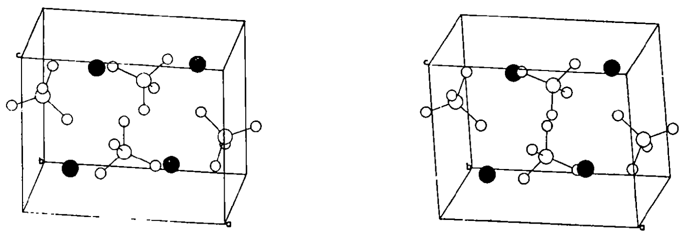

Fig. 1. Stereoscopic diagram of the unit-cell of $SnSO_4$. Atom code as for Fig. 2.

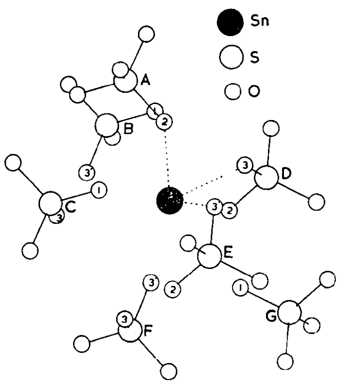

Fig. 2. The environment of the tin atoms in $SnSO_4$.

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A Study on the Diffraction Enhancement of Symmetry

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The condition for the diffraction enhancement of symmetry has been re-examined. From a general expression for the square of the structure amplitude for the structures composed of two kinds of parallel layers, it has been shown that the diffraction enhancement of symmetry may occur much more generally than previously supposed. Two kinds of constituent layers can have arbitrary thickness. It has been shown that the twofold rotational axis previously assumed for the local symmetry of each layer can be replaced by a twofold screw axis, a mirror plane, or a glide plane. The enhancement can take place not only from triclinic symmetry to the monoclinic Laue symmetry, but also from monoclinic symmetry to the orthorhombic Laue symmetry.

Introduction

Rose, Takeda & Wones (1966) reported that a triclinic polytype of mica produced monoclinic X-ray diffraction patterns. Sadanaga & Takeda (1968) called this phenomenon the 'diffraction enhancement of symmetry', which is caused by a particular structure of the crystal. According to the latter authors, a triclinic crystal gives an X-ray diffraction pattern with the monoclinic Laue symmetry if: (1) the structure consists of a stack of parallel layers of two kinds, (2) every layer possesses a twofold rotational symmetry axis in a certain direction parallel to the layer, (3) the layers are stacked in such a way that the origins of all layers are arranged along a straight line perpendicular to the twofold rotational axis, and (4) the thickness of one kind of layer is an integral multiple of that for the other kind of layer. The crystal should have a metrically monoclinic lattice in order to satisfy these conditions.

The present authors have re-examined the problem and extended it more generally. It has been shown that the diffraction enhancement of symmetry can occur more generally than was previously believed.

Formulation of the problem

With a closer examination of model structures, it was revealed that the condition (4) for the thicknesses of layers assumed by Sadanaga & Takeda (1968) is unnecessary for the diffraction enhancement of symmetry. In order to clarify this situation, a general expression for the structure amplitude of the crystals with structures composed of two kinds of layers should be examined in detail.

Let us assume a structure satisfying the following conditions:

(i) the structure is composed of two kinds of parallel layers A and B,

(ii) the origin of each layer lies on a straight line which is not parallel to the layers.

If the c axis is taken along this line, and the a and b axes parallel to the layers, the structure factor of the crystal can be expressed as

$$F(hkl)=\sum_j F_j(hkl)\exp 2\pi i l z_j\,, \tag{1}$$

where $F_j(hkl)$ is the layer structure factor and z_j the z coordinate of the origin of the jth layer. The intensity of diffracted X-rays is proportional to the square of the amplitude,

$$|F(hkl)|^2=\sum_i\sum_j F_i(hkl)F_j(hkl)^*\exp 2\pi i l(z_i-z_j)\,. \tag{2}$$

Now, let us designate by $r_{A(A^mB^n)A}$ the distance between the origins of two A-layers separated by m A-layers and n B-layers in fraction of the length of the c axis, by $r_{A(A^mB^n)B}$ the distance between A and B layers separated by m A-layers and n B-layers, and so forth. These distances are determined by m, n and the kinds of the terminal layers, and do not depend on the stacking sequence of the intervening $m+n$ layers. Suppose that there are N_A A-layers and N_B B-layers in a period along the c axis. If, for example, the number of the pairs A–A separated by m A-layers and n B-layers are $N_{A(A^mB^n)A}$ per unit period, the equation (2) can be rewritten as

