Short Communications

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On the definition and practical use of crystal-based azimuthal angles. Erratum. By D. SCHWARZENBACH, Institut de Cristallographie, University of Lausanne, BSP Dorigny, CH-1015 Lausanne, Switzerland, and H. D. FLACK, Laboratoire de Cristallographie, University of Geneva, 24 quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

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Abstract

In the paper by Schwarzenbach & Flack [J. Appl. Cryst. (1989), 22, 601-605], the equation describing the transformation properties of the crystal-based azimuthal angle \( \psi \) is incorrect. The correct formula is derived.

The argument in the section Unit-cell transformations on p. 603 of the paper is erroneous since \( |q_x \times q_y| = |\sin \Delta \psi| \) and not \( \sin \Delta \psi \). Similarly, equation (10) is wrong since

\[
V_a^T G_n^T V_v = V_a^T S^{-2} \sin^2 \Delta \psi \quad V_v = a_n \times b_n \cdot c_n = [G_n]^{1/2}
\]

is the volume of the new unit cell. In terms of physical vectors, \( \sin \Delta \psi = q_x \times q_y \cdot f \). Relative to the new cell, the reciprocal-space coordinates of vectors proportional to \( q_x \times q_y \) and \( f \) are, respectively, the algebraic vector product \( v_n = o_n \times u_n \) and \( h_n \). Moreover, \( v_n \) is proportional to \( h_n \), \( v_n = ch_n \). The sign of \( \sin \Delta \psi \) is \( \text{sign}(\sin \Delta \psi) = \text{sign}(c) = \text{sign}(v_n \cdot b_n) \). Equation (10) thus becomes

\[
\Delta \psi^T = (\sin \Delta \psi, 0, \cos \Delta \psi)
\]

\[
= s\{\text{sign}(v_n^T h_n) V_v^T G_n^T V_v)^{1/2}, 0, (o_n^T G_n u_n)\}, \quad (10)
\]

\[
S^{-2} = (o_n^T G_n o_n) (u_n^T G_n u_n), \quad v_n^T G_n^T v_n = [2c(\sin \theta)/2]^2.
\]

Computer Programs


MRIAAU – a program for autoindexing multiphase polycrystals. By V. B. ZLOKAZOV, Joint Institute for Nuclear Research in Dubna, Laboratory of Computing Techniques and Automation, Head Post Office, PO Box 79, Moscow, USSR

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Abstract

A method and algorithm are described for solution of the autoindexing problem of multiphase polycrystals. A Fortran program, called MRIAAU, which implements the algorithm, runs on a PC and can solve the problem in some minutes (IBM PC with 80286 and higher).

1. Introduction

Autoindexing is the determination of the lattice parameters and Miller indices of reflections. In a multiphase polycrystalline sample this can be done on the basis of a set (incomplete) of experimentally observed diffraction reflection positions.

The method, described below, is universal, straightforward and uses the analytical technique of approximation, which allows the user to get an acceptable problem solution quickly even in complicated cases [the program run takes on average a few minutes on a PC like the Wang 250/16 (IBM compatible, with an 8 MHz coprocessor)].

Let a diffraction (neutron or X-ray) measurement produce a spectrum where (approximate) positions of intensity maxima give the set \( R = \{r_i\}, i = 1, 2, \ldots, m \), the assumption being that the crystalline sample has \( n \) phases, i.e. \( n \) different lattices, each described by six quantities:

\[
a, b, c, \cos \alpha, \cos \beta, \cos \gamma,
\]

some of which can be dependent on one another. Each reflection position is formally given by the formula

\[
r = f(P, l),
\]

where \( P \) is vector (1) and \( l \) is a vector of three integer numbers from a set of groups of three \( M_k \) (Miller indices), \( k = 1, 2, \ldots, n \), for any unknown phase.

The problem is: \( R \) being given and \( n \) fixed, determine \( P_k \) and \( M_k \) for each \( k \). This problem is difficult even for a 'monocrystal sample, \( n = 1 \)' and particularly for a 'powder sample, \( n > 1 \)'.

