direct-methods solutions are indicated often fail at low resolution (Woolfson & Yao, 1990; Gilmore, Henderson & Bricogne, 1991), making it difficult to identify the more likely solution sets among the 100 that were computed. *SnB* recycling has been formulated to produce a single density map with the likelihood that it is a marked improvement over the best of those computed by multisolution tangent-formula recycling methods.

Concluding remarks

The minimal function has been shown to be a powerful new tool in fragment-recycling applications involving small fragments, large unknown r.m.s. displacement errors in the model and low-resolution data. Although *SnB* fragment-recycling calculations are five to ten times more computer costly than tangent-formula recycling methods, they may provide a solution when the more economic tangent-based solution methods fail.

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Determination of Laue Class from Diffraction Data of Polycrystalline Materials

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Abstract

It has long been believed that superposition of Debye–Scherrer lines caused by symmetry of the reciprocal lattice should suppress true information on Laue symmetry of crystal systems with high symmetry: trigonal, tetragonal, hexagonal and cubic. An interpretation of intensities at superposed reciprocal-lattic points reveals that Laue classes of polycrystalline materials can be identified from con-

centrations of vectors in vector space, that is, from distributions of Patterson peaks. Determination of Laue class enables us to make structural studies of polycrystalline materials with the same process used in single-crystal studies.

Introduction

A diffraction method for polycrystalline materials (Debye & Scherrer, 1916; Hull, 1917) has so far been utilized in various fields of research and industry. The role played by the powder method in identification of crystalline materials is very important. On the other hand, because of the development of single-crystal diffractometers controlled by small electronic computers, structure determination with single-crystal specimens has become the mainstream of structural studies. Structure determination by the Debye–Scherrer method has only been applied to samples for which single crystals with sufficient volume are unavailable, samples for which reduction of extinction effects is necessary and samples having distinct problems.

Recently, the Rietveld method has been developed for structural studies of polycrystalline materials by neutron diffraction (Rietveld, 1967, 1969). Since then, the method has also been applied to studies of crystal structures by X-ray diffraction. Recent progress in developing new equipment, especially that installed at synchrotron-radiation facilities, enables us to measure many more intensities diffracted from a very strong and highly parallel incident beam. The shortening of the time necessary for measurement of diffraction with such strong intensity and improvements in sample preparation techniques have also promoted structural studies of polycrystalline materials.

The process of structure determination with diffraction data of a single crystal consists of: (1) construction of the reciprocal lattice from diffraction angles; (2) determination of Laue class; (3) assignment of possible space groups from observed extinction rules; and (4) determination of phases of $|F_{obs}|$'s. However, the process of structure determination of polycrystalline materials encounters two difficult problems. The first problem to be solved is that of the indexing of a set of observed powder lines; that is, the reconstruction of a three-dimensional reciprocal lattice from the one-dimensional data set. The second is determination of the Laue class from the symmetry of the intensity distribution. There are two possible Laue classes, holohedral and hemihedral, for the crystal systems with trigonal symmetry of symmetries higher than trigonal. Although the first problem was resolved for crystals with symmetry higher than monoclinic (see e.g. Hull & Davey, 1921), it has long been believed

that it is impossible to distinguish hemihedral Laue classes from holohedral ones when only diffraction data for polycrystalline materials are available. However, we have discovered a method to identify Laue classes using symmetry information extracted from diffraction data of polycrystalline materials. We report the details of this discovery in the following sections.

Symmetry of intensity distribution in reciprocal space

Let us consider the reciprocal lattice weighted by $|F(hkl)|^2$ of a single crystal for interpreting symmetry of diffraction of polycrystalline materials. In cases where the symmetry of the crystal system is trigonal or higher than trigonal, unit lengths of two or three reciprocal axes are equal and the plane bisecting the axial angle of those axes is a mirror plane when the symmetry of the weighted reciprocal lattice is holohedral. For hemihedral symmetry, the weights of reciprocal-lattice points are not equal to those of the points corresponding to their mirror image, for example, $|F(hkl)|^2$'s are not equal to $|F(khl)|^2$'s when the Laue class is $4/m$. Hereinafter, we denoted the holohedral symmetry of the reciprocal lattice G and hemihedral symmetry L. L is a subgroup of G in those cases. Since the same coordinate system as the hexagonal one can be chosen for the trigonal system, we may consider that there are three L's and one common G for both systems. If G and L are decomposed into each irreducible system of generators, G has n extra generators g_n that are not included in L. n is usually 1 but is 2 when we compare the numbers of generators of $6/mmm$ and of $\bar{3}$. Thus, $\bar{3}$ can be regarded as tetartohedry of $6/mmm$.

