A new computer program for Rietveld analysis of X-ray powder diffraction patterns. By D. B. Wiles and R. A. Young, School of Physics and Engineering Experiment Station, Atlanta, Georgia 30332, USA

(Received 21 April 1980; accepted 13 October 1980)

Abstract

The Rietveld [J. Appl. Cryst. (1969), 2, 65-71] method of structure refinement from powder diffraction patterns is widely used with neutron data and increasingly so with X-ray data. A computer program for the application of the method with X-ray data, or with neutron nuclear scattering data, has been written ab initio in an effort to make it versatile, user oriented, portable, convenient, and largely self-contained yet reasonably comprehensive. It is of modular construction to facilitate user-desired modifications, one of which may be reasonably comprehensive. It is of modular construction to

Description

For portability, the program has been written in Fortran IV in conformity with ANSI 1966 standards. Since it was written for a computer with a 60-bit word length, users with shorter word-length machines may have to use double precision. The total program contains more than 5000 Fortran statements. With the automatic segmented loading capability on a CDC CYBER 70/74 machine, it requires less than 150 K words (octal) random-access memory to handle a refinement with

The program accommodates either one or two wavelengths (e.g. \( \lambda \) and \( \lambda/2 \)). It permits simultaneous refinement of the structures of two phases and the background.

Convenience features include single-pass operation (no preparatory program is needed) and built-in direct applicability with all space groups and with all atoms for which the required scattering factors are listed in International Tables for X-ray Crystallography (1974) as either (i) coefficients of an exponential series generating the X-ray scattering factors, plus anomalous scattering corrections as appropriate, or (ii) nuclear scattering lengths for thermal neutrons. One enters the space-group designation with a computer-compatible version of the standard space-group symbol. The program then generates the multiplicities in the powder pattern and the symmetry operations for structure factor calculations.

As with the Rietveld (1967, 1969) program, the quantity minimized in the least squares sense is the residual, \( R \),

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

where \( y_i(o) \) is the intensity observed at the \( i \)th step in the step-scanned powder diffraction pattern, \( y_i(c) \) is that calculated, and the weight \( w_i \) is given by

\[
(w_i)^{-1} = \sigma_i^2 = \sigma_i^2 + \sigma_{ib}^2;
\]

here taken as \( y_i + \gamma_i b \). Here \( \sigma_i \) is the standard deviation (usually based only on counting statistics) in the gross intensity, \( y_i \), and \( \sigma_{ib} \) is that for the background intensity, \( y_{ib} \), at the \( i \)th step.

The \( y_i(c) \) are determined from summation of the contributions from neighboring Bragg reflections and the background as

\[
y_i(c) = s \sum_k p_k I_{k}\bar{F}_k^2 G(\Delta \theta_{k}) P_k + y_{ib}(c),
\]

where \( s \) is a scale factor, \( L_k = \) Lorentz and polarization factors for the \( K \)th Bragg reflection, \( F_k = \) structure factor, \( p_k = \) multiplicity factor, \( P_k = \) preferred orientation function (currently implemented only for platy habit), \( \theta_k = \) Bragg angle for the \( K \)th reflection, \( K = h,k,l \), the indices identifying the Bragg reflection for which each of the above is evaluated, and \( G(\Delta \theta_{k}) = G(2\theta - 2 \theta_{k}) \) is the reflection profile function consisting, in the present version, of a symmetric profile function \( g(\Delta \theta_{k}) \) multiplied by an asymmetry function \( a(\Delta \theta_{k}) \) given by

\[
a(\Delta \theta_{k}) = 1 - \frac{A (\text{sign} \, \Delta \theta_{k}) (2 \Delta \theta_{k})^2}{\tan \theta_k},
\]

where \( A \) is the (adjustable) asymmetry parameter.

Physically, \( G(\Delta \theta_{k}) \), consists of the convolution of an instrumental profile and an intrinsic diffraction profile, which in turn may be the convolution of several broadening functions (profiles) arising from various diffraction effects. The angular range over which the summation is taken for any \( y_i \) is specified as a multiple, usually non-integer, of \( H_k \), the full-width-at-half-maximum (FWHM) of the function evaluated for the \( K \)th Bragg reflection.