$$\begin{aligned}|F(hkl)|^2&=N_A|F_A|^2+N_B|F_B|^2\\
&+\tfrac{1}{2}\sum_m\sum_n N_{A(A^mB^n)A}|F_A|^2\,[\exp 2\pi i l r_{A(A^mB^n)A}\\
&+\exp(-2\pi i l r_{A(A^mB^n)A})]\\
&+\tfrac{1}{2}\sum_m\sum_n N_{B(A^mB^n)B}|F_B|^2\,[\exp 2\pi i l r_{B(A^mB^n)B}\\
&+\exp(-2\pi i l r_{B(A^mB^n)B})]\\
&+\tfrac{1}{2}\sum_m\sum_n N_{A(A^mB^n)B}F_AF_B^*\exp 2\pi i l r_{A(A^mB^n)B}\\
&+\tfrac{1}{2}\sum_m\sum_n N_{B(A^mB^n)A}F_BF_A^*\exp 2\pi i l r_{B(A^mB^n)A}\\
&+\tfrac{1}{2}\sum_m\sum_n N_{A(A^mB^n)B}F_A^*F_B\\
&\times\exp(-2\pi i l r_{A(A^mB^n)B})\\
&+\tfrac{1}{2}\sum_m\sum_n N_{B(A^mB^n)A}F_B^*F_A\\
&\times\exp(-2\pi i l r_{B(A^mB^n)A})\,,\end{aligned} \tag{3}$$

where F_A and F_B are the layer structure factors of A and B layers, respectively, and the summation is taken over all the possible combinations of m and n.

The numbers $N_{A(A^mB^n)B}$ *etc.* depend on the mode of stacking. However, the equality, $N_{A(A^mB^n)B}=N_{B(A^mB^n)A}$, holds for any combination of m and n in any periodical structure, as shown in the Appendix. Substituting this relation into equation (3), we get finally

$$\begin{aligned}|F(hkl)|^2&=N_A|F_A|^2+N_B|F_B|^2\\
&+\sum_m\sum_n N_{A(A^mB^n)A}|F_A|^2\cos 2\pi l r_{A(A^mB^n)A}\\
&+\sum_m\sum_n N_{B(A^mB^n)B}|F_B|^2\cos 2\pi l r_{B(A^mB^n)B}\\
&+\sum_m\sum_n N_{A(A^mB^n)B}(F_AF_B^*+F_A^*F_B)\\
&\times\cos 2\pi l r_{A(A^mB^n)B}\,.\end{aligned} \tag{4}$$

The cosine factors in equation (4) have identical values for l and $-l$. Therefore, the diffraction enhancement of symmetry may occur if there exist appropriate relations between $F_A(hkl)$ and $F_A(hk\bar{l})$, and also between $F_B(hkl)$ and $F_B(hk\bar{l})$.

Examples

Enhancement from triclinic to monoclinic symmetry

To begin with, let us consider a triclinic crystal whose structure satisfies the conditions (i) and (ii) assumed in the derivation of equation (4). The crystal axes are also taken as in the previous section.

(I) Besides the above assumptions, we assume that the structure satisfies the following conditions as in the case treated by Sadanaga & Takeda (1968): (iii) the b axis is perpendicular to the a and c axes, and (iv) each layer possesses a twofold rotational axis along the

b axis as a local symmetry. Then the following equalities hold between the layer structure factors:

$$F_A(hkl)=F_A(\bar{h}k\bar{l}) \text{ and } F_B(hkl)=F_B(\bar{h}k\bar{l}),$$

where the origin of each layer is taken on the twofold rotational axis. We readily obtain from equation (4) the relation,

$$|F(hkl)|=|F(\bar{h}k\bar{l})|.$$

Since the crystal has a metrically monoclinic lattice according to the assumption (iii), the X-ray diffraction pattern of the crystal has obviously the monoclinic Laue symmetry $2/m$. The structure satisfying the conditions assumed above can have monoclinic symmetry as a whole in special cases. It is, however, possible that the layers are stacked in such a way that the resultant structure has no twofold rotational axis of symmetry. In this case, the structure is triclinic, whereas the Laue

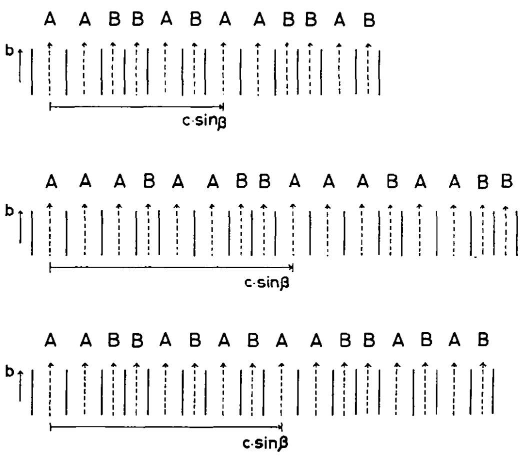

Fig. 1. Some examples of stacking modes which yield triclinic structures giving monoclinic diffraction patterns when each layer has twofold rotational axes of symmetry parallel to the layer. The local twofold axes are indicated by broken lines with arrows.