Each crystallite of a polycrystalline sample for diffraction measurement is oriented randomly and its reciprocal-lattice points are distributed on spheres with a common centre at the origin of reciprocal space. Every Debye–Scherrer line is consequently a superposition of diffracted beams from the reciprocal-lattice points at equal distances from the origin. Hereinafter, we discuss only the cases where the superposition is caused by rotation or rotatory inversion symmetry of the reciprocal lattice. The intensity of a peak is therefore a sum of the intensities of the superposed reciprocal-lattice points and the number of superposed equivalent lattice points is the multiplicity factor. For holohedral symmetry G, we can determine possible space groups of the specimen and correct $|F(hkl)|^2$'s from powder diffraction data because the intensities of all reciprocal-lattice points superposed by the symmetry operations are equal. However, those intensities are not equal for hemihedral symmetry L and we cannot obtain correct $|F(hkl)|^2$'s from powder diffraction unless the

crystal structure is known. Therefore, it is impossible for us to know if the observed intensities of an unknown structure are sums of equal intensities (holohedry) or of unequal ones (hemihedry or tetratohedry) and it is impossible to determine its Laue class.

Since a powder diffraction data set in one-dimensional space is essentially a degenerate set of data from three-dimensional space and since Laue symmetries are symmetries in three-dimensional space, the problems are: (1) how to convert the one-dimensional data set to three-dimensional space, that is, how to distribute summed intensities among the reciprocal-lattice points; and (2) how to extract intrinsic information of three-dimensional space from one-dimensional data.

Now, let the Laue symmetry in reciprocal space derived from diffraction of polycrystalline materials be holohedral symmetry and let each reciprocal-lattice point be weighted by $|F_1(hkl)|^2 + ... + |F_{2n}(hkl)|^2$ (n is the number of generators) because the information indicating hemihedral symmetry is lost in intensity data as indicated above. The sum is $2n|F(hkl)|^2$ for holohedral symmetry. For hemihedral or tetratohedral symmetry, the reciprocal lattice weighted by the summed $|F(hkl)|^2$'s can be regarded as a superposition of $2n$ sets of the same reciprocal lattices weighted with the proper $|F(hkl)|^2$'s and each of them are related by n extra generators g_n of holohedral symmetry: $2n$ intensity data sets are superposed upon each other with the relationship caused by the generators g_n. The holohedral symmetry assumed above can therefore be regarded as an apparent symmetry caused by g_n's in cases where the symmetry is hemihedral or tetratohedral. The superposed reciprocal lattice can therefore be called a *composite reciprocal lattice* and the diffraction pattern of the composite reciprocal lattice is a *composite diffraction pattern*. Information on symmetry that can be derived from a composite reciprocal lattice is given in the next section.

Symmetry derived from diffraction of polycrystalline materials

The intensity of the diffracted beam is given by the following relations:

$$I(\mathbf{R}) = \int P(\mathbf{u}) \exp (2\pi i \mathbf{R} \cdot \mathbf{u}) dv_u,$$

where $\mathbf{R}$ denotes a vector in a reciprocal space, $P(\mathbf{u})$ is the Patterson function and dv_u is the volume element in Patterson space.

