A Computer Program for Refinement of Crystal Orientation Matrix and Lattice Constants from Diffractometer Data with Lattice Symmetry Constraints

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Abstract

A linear least-squares computer program that implements the procedure described by Shoemaker & Bassi [Acta Cryst. (1970), A26, 97–101] has been written. With this technique constraints appropriate to the lattice symmetry may be imposed during refinement of the coefficients of the orientation matrix. Cell parameters and variances with the assumed lattice symmetry and the best least-squares agreement result from this calculation.

Introduction

Two methods of refining crystal orientation and lattice parameters have been proposed. Busing & Levy (1967) and Busing (1970) describe a technique whereby the refinement is accomplished by adjusting the reciprocal-lattice parameters and three of six angles that define the orientations of a primary and a secondary reflection to minimize the sum of squares of angular residuals. This approach has the advantage that constraints required by lattice symmetry are applied in a straightforward manner and partial data such as 20 peak positions can be used. The disadvantages are that (1) the equations are nonlinear and several cycles must be performed, and (2) the least-squares problem may be as large as rank 9 and may lead to very long computing times for slow computers.

A second method of refining the orientation matrix was presented by Shoemaker & Bassi (1970) and Tichý (1970), and elaborated by Gabe (1980). With this technique, the coefficients of the matrix are refined by direct least-squares calculations, minimizing the sum of squares of residuals of diffractometer-system vector components. This approach, which is widely available in commercial and custom diffractometer software, has the advantage that the observational equations are linear, so that a single cycle is sufficient and the nine normal equations separate into three sets of three to minimize computation time. The disadvantage is that the resultant lattice parameters are unconstrained and all crystal lattice constants are refined as though they were triclinic. Shoemaker & Bassi (1970) presented equations for applying lattice symmetry constraints during refinement of the orientation matrix; this report describes a computer program that implements their formalism.

Method

In the notation of Busing & Levy (1967), the coordinates of a reciprocal-lattice point, \( h_\phi \), in a Cartesian coordinate system attached to the \( \phi \) circle of the machine are related to the Miller indices of the reciprocal lattice by

\[
\mathbf{h}_\phi = \mathbf{U} \mathbf{B} \mathbf{h} = \mathbf{V} \mathbf{h},
\]

where \( \mathbf{U} \) is an orthogonal matrix that relates the \( \phi \)-axis system to a crystal Cartesian system, \( \mathbf{B} \) is a matrix that transforms the reciprocal lattice into such a crystal Cartesian system, \( \mathbf{h} \) is a vector of Miller indices, and \( \mathbf{V} = \mathbf{U} \mathbf{B} \) is commonly called the orientation matrix. If \( n \) different vectors \( \mathbf{h}_\phi \) are calculated from measured setting angles for \( n \) centered reflections and used to construct a \( 3 \times n \) matrix \( \mathbf{H}_\phi \), with the corresponding Miller indices used to form \( \mathbf{H} \), the \( 3 \times n \) observational equations may be represented by the vector equation

\[
\mathbf{H}_\phi = \mathbf{VH}.
\]
REFINEMENT OF CRYSTAL ORIENTATION MATRIX

In vector notation, with subscripts indicating rows of the corresponding matrices and \( \mathbf{H}' \) representing the transpose of \( \mathbf{H} \), this equation may be rewritten as

\[
\begin{pmatrix}
  \mathbf{H}' & 0 & 0 \\
  0 & \mathbf{H}' & 0 \\
  0 & 0 & \mathbf{H}'
\end{pmatrix}
\begin{pmatrix}
  \mathbf{V}'_1 \\
  \mathbf{V}'_2 \\
  \mathbf{V}'_3
\end{pmatrix} =
\begin{pmatrix}
  \mathbf{H}'_{1 \varphi} \\
  \mathbf{H}'_{2 \varphi} \\
  \mathbf{H}'_{3 \varphi}
\end{pmatrix}.
\]

(4)