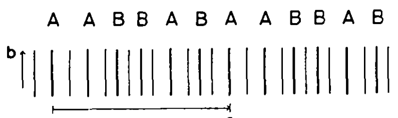

Fig. 2. An example of a triclinic structure which gives monoclinic diffraction patterns when each layer has a mirror plane parallel to the layer. The local mirror planes are indicated by thick lines.

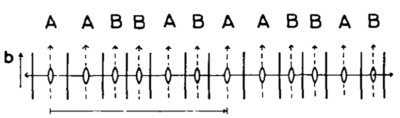

Fig. 3. An example of a monoclinic structure which gives orthorhombic diffraction patterns. The structure has twofold rotational axes perpendicular to the layers. The local twofold rotational axes are indicated by broken lines and open spindles.

symmetry of the diffraction pattern is monoclinic. Some simple examples of such stackings are given in Fig. 1.

(II) If each layer has a twofold screw axis in place of the twofold rotational axis, the following relations hold between the layer structure factors:

$$F_A(hkl)=F_A(\bar{h}k\bar{l}), \quad F_B(hkl)=F_B(\bar{h}k\bar{l}) \quad \text{for } k=\text{even},$$
$$F_A(hkl)=-F_A(\bar{h}k\bar{l}), \quad F_B(hkl)=-F_B(\bar{h}k\bar{l}) \quad \text{for } k=\text{odd}.$$

In either case of k, we obtain the relation $|F(hkl)|=|F(\bar{h}k\bar{l})|$. Therefore, in this case the crystal also gives a strictly monoclinic diffraction pattern, even if the structure is triclinic as the result of a specific mode of stacking sequence.

(III) If the conditions (iii) and (iv) are replaced respectively by the conditions: (iii′) the c axis is perpendicular to the layer, and (iv′) the constituent layers have twofold rotational axes parallel to **c**, we get the relation $|F(hkl)|=|F(\bar{h}\bar{k}l)|$. This relation is, however, not relevant to the diffraction enhancement, since the structure is really monoclinic with the unique axis along **c**. A similar situation occurs when each layer has a mirror plane perpendicular to the layer and parallel to the c axis.

(IV) Next let us assume the following conditions in place of (iii) and (iv): (iii″) the c axis is perpendicular to the layer, and (iv″) each layer possesses a mirror plane parallel to the layer (Fig. 2). Then the following relation holds:

$$F_A(hkl)=F_A(hk\bar{l}), \quad F_B(hkl)=F_B(hk\bar{l}).$$

From equation (4), we obtain the relation $|F(hkl)|=|F(hk\bar{l})|$, and accordingly the symmetry of the diffraction pattern is monoclinic as in the previous cases, even if the stacking sequence of layers is such as results in a triclinic symmetry of the structure. The unique axis is c in this case. We can get similarly a monoclinic diffraction pattern when the mirror plane in each layer is replaced by a glide plane.

It should be noted that, for the symmetry enhancement to occur, both kinds of layers should have the same symmetry. For example, if the symmetry element in the type A layer is a twofold rotational axis while that in the type B layer is a twofold screw axis, $|F(hkl)|$ is not equal to $|F(\bar{h}k\bar{l})|$ owing to the fourth term in equation (4).

Enhancement from monoclinic to orthorhombic symmetry

It is easily seen from equation (4) that the diffraction enhancement of symmetry can be, in principle, observed not only with triclinic crystals but also with monoclinic crystals. If a monoclinic crystal satisfies the following conditions in addition to the conditions (i) and (ii) assumed in the derivation of equation (4), it gives orthorhombic diffraction patterns: (iii‴) the lattice of the crystal is metrically orthorhombic, and (iv‴) both kinds of layers have an orthorhombic local symmetry. It is obvious that each layer can have neither screw axis nor glide plane inclined to the layer.