$P(\mathbf{u})$ is expressed as

$$P(\mathbf{u}) = \int d(\mathbf{r})d(\mathbf{u} + \mathbf{r})dv_r$$

$$= d(\mathbf{r}) * d(\mathbf{r}),$$

where $d(\mathbf{r}) * d(\mathbf{r})$ is the self-convolution of $d(\mathbf{r})$, the

distribution of scatterers of atoms at $\mathbf{r}$. The inverse Fourier transform of $I(\mathbf{R})$ is then

$$\int I(\mathbf{R}) \exp (-2\pi i \mathbf{R} \cdot \mathbf{r}) dv_R = d(\mathbf{r}) * d(\mathbf{r}). \qquad (1)$$

Since the term on the right of the formula is not equal to zero when $\mathbf{r}$ coincides with an interatomic vector, the Fourier transform of a diffraction pattern can be regarded as the vector set of a structure. $I(\mathbf{R})$ is replaced by $I_c(\mathbf{R}) = I_1(\mathbf{R}) + ... + I_{2n}(\mathbf{R})$ for a composite diffraction pattern. Then, the left term is written

$$\int I_c(\mathbf{R}) \exp (-2\pi i \mathbf{R} \cdot \mathbf{r}) dv_R$$

$$= \int I_1(\mathbf{R}) \exp (-2\pi i \mathbf{R} \cdot \mathbf{r}) dv_R + ...$$

$$+ \int I_{2n}(\mathbf{R}) \exp (-2\pi i \mathbf{R} \cdot \mathbf{r}) dv_R. \qquad (2)$$

As $I_{2n}(\mathbf{R}) = I_1(g_n\mathbf{R})$, the $2n$'th integral in the right term of (2) is written with the similar formula given by Ohsumi & Nowacki (1981):

$$\int I_1(g_n\mathbf{R}) \exp (-2\pi i g_n\mathbf{R} \cdot g_n\mathbf{r})(1/|g_n|) dv_{g_n R},$$

where $|g_n| = 1$ and $dv_{g_n R} = dv_R$. Then, the above formula is

$$\int I_1(g_n\mathbf{R}) \exp (-2\pi i g_n\mathbf{R} \cdot g_n\mathbf{r}) dv_R.$$

Consequently, (2) is written

$$\int I_1(\mathbf{R}) \exp -(2\pi i \mathbf{R} \cdot \mathbf{r}) dv_R + ...$$

$$+ \int I_1(g_n\mathbf{R}) \exp (-2\pi i g_n\mathbf{R} \cdot g_n\mathbf{r}) dv_R$$

$$= d_1(\mathbf{r}) * d_1(\mathbf{r}) + ... + d_1(g_n\mathbf{r}) * d_1(g_n\mathbf{r}).$$

Thus, the Fourier transform of the intensity of the composite diffraction pattern is a sum of the constituent $d(\mathbf{r}) * d(\mathbf{r})$'s and no interaction among them occurs.

When a specimen has holohedral symmetry G, its vector set derived from powder diffraction data is therefore a simple superposition of $2n$ holohedral vector sets, while, for a specimen with hemihedral or tetratohedral symmetry L, the derived vector set is a superposition of $2n$ hemihedral or tetratohedral vector sets that are related by n generators g_n. The superposed vector set may be called a *composite vector set*. The extra generators g_n play their symmetrical roles as intrinsic characteristics for G. On the other hand, they do act as extrinsic characteristics for L. Consequently, the vectors between atoms related by g_n's exist in vector sets of G but no vectors related by g_n's can be found in vector sets and composite vector sets of L.

Fig. 1 shows the fundamental sets (the points of the general equivalent positions of $4/mmm$ and $4/m$, respectively, Figs. 2(a) and (b) their vector sets. Fig. 2(c) indicates the composite vector set of $4/m$: one of the two vector sets given in Fig. 2(b) is transformed by the extra generator m parallel to c and then superposed on another one. Since Laue class $4/mmm$

has additional mirror planes parallel to the fourfold axis, the vectors related by those mirror planes occur in the direction perpendicular to the mirrors, that is, along $\langle 100 \rangle$ and $\langle 110 \rangle$. No such vectors occur along those zones in the composite vector set (Fig. 2c). Therefore, if we evaluate Patterson functions $P(u00)$ and $P(uu0)$, we can distinguish whether the Laue class of the specimen is $4/m$ or $4/mmm$.