A natural algorithm which offers itself here is as follows. Let bounded vector sets \( \{P_k\} \) and sets of three integer numbers \( \{M_{jk}\} \) \( k = 1, 2, \ldots, n \); \( j = 1, \ldots, m \), be given such that

\[
Q_k \subset \{P_k\}, \quad \{N_j\} \subset \{M_{jk}\},
\]

where \( Q_k \) and \( \{N_j\} \) are true parameters of the lattice and jth Miller indices for the kth phase. For components of vectors \( P_k \) the following relations are true:

\[
P_{kl} \leq p_k \leq P_{kw}.
\]

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Then the estimates of $Q_k$ and sets $\{N_{jk}\}$ can be obtained as a solution of the problem: find
\begin{equation}
\min \sum_{j=1}^{m} \rho_j[r_j, f(P_k, M_{jok})],
\end{equation}
where $M_{jok}$ is a solution of the problem
\begin{equation}
\min \rho_j[r_j, f(P_k, M_{jok})]
\end{equation}
and $\rho_1$ and $\rho_2$ are some distance functions and the minimum of (5) is searched over pairs of $P_k$ and related $\{M_{jk}\}$. The problem is well posed if, say, the set of experimental reflection positions is sufficiently accurate and complete and simplices (3) (or Miller-index sets) are disjoint for different phases.

This problem can be solved by, say, trying points of the simplex (3) and Miller indices $\{M_{jok}\}$ from a set which definitely includes indices observable for these lattices. However, this is a time- and effort-consuming procedure; even for two phases there are 12 parameters and no less index vectors. This requires huge numbers of tries to be carried out even for rather rough grids (hence providing a low accuracy of parameter estimates).

A more attractive idea is to use a look-up procedure for obtaining initial guesses about the parameters and then to use the refinement procedure of analytical minimization of the functional (4), (5) in the space of parameters and Miller-index vectors. For the multiphase case the analytical minimization is strictly necessary. However, this poses a problem: how to compute variations of (i.e. differentiate) formulae like (5) where a minimization operation is encountered.

2. On combining the differentiation and non-analytical operations
We pose the problem in a more general way: let a functional
\begin{equation}
G = G[y(x)],
\end{equation}
defined in a space of function vectors $\{x\}$, be given, and assume that some functions $y(x)$ are differentiable with respect to $x$, while others are not. How can the problem of minimization of (6) in the space $\{x\}$ be solved by gradient-like methods?

We shall proceed as follows. Let us take a set of functions $\{z(x)\}$, which is $\delta$ dense in the function set $\{y(x)\}$. Then, if the functional (6) is strictly convex in the space $\{x\}$ and has a minimum of $X_0$, its minimum on $\{z(x)\}$, if any, will be achieved at an $x$ which is close to $x_0$ and differs from it by a quantity continuously dependent on $\delta$.

This poses another problem: how to replace the widely used non-differentiable functions such as the absolute value, the function $\text{sign}(x)$, the minimum and maximum etc. by differentiable ones, which would be arbitrarily close to the former ones.

One can suggest the following approach.
1. Function $|x|$. This can be approximated by
\begin{equation}
|x| \simeq (x^2 + \delta)^{1/2}.
\end{equation}
2. Function $\text{sign}(x)$.
\begin{equation}
\text{sign}(x) = \begin{cases} x/|x| & \text{if } x \neq 0, \\ 0 & \text{if } x = 0. \end{cases}
\end{equation}
This can be approximated by
\begin{equation}
\text{sign}(x) \simeq x/(x^2 + \delta)^{1/2}.
\end{equation}
3. Function $\min(x_i), i = 1, 2, \ldots, n$. Let us start with $n = 2$. Then one can write
\begin{equation}
\min(a, b) = \{a[\text{sign}(b - a) + 1] + b[\text{sign}(a - b) + 1]\}/2.
\end{equation}
One can easily see that for an arbitrary $n$ we have
\begin{equation}
\min(x_i) = \min(\min(\cdots \min(\min(x_1, x_2), x_3), \ldots), x_n).
\end{equation}
The function $\max(x_i)$ is built similarly:
\begin{equation}
\max(a, b) = \{a[\text{sign}(a - b) + 1] + b[\text{sign}(b - a) + 1]\}/2.
\end{equation}
Substituting (7) into (8) and (8) into (9) and (10), we get the expressions needed.

We restrict ourselves to these functions, bearing in mind that, if necessary, other functions may be dealt with in a similar way.