The first matrix, which is block diagonal in this special case, is the \( 3n \times 9 \) matrix of observational equations, the second matrix is the \( 9 \times 1 \) vector of unknowns, and the third matrix is the \( 3n \times 1 \) vector of observations. The least-squares equation to be solved, assuming equal weights for all observations, is

\[
\begin{pmatrix}
  \mathbf{H} \mathbf{H}' & 0 & 0 \\
  0 & \mathbf{H} \mathbf{H}' & 0 \\
  0 & 0 & \mathbf{H} \mathbf{H}'
\end{pmatrix}
\begin{pmatrix}
  \mathbf{V}'_1 \\
  \mathbf{V}'_2 \\
  \mathbf{V}'_3
\end{pmatrix} =
\begin{pmatrix}
  \mathbf{H} \mathbf{H}'_{1 \varphi} \\
  \mathbf{H} \mathbf{H}'_{2 \varphi} \\
  \mathbf{H} \mathbf{H}'_{3 \varphi}
\end{pmatrix}.
\]

(5)

with the first matrix being the \( 9 \times 9 \) matrix of normal equations, and the second, the least-squares solution vector \( \mathbf{V} \). Explicitly,

\[
\begin{pmatrix}
  \mathbf{V}'_1 \\
  \mathbf{V}'_2 \\
  \mathbf{V}'_3
\end{pmatrix} =
\begin{pmatrix}
  (\mathbf{H} \mathbf{H}')^{-1} & 0 & 0 \\
  0 & (\mathbf{H} \mathbf{H}')^{-1} & 0 \\
  0 & 0 & (\mathbf{H} \mathbf{H}')^{-1}
\end{pmatrix}
\begin{pmatrix}
  \mathbf{H} \mathbf{H}'_{1 \varphi} \\
  \mathbf{H} \mathbf{H}'_{2 \varphi} \\
  \mathbf{H} \mathbf{H}'_{3 \varphi}
\end{pmatrix},
\]

(6)

if \( \mathbf{H} \mathbf{H}' \) is nonsingular. After some manipulation this expression becomes

\[
(\mathbf{V}_1 \mathbf{V}_2 \mathbf{V}_3) = (\mathbf{H}_{1 \varphi} \mathbf{H}_{2 \varphi} \mathbf{H}_{3 \varphi}) \mathbf{H}' (\mathbf{H} \mathbf{H}')^{-1}.
\]

(7)

Interpreting \( \mathbf{V} \) as a \( 3 \times 3 \) matrix rather than as a \( 9 \times 1 \) vector, the unconstrained solution for the orientation matrix may be written as

\[
\mathbf{V} = \mathbf{H}_{\varphi} \mathbf{H}' (\mathbf{H} \mathbf{H}')^{-1}.
\]

(8)

Lattice constants are derived from \( \mathbf{V} \) in the manner described by Busing & Levy (1967).

To apply lattice symmetry constraints, Shoemaker & Bassi (1970) proposed a matrix \( \mathbf{D} \) that would transform the unconstrained system into the constrained one by

\[
\mathbf{V}' = \mathbf{V} \mathbf{D},
\]

(9)

where primed quantities represent the case where symmetry is applied. This matrix will also transform the Miller indices according to

\[
\mathbf{H}' = \mathbf{D} \mathbf{H},
\]

(10)

which represents, in the same shorthand as (2), the new observational equations. Some of the details of the transformation may be seen by writing

\[
\mathbf{D} = \mathbf{V}^{-1} \mathbf{V}' = (\mathbf{U} \mathbf{B})^{-1} \mathbf{U}' \mathbf{B}' = \mathbf{B}^{-1} \mathbf{U}' \mathbf{B}' = \mathbf{B}^{-1} \mathbf{d} \mathbf{B}',
\]

(11)

where \( \mathbf{d} = \mathbf{U}^{-1} \mathbf{U}' \) is a matrix that approximates a small rotation and to first order is the orientation correction of the crystal Cartesian system with respect to the \( \varphi \)-axis system.