Fundamental sets of the four Laue classes belonging to hexagonal and trigonal systems are given in Fig. 3 and their vector set and composite vector sets are shown in Fig. 4. Identification of the four Laue classes is possible by the following process. Concentration of vectors along $\langle 100 \rangle$ and $\langle 110 \rangle$ should be examined to distinguish $6/mmm$ from $6/m$ and $\bar{3}$, and concentration along $\langle 100 \rangle$ or $\langle 110 \rangle$ to distinguish $\bar{3}m1$ or $\bar{3}1m$ from the other three Laue classes, $6/mmm$, $6/m$ and $\bar{3}$. Vectors generated by the mirror plane of $6/m$ are concentrated along $\langle 001 \rangle$, while no concentration occurs along $\langle 001 \rangle$ of the vector set of $\bar{3}$.
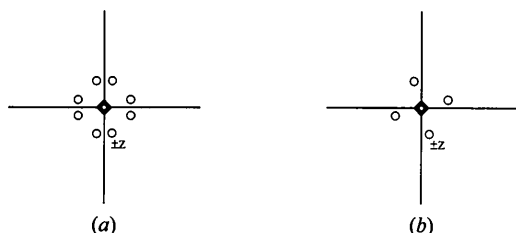
Cubic Laue casses $m\bar{3}$ and $m\bar{3}m$ can be distinguished when the concentrations of the vectors are checked along the directions parallel to $\langle 110 \rangle$. A table was published by Buerger (1959) that lists the characteristics of the vector concentrations of the 230 space groups. We can find details of the vector concentrations characteristic of the point symmetry corresponding to each Laue class and also that of each space group using the table.

We have also to consider the superposition of reciprocal-lattice points caused by other metrical characteristics of a reciprocal lattice with symmetry higher than orthorhombic. Distances of reciprocal-lattice points from the origin are expressed with the

Fig. 1. Distribution of the points at general equivalent positions: (a) 4/mmm; (b) 4/m.

Fig. 3. Distribution of the points at general equivalent positions: (a) 6/mmm; (b) 6/m; (c) $\bar{3}m1$; (d) $\bar{3}$.
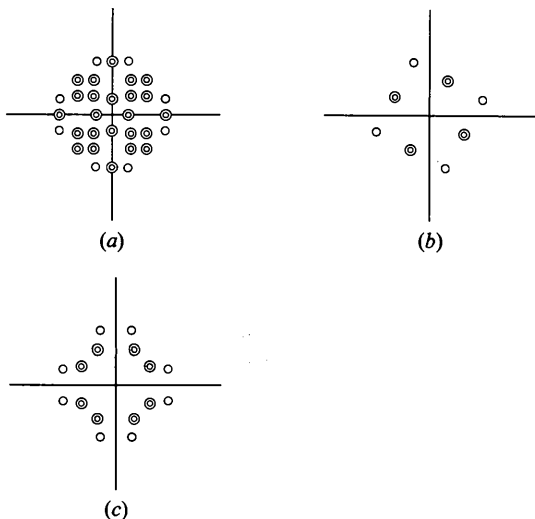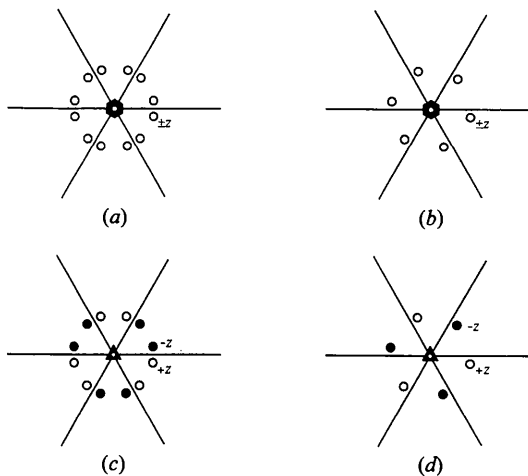

Fig. 2. Distribution of ends of vectors in vector space. The vectors perpendicular to c are shown. Single and double circles indicate double and quadruple weights of the vectors, respectively. The peaks at origins are not shown. (a) Vector set of 4/mmm. (b) Vector set of 4/m. (c) Superposition of the vector sets 4/m by the generator m, a composite vector set.
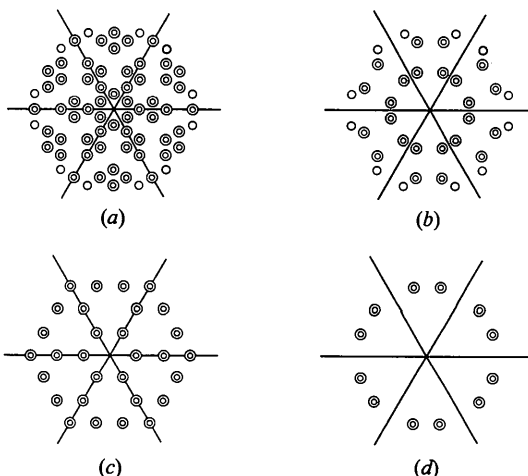