The definition of \( y_i(c) \) and the correctness of the weights, \( w_i \), depend on whether the background is being refined or is fixed. In the current version (2.9), the background function may be obtained from the function

\[
y_i(c) = B_0 + B_1(2\theta) + B_2(2\theta)^2 + B_3(2\theta)^3 + B_4(2\theta)^4 + B_5(2\theta)^5
\]

or from an operator-supplied table of background intensities, or from linear interpolation between operator-selected points in the pattern. When the background is fixed, the \( y_{ib}(c) \) are defined to be those fixed values, even though they may have come from observation, and the weighting taken in (2) is correct.

The minimization is done with the Newton Raphson algorithm. The normal matrix elements formally given by

\[
M_{jk} = -\sum_i 2w_i \left\{[y_i(o) - y_i(c)][\frac{\partial^2 y_i(c)}{\partial x_j \partial x_k} - \frac{\partial y_i(c)}{\partial x_j}\frac{\partial y_i(c)}{\partial x_k}]\right\}
\]

are approximated by deleting the term in \( [\partial y_i(o) - \partial y_i(c)] \). \( x_j \) and \( x_k \) represent the parameters varied.

The standard deviation, \( \sigma_j \), for the \( j \)th adjusted parameter is calculated as

\[
\sigma_j = \{M_{jj}^{-1} \sum_i w_i [y_i(o) - y_i(c)]^2 / (N - P - C) \}^{1/2},
\]

where \( M_{jj}^{-1} \) is the diagonal element in the inverse of the normal matrix, \( N \) is the number of observations \( [i.e. \, y_i(o)] \), \( P \) is the number of parameters adjusted, and \( C \) is the number of constraints imposed.

Three 'goodness-of-fit' indicators are calculated:

\[
R_B = \frac{\sum K [I_k(o) - I_k(c)]^2}{\sum K I_k(o)} \quad (\text{R-Bragg})
\]

\[ \copyright \, 1981 \text{ International Union of Crystallography} \]
Required input information includes least-squares refinement include (Young, 1980). One reason for the modular construction of the profile functions. program was to facilitate the incorporation of improved certainly needed (Suortti, 1980), particularly for the X-ray case.

The procedure used is that of Rietveld (1969).

The profile functions $G(\theta K)$ presently implemented are

$$\frac{C_0^{1/2}}{\sqrt{\pi H_k}} \exp \left[ -C_0 (2\Delta \theta K)^2 / H_k^2 \right]$$

(Gaussian) (11)

$$\frac{C_1^{1/2}}{\pi H_k} \left[ 1 + C_1 (2\Delta \theta K)^2 / H_k^2 \right]^{-1}$$

(Lorentzian) (12)

$$\frac{2C_r^{1/2}}{\pi H_k} \left[ 1 + C_r (2\Delta \theta K)^2 / H_k^2 \right]^{-2} \mod 1 \text{Lorentzian}$$

(13)

$$\frac{C_s^{1/2}}{2H_k} \left[ 1 + C_s (2\Delta \theta K)^2 / H_k^2 \right]^{-1.5} \mod 2 \text{Lorentzian}$$

(14)

where $H_k$ is the full-width-at-half-maximum, $C_0 = 4 \ln 2$, $C_1 = 4$, $C_2 = 4(2^{1/2} - 1)$, and $C_3 = 4(2^{3/2} - 1)$.

The functional form of $H_k$ is approximated by $H_k^2 = U \tan^2 \theta_k + V \tan \theta_k + W$, where $U$, $V$, and $W$ are constants for any one diffraction pattern. Better profile functions are certainly needed (Suortti, 1980), particularly for the X-ray case (Young, 1980). One reason for the modular construction of the program was to facilitate the incorporation of improved profile functions.

The parameters that can be adjusted simultaneously in the least-squares refinement include

- lattice
- atom position $(x, y, z)$
- atom site occupancy
- atom thermal vibrational (isotropic or anisotropic)
- profile $(U, V, W$ and asymmetry)
- preferred orientation
- background function
- $2\theta$-zero correction
- overall scale (one for each phase)
- overall isotropic thermal $(B)$.