The first step of the calculation performed by the program is to determine \( \mathbf{V}, \mathbf{U}, \mathbf{B} \) and unconstrained (i.e. 'triclinic') lattice parameters by application of (8). A trial value of \( \mathbf{V}' \), denoted as \( \mathbf{V}_0 \), is formed by forcing the lattice parameters determined above to conform to the symmetry, calculating matrix \( \mathbf{B}_0 \) from this lattice, and \( \mathbf{V}_0 \) from

\[
\mathbf{V}_0 = \mathbf{U} \mathbf{B}_0.
\]

(12)

The left-hand side of (10) may be found by solving the equivalent of (2) to obtain

\[
\mathbf{H}' = (\mathbf{V}_0)^{-1} \mathbf{H}_\varphi.
\]

(13)

The observational equations solved by least squares are

\[
(\mathbf{V}_0)^{-1} \mathbf{H}_\varphi = \mathbf{D} \mathbf{H},
\]

(14)

where the elements of \( \mathbf{D} \) are the unknowns, which must satisfy the constraints imposed by symmetry. Shoemaker & Bassi (1970) list the constraining equations for most cases of interest, and the others may be obtained by cyclic permutation of axes. For crystal systems in which all axes are mutually perpendicular, the constraint equations involve only two of \( D_{ij} \) and could be applied by direct substitution before the normal equations are solved, thus reducing the rank of the problem. For monoclinic or hexagonal systems, however, the constraint equations involve three terms from \( D_2 \); thus a method such as Lagrangian multipliers must be used. To minimize special code in the program, the latter method is used in all cases; the rank of the normal equations is equal to \( 9 + m \), where \( m(\leq 5) \) is the number of constraints.

A program is more easily understood and maintained if the number of decision branches is minimized. Such branches in the constraint routine were avoided by noting that only 14 different terms are used...
as multipliers of the coefficients of $D$. It is possible, therefore, to evaluate all these terms and to apply them as required to the appropriate element of the normal equations matrix without any testing or branching on symmetry type. Sets of indices and pointers are used to specify the type of term and the element to which it is to be applied.

The least-squares normal equations are

$$
\begin{bmatrix}
HH' & 0 & 0 & c_{111} & \ldots & c_{11m} \\
0 & HH' & 0 & \ldots & \ldots & \ldots \\
0 & 0 & HH' & c_{331} & \ldots & c_{33m} \\
c_{111} & \ldots & c_{331} & \vdots & \vdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
c_{11m} & \ldots & c_{33m}
\end{bmatrix}
\begin{bmatrix}
D_1' \\
D_2' \\
D_3' \\
L_1 \\
L_2 \\
L_m
\end{bmatrix}
= \begin{bmatrix}
[(V_0)^{-1}HH']_1 \\
[(V_0)^{-1}HH']_2 \\
[(V_0)^{-1}HH']_3 \\
0 \\
0 \\
0 \\
0
\end{bmatrix},
$$

where the $L_1, \ldots, L_m$ are the Lagrangian multipliers, $m$ is the number of constraint equations, and $c_{ijk}$ represents the coefficient of $D_{ij}$ in the $k$th constraint equation. The system of equations has rank $9 + m$ and is solved by normal procedures. The final step is to calculate $V'$ from (9) and the constrained lattice constants according to the method of Busing & Levy (1967). Partial derivatives of the lattice parameters with respect to the elements of $D$ are obtained by numerical differentiation. Estimated standard deviations for the parameters propagated from the variance–covariance matrix of $D$ are obtained in the usual manner from the inverse of the normal equations matrix.

**Discussion**

It matters little whether the constrained or unconstrained orientation matrix is used to position a crystal during the collection of intensity data with a diffractometer. Cell parameters extracted from the unconstrained matrix, however, cannot be transformed by any subsequent manipulation into quantities that have both the assumed lattice symmetry and the best agreement (in the sense of least squares). The difficulty, for example, of correcting the calculated axial lengths of an orthorhombic crystal for the effects of small deviations from orthogonality cannot be overcome, except for the procedure described here. Cell parameters derived from the constrained orientation matrix or calculated by symmetry-constrained, nonlinear least-squares methods from the 2θ observations alone meet both criteria simultaneously. Such cell parameters can be compared to characterize systematic lattice variations under different conditions of pressure, temperature, or composition within a single-phase region, and to discover the structural invariants of phase transformations.

**Availability of program**

Several versions of the program, which is written in Fortran, are available, including a batch version and interactive implementations for a PDP-11/34 under RSX-11M, for a VAX-11/780 under VMS, and for a CDC Cyber 170/750 under NOS. To obtain copies of the program and a test data set with results, a small magnetic tape (150 feet long) should be sent to the second author with instructions regarding the format of the tape to be returned. There will be no charge for this service.

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**References**