Fig. 4. Distribution of ends of vectors in vector space. The vectors perpendicular to c are shown. Single and double circles indicate double and quadruple weights of the vectors, respectively. The peaks at origins are not shown. (a) Vector set of 6/mmm. (b) Composite vector set of 6/m. (c) Composite vector set of $\bar{3}m1$. (d) Composite vector set of $\bar{3}$.

following relations for those cases:

$$Q^{1/2} = 1/d = (Na^{*2} + l^2 c^{*2})^{1/2}.$$

The term $l^2 c^{*2}$ is neglected for the cubic system. N is $h^2 + k^2 + l^2$ for cubic, $h^2 + k^2$ for tetragonal and $h^2 + hk + k^2$ for trigonal and hexagonal systems, respectively. Since indices h, k and l are integers, different combinations of h, k and l give the same values for N and give rise to superposition of Debye–Scherrer lines (*e.g.* 333 and 511 reflections for the cubic lattice). For evaluation of the Patterson function we should exclude Debye–Scherrer lines that are superpositions of lines caused by such metrical characteristics of the reciprocal lattice.

Determination of Laue classes from diffraction data of polycrystalline materials is thus possible and it is now feasible to study crystal structures of those materials with the same process applied to single crystals.

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SHORT COMMUNICATIONS

Comment on *Enantiomorphism and multiple-beam X-ray diffraction* by Roberto Colella (1994). By HANS BURZLAFF, JOACHIM LANGE and HELMUTH ZIMMERMANN, *Institut für Angewandte Physik, Lehrstuhl für Kristallographie der Universität Erlangen–Nürnberg, Bismarckstrasse 10, D-91054 Erlangen, Germany*

Abstract

For the transition of the structure factors of benzil (B) to benzil (A), Colella [*Acta Cryst.* (1994), A50, 55–57] employs the relation

$$F_A(h, k, l) = F_B(-h-k, k, -l), \qquad (1)$$

i.e., in matrix notation,

$$\begin{aligned}(h, k, l)_A &= H_A \\ &= H_B \begin{pmatrix} -1 & 0 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\ &= H_B A \\ &= (-h-k, k, -l). \end{aligned} \qquad (2)$$

This relation is wrong since det $(A) = 1$. It is *not* a mapping onto an enantiomorph; for the change of handedness, det (A) must be -1. Moreover, matrix A is an element of the related point group 321. Thus, the result is symmetrically equivalent to the starting set of structure factors. As a consequence, all arguments presented on the basis of (1) are invalid.

To avoid confusion, it is convenient to give some further explanations with respect to the problem.

Enantiomorphic objects are defined by their symmetry; their symmetry operations are only proper rotations R, *i.e.* det $(R) =$ 1. The transition from one enantiomorph to the other is described by a pair of matrices (A, S). The application of (A, S) acts on the coordinates by

$$X = (A, S)^{-1} X = A^{-1}(X - S) \qquad (3)$$

and on the symmetry operations by

$$\begin{aligned}(R, T) &= (A, S)(R, T)(A, S)^{-1} \\ &= \{ARA^{-1}, AT + [(E - A)RA^{-1}]S\}. \end{aligned} \qquad (4)$$

For the mapping (A, S), det (A) must be equal to -1 (see above). The simplest matrix of this type is the matrix for a center of inversion. It can be separated from any improper rotation. With this center of symmetry, the transformation relations can be simplified significantly:

$$X_j = S - X_j; \quad R_k = R_k; \quad T_k = (E - R_k)S - T_k. \qquad (5)$$

Here, j counts the atoms in the unit cell and k the symmetry operations of the space group. Inserting these expressions into the structure-factor equation, we get the structure factor F of the enantiomorph:

$$F(H) = F(-H)\exp(2\pi i H S) \qquad (6a)$$