((DF(I,J),I=1,2),J=1,5)
      END IF
    GO TO 9
  END IF
  GO TO 1
9 CLOSE(UNIT=NUNIT)
END

```

Contents of dummy arguments

- NAME: name of a chemical species (input).
- NUNIT: unit identifier (input).
- ATWT: atomic weight (zero is returned for ions).
- ABC: nine coefficients when each atomic scattering factor is represented by the sum of four exponential functions and a constant (*International Tables*, Vol. IV, 1969).
- B: coherent scattering length, b/fm (Sears, 1986).
- DF(1,1): real part of the correction term for anomalous dispersion (*International Tables*, Vol. IV, 1969) ($\text{CrK}\alpha$), $\Delta f'$.
- DF(2,1): imaginary part of the correction term for anomalous dispersion (*International Tables*, Vol. IV, 1969) ($\text{CrK}\alpha$), $\Delta f''$.
- DF(1,2): real part of the correction term for anomalous dispersion ($\text{FeK}\alpha$), $\Delta f'$.
- DF(2,2): imaginary part of the correction term for anomalous dispersion ($\text{FeK}\alpha$), $\Delta f''$.
- DF(1,3): real part of the correction term for anomalous dispersion ($\text{CuK}\alpha$), $\Delta f'$.
- DF(2,3): imaginary part of the correction term for anomalous dispersion ($\text{CuK}\alpha$), $\Delta f''$.
- DF(1,4): real part of the correction term for anomalous dispersion ($\text{MoK}\alpha$), $\Delta f'$.
- DF(2,4): imaginary part of the correction term for anomalous dispersion ($\text{MoK}\alpha$), $\Delta f''$.
- DF(1,5): real part of the correction term for anomalous dispersion ($\text{AgK}\alpha$), $\Delta f'$.
- DF(2,5): imaginary part of the correction term for anomalous dispersion ($\text{AgK}\alpha$), $\Delta f''$.
- SA: absorption cross section for 2200 m/s neutrons, σ_a/fm^2 (Sears, 1986).
- SI: incoherent scattering cross section, σ_i/fm^2 (Sears, 1986).
- IERR: = 0, data have been input successfully.
 = 1, data for NAME input by the user are absent.

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Rietveld Analysis System

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