The question then arises of how to compute the partial derivatives with respect to the arguments. This is to be done as follows.
1. \begin{equation}
\partial |x|/\partial x \simeq x/(x^2 + \delta)^{1/2}.
\end{equation}
2. \begin{equation}
\partial \text{sign}(x)/\partial x \simeq \delta/(x^2 + \delta)^{1/2}.
\end{equation}
3. Let us first compute the derivative of the function, approximate to $\min(a, b)$, with respect to one parameter ($a$ or $b$); we have
\begin{equation}
\partial \min(a, b)/\partial a = [(b - a)/2](1/s + 1 + \delta/q),
\end{equation}
where
\begin{equation}
\delta = [(b - a)^2 + \delta^2]^{1/2}, \quad q = s^2.
\end{equation}
Then, applying this formula to (9), we get the following recurrent algorithm:
\begin{equation}
\frac{\partial \min(x_1, x_2, \ldots, x_n)}{\partial x_i} = \prod_{k=i+1}^{n} \frac{\partial \min(x_1, x_2, \ldots, x_k)}{\partial x_i} \frac{\partial \min(x_1, \ldots, x_i)}{\partial x_i}.
\end{equation}

3. Program MRIAIAU for autoindexing and instances of its application
Let us return to the problem (3)-(5). We can consider the following cases of distance functions $\rho_1$ and $\rho_2$.
1. $\rho_1$ = quadratic distance, $\rho_2$ = modulus distance. This selection is relevant if the experimental reflection positions (peaks) are given with 'normal' errors, but without mistakes - large deviations from the true values.
2. $\rho_1$ = modulus distance, $\rho_2$ = modulus distance. This selection is relevant if experimental peaks are given with large uncertainties or mistakes.
3. $\rho_1$ and $\rho_2$ are intermediate distance functions. A concrete choice is determined by the degree of the uncertainty of the experimental data.

4. $\rho_1 = \text{quadratic distance}, $ $\rho_2 = \text{entropy quasi-distance}:$

$$\rho_2(a, b) = (a - b)^2LN^2[((a - b)/N)]^2/N^2,$$

where $N = \text{error norm of } a - b.$

The entropy quasi-distance is more robust to data errors and sometimes more efficient than the modulus distance.

To find the minimum of (4) by gradient-like methods one needs initial guesses of the lattice parameters because (4) can be strictly convex only in a small neighborhood of the argument of this minimum.

Thus, one can apply a two-stage process for the minimum computation:

1. Use a random pickup of points from a compact defined by the inequalities (3) and save the vector which gives a minimal value of (4).

2. Using this vector as an initial item, apply a gradient-like method to compute the argument of the true minimum.

The partial derivatives of (4) with respect to the parameters can be computed on the basis of the above-given formulae.

A program called MRIAASU was developed which implements an algorithm to determine lattice parameters for a polycrystalline sample. The steps of this algorithm are as follows.

1. Reflection positions in an experimental diffraction spectrum are either given or found by an algorithm, described by Zlokazov (1982).

2. Miller indices are generated, including those covering the experimental diffraction maxima.

3. A compact set of lattice-parameter values to be looked through is determined using the inequalities (3) under condition that this set contains the true values of the lattice parameters.

4. Additional a priori information, if any available, is used, such as syngony and type of lattice etc., to simplify and accelerate the analysis.

5. For a single phase a grid, defined on the compact set (3), is searched and lattice parameters, providing the minimal value of the functional (4)-(5), are taken as a preliminary solution.

6. For several phases a random parameter vector is tried and a vector which provides the minimal value of the functional (4)-(5) is taken as the preliminary solution. These points can be taken from the compact (3) according to either a uniform law or a normal one. The latter procedure can be performed in a Bayesian way.

7. In both cases (one or many phases) then the gradient-descent-based method for the minimization of (4)-(5) on (3) is used, which gives us the best final estimate of the lattice parameters.

Also, various filtration algorithms for the determination of lattice parameters in the case of many phases can be used, i.e. the extraction of single phases from the experimental peak set in succession and the analysis of one-phase reflection sets.

Examples of the analysis are given below.

A neutron diffraction spectrum from a powder of Cu, CuO$_2$ and CuO, obtained on a time-of-flight diffractometer (Balagurov, 1984), was analyzed and the following series of reflections, corresponding to the interplanar distances $3.0154\ 2.7580\ 2.5269\ 2.4638\ 2.3377\ 2.0961\ 2.0856\ 1.9648\ 1.8702\ 1.7914\ 1.7231\ 1.5970\ 1.5077\ 1.4132\ 1.3869\ \text{Å},$ taken.