A simple example of a monoclinic structure giving orthorhombic diffraction patterns is shown in Fig. 3. In this structure each layer has three twofold rotational axes which are mutually perpendicular. However, only the twofold axis perpendicular to the layer is the symmetry element of the whole structure. Accordingly the structure is monoclinic having the unique axis along **c**. There are the relations $F(hkl)=F(hk\bar{l})=F(\bar{h}\bar{k}\bar{l})=F(\bar{h}\bar{k}l)$ between the structure factors. Since each layer has a twofold rotational axis along b passing through the origin of the layer, we have the relations

$$F_A(hkl)=F_A(\bar{h}k\bar{l}),\quad F_B(hkl)=F_B(\bar{h}k\bar{l}).$$

Therefore we obtain the relation $|F(hkl)|=|F(\bar{h}k\bar{l})|$ from equation (4) as in the triclinic case. Accordingly the diffraction pattern of the crystal should have the orthorhombic Laue symmetry *mmm* irrespective of the stacking sequence.

Conclusion

Diffraction enhancement of symmetry may appear more frequently than conceived by Sadanaga & Takeda (1968). No special relation is required in thickness between two kinds of constituent layers to yield the enhancement. Further the twofold rotational axis assumed by Sadanaga & Takeda in each layer can be replaced by a twofold screw axis, a mirror plane, or a glide plane. Diffraction enhancement where a monoclinic crystal produces an orthorhombic diffraction pattern is also possible in principle.

APPENDIX

When two kinds of layer, *e.g.* A and B layers, are stacked with a certain periodicity, an equality holds between the number of the A–B pairs separated by mA and nB layers and that of the B–A per repeating unit. The equality can be easily proved by mathematical induction, as shown below.

The number of a certain kind of pairs is designated by N, and the kind concerned is shown with the subscript of a form such as $A(A^mB^n)B$, $AA(A^mB^n)B$ *etc.* The subscript $A(A^mB^n)B$ is used for the number N of the pairs A–B separated by mA and nB layers, where the stacking sequence of the intervening $m+n$ layers is disregarded. The subscript $AA(A^mB^n)B$ stands for the stacks of $(m+2)A$ and $(n+1)B$ layers, where the first two layers are A and the last one is B. The sequences of the mA and nB layers denoted in parentheses are disregarded as before. The relation to be proved is written with this notation as

$$N_{A(A^mB^n)B}=N_{B(A^mB^n)A}. \qquad \text{(A 1)}$$

If the numbers of A and B layers are N_A and N_B per repeating unit, the following relations must exist:

$$N_A=N_{AA}+N_{AB}=N_{AA}+N_{BA}.$$

Accordingly,

$$N_A(A^0B^0)=N_B(A^0B^0)_A.$$

This means that equation (A 1) holds when $m=n=0$.

Now let us assume that equation (A 1) holds for a certain combination of m and n. Then we will show that equation (A 1) also holds when m is replaced by $m+1$. From the definition the following relations are obvious:

$$\begin{aligned}N_{A(A^{m+1}B^n)B}&=N_{AA(A^mB^n)B}+N_{AB(A^{m+1}B^{n-1})B}\\&=N_{A(A^mB^n)B}-N_{BA(A^mB^n)B}+N_{B(A^{m+1}B^{n-1})B}\\&\quad-N_{BB(A^{m+1}B^{n-1})B}\end{aligned}$$

and

$$\begin{aligned}N_{B(A^{m+1}B^n)A}&=N_{B(A^mB^n)AA}+N_{B(A^{m+1}B^{n-1})BA}\\&=N_{B(A^mB^n)A}-N_{B(A^mB^n)AB}+N_{B(A^{m+1}B^{n-1})B}\\&\quad-N_{B(A^{m+1}B^{n-1})BB}.\end{aligned}$$

Therefore,

$$\begin{aligned}&N_{A(A^{m+1}B^n)B}-N_{B(A^{m+1}B^n)A}\\&\quad=N_{A(A^mB^n)B}-N_{BA(A^mB^n)B}\\&\quad\quad-N_{BB(A^{m+1}B^{n-1})B}-N_{B(A^mB^n)A}\\&\quad\quad+N_{B(A^mB^n)AB}+N_{B(A^{m+1}B^{n-1})BB}.\end{aligned}$$

From the assumption we get,

$$\begin{aligned}&N_{A(A^{m+1}B^n)B}-N_{B(A^{m+1}B^n)A}\\&\quad=-N_{BA(A^mB^n)B}-N_{BB(A^{m+1}B^{n-1})B}\\&\quad\quad+N_{B(A^mB^n)AB}+N_{B(A^{m+1}B^{n-1})BB}\\&\quad=-N_{B(A^{m+1}B^n)B}+N_{B(A^{m+1}B^n)B}\\&\quad=0.\end{aligned}$$

i.e.

$$N_{A(A^{m+1}B^n)B}=N_{B(A^{m+1}B^n)A}.$$

In the same way we can obtain the relation,

$$N_{A(A^mB^{n+1})B}=N_{B(A^mB^{n+1})A}.$$

Consequently equation (A 1) should hold for any combination of m and n.

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