Required input information includes

- initial values of all variable parameters
- step-scan data in equal increments in $2\theta$
- $2\theta$ limits and excluded regions in the data
- wavelength data
- background specification
  - [either values at selected points defining straight line segments, or complete table, or values of the $B$'s in (5)]
- space-group symbol
- chemical symbol and valence of each atom (used to enter stored scattering factor tables, special tables can be added as needed)

Of these, $R_{wp}$ probably should be considered the most meaningful, at least for following the progress of a refinement, because its numerator is the quantity being minimized.

In the R-Bragg expression the symbol $I_K(o)$ for the observed Bragg intensity is placed in quotation marks because it is not actually observed. Instead, it is calculated by allocating the actually observed intensities $I(o)$ to Bragg intensities, $I_K(o)$, on the basis of the calculated intensities $I_K(c)$. The procedure used is that of Rietveld (1969).

The off-line plots show the observed $I_o$'s separately and the calculated ones are connected by a continuous line in the same field. Markers indicating Bragg-reflection positions are placed below these and plotted below the markers is the difference $I(o) - I(c)$. Fig. 1 gives an example of such a plot resulting from a refinement (R-185) with this program of pure synthetic fluorapatite, $Ca_4(PO_4)_3F$, for which the structure is well known from single-crystal work (e.g. Sudarsanan, Mackie & Young, 1972). Here, six background parameters were refined simultaneously with the 19 structural and nine other parameters, $R_{wp} = 11.9\%$, and $R_B = 2.6\%$. For the adjustable positional parameters, the indicated standard deviations ranged from 0.0001 to 0.0003. Their differences from the values found for a synthetic single crystal (Sudarsanan, Mackie & Young, 1972) (which would not necessarily have physically identical atomic coordinates) were $\leq 3\sigma$ for all but one case (5o).

When the background is refined, all points, except those in pre-designated excluded regions, are considered. When the background is fixed, all data points farther than $q H_K$ (q is a small number, not necessarily integer, selected by the operator) from the nearest Bragg position (in the model) are ignored. This has the effect of reducing $R_{wp}$ in a non-significant way. For example, a fixed-background structure refinement with the same data shown in Fig. 1 led to $R_{wp} = 8.2\%$ and $R_B = 3.1\%$. This result suggests that the Bragg intensities were actually better fit in the background-refined case, even though $R_{wp}$ was higher.

The new program has now been used for Rietveld refinements with more than 200 sets of X-ray data and a few sets of neutron data, mostly, but not solely, for variously substituted synthetic and biological apatites. The convenience features have been shown to be real and to save substantial operator time while increasing the throughput. The new program also runs faster than a previous one (Mackie, Young & von Dreele, 1977), 30% faster in a test case with fluorapatite.

The program in versions DBW2.6 (without the multiphase, preferred orientation, $R_B$ and background refinement features) and 2.8 (without background refinement) has been used successfully by workers at other locations on both CDC and IBM machines. The current version (DBW 2.9) is available
from the authors either without charge or, if necessary, with simple cost reimbursement for reproduction and mailing.

The authors are grateful to Dr P. E. Mackie, Dr K. Ann Kerr, and Dr D. Cromer for discussions and information, to Dr Allen C. Larson for having written his SPGP program on which the space-group handling part of this program was modeled, and to the USPHS for financial support through NIH-NIDR grant DE-01912.

References


BLOKJE, a computer program to calculate the domain of an atom in a structure. By Louise Gelato, Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

(Received 28 August 1980; accepted 27 October 1980)

Abstract
A computer program has been written with the aim of calculating the domain of an atom in a structure. The domain may be limited by planes situated half-way between the atoms, or at a distance that takes into account the relative radii of the atoms. Data concerning this domain and the corresponding coordination polyhedron are computed and printed. Punched cards, to be used in a special plotting program, can also be produced. Three types of weighted coordination number are calculated.

Introduction
The description of crystal structures in terms of the domains of the atoms can aid in finding relationships between different structures.

The word 'domain' is used to indicate a certain space, defined by some geometrical law, around a given atom in a structure. This concept is based on work of G. Lejeune-Dirichlet, G. Voronoi, P. Niggli and others.

Lejeune-Dirichlet (1850), in his work on the reduction of positive quadratic forms, proved that the region containing all