The syngonies suggested were

1st phase: cubic
2nd phase: cubic
3rd phase: monoclinic.

The parameter compact was bounded thus: $(\text{Å, °})$

1st phase: $3 < a < 4$
2nd phase: $4 < a < 5$
3rd phase: $4 < a < 5$

$3 < b < 4$
$4 < c < 6$
$90 < \beta < 100.$

Miller indices were tried:

9 $hkl$ indices for the 1st phase
9 $hkl$ indices for the 2nd phase
47 $hkl$ indices for the 3rd phase.

The identification gave the following results.

Parameters of phase 1 were estimated as $(\text{Å, °})$

$$a \quad b \quad c \quad \alpha \quad \beta \quad \gamma$$

3·6136 3·6136 3·6136 90·000 90·000 90·000.

Parameters of phase 2 were estimated as $(\text{Å, °})$

$$a \quad b \quad c \quad \alpha \quad \beta \quad \gamma$$

4·2655 4·2655 4·2655 90·000 90·000 90·000.
Parameters of phase 3 were estimated as (Å, °)

\[
\begin{array}{cccccc}
    a & b & c & \alpha & \beta & \gamma \\
    4.7078 & 3.4253 & 5.1616 & 90.000 & 99.091 & 90.000 \\
    (4.6837 & 3.4226 & 5.1288 & 99.54) & \\
\end{array}
\]

The numbers in brackets are the estimates obtained by the Rietveld method and published by Åsbrink & Norrby (1970).

The table of autoindexing is given as Table 1.
An artificial example was also analyzed. Data were simulated for a two-phase powder. 16 peaks were produced (disturbed interplanar distances, errors about 0.001-0.003 Å): 4.9225 3.8793 3.3446 3.2659 2.9514 2.5687
2.4586 2.8308 2.5687 2.5677 2.4607 2.2647 2.1703 2.0812 2.0025 1.9396 1.9187 1.7352 1.7037 Å.

The syngonies suggested were

1st phase: triclinic
2nd phase: rhombohedral.

The true parameter values were (Å, °)

1st phase: 3, 4, 5, 80, 100 (a, b, c, α, β, γ)
2nd phase: 4, 4, 4, 60, 60, 60 (a, b, c, α).

The parameter compact was bounded thus (Å, °):

1st phase: 2.5 < a < 3.5
        3.5 < b < 4.5
        4.5 < c < 5.5
        70 < α < 90
        80 < β < 100
        90 < γ < 110
2nd phase: 3.5 < a < 4.5
        50 < α < 70.

Miller indices were tried:

17 hkl indices for the 1st phase
8 hkl indices for the 2nd phase.

The identification gave the following results.

Parameters of phase 1 were estimated as (Å, °)

\[
\begin{array}{cccccc}
    a & b & c & \alpha & \beta & \gamma \\
    3.0004 & 4.0093 & 4.9976 & 80.1454 & 90.0001 & 100.1607 \\
\end{array}
\]

Parameters of phase 2 were estimated as (Å, °)

\[
\begin{array}{cccccc}
    a & b & c & \alpha & \beta & \gamma \\
    4.0055 & 4.0055 & 4.0055 & 59.8816 & 59.8816 & 59.8816 \\
\end{array}
\]

Table 2 shows the autoindexing results. **Remark.** Since the problem was very difficult, 210 000 tries and 100 iterations were used; using the entropy quasi-distance gave results of the same quality with half the number of tries.

The program runs on any IBM-compatible PC under the MSDOS operating system. It is written in a standard set of Fortran77 and can be compiled by such IBM PC compilers as RMFORT or MS-FORTRAN. No overlays and libraries are used. Up to four phases can be in the sample. The deck includes the *MRIAUAU* program, file MAU.HLP — documentation for *MRIAUAU* and a number of test input files for *MRIAUAU*. The program (all or its parts) is available upon request.

**Concluding remarks**

This work testifies to the efficiency of the method described. Estimates of lattice parameters, obtained by this method, can serve as initial guesses for their refinement by other methods using fuller information about the sample crystals (structure factors etc.).

The author expresses his great gratitude to the physicists Dr A. M. Balagurov and Dr V. V. Chernyshev for their fruitful help in providing a practical test of the method and program described.

**References**