134. *On the Diffraction Enhancement of Symmetry for Two-Layer Structures*

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It had long been a general belief in the field of X-ray crystallography that the symmetry of the diffraction pattern of a crystal is the same as either the point-group symmetry of the crystal or that derived by adding a centre of inversion to it, until Ito (1950) showed that for certain cases some sets of X-ray reflections from a crystal exhibit, besides the centrosymmetry due to the Friedel law, a symmetry higher than that of the crystal. In 1951, Ramsdell and Kohn found that a new type of SiC, 10H, then discovered shows an X-ray pattern hexagonal in symmetry, while its crystal structure is definitely trigonal. They explained this disagreement as due to a special mode of layer-stacking peculiar to this and some other SiC polytypes (Ramsdell and Kohn, 1951).

Ross, Takeda and Wones (1966) reported that the triclinic mica polytype $10Tc_3$ produces an X-ray pattern monoclinic in symmetry. Sadanaga and Takeda (1968) then carried out a theoretical study of the conditions for a triclinic crystal to produce a monoclinic diffraction pattern, established that this is indeed possible for certain mica polytypes, proposed to call this phenomenon the '(total) diffraction enhancement of symmetry', and also discussed about some other types of enhancement such as quasi and partial. The type of triclinic structure which they showed as having the property of producing a diffraction pattern completely monoclinic in symmetry and which corresponds to the case of the mica polytype $10Tc_3$ was the one satisfying the following conditions:

(1) It consists of a stack of parallel layers of two kinds,

(2) Every layer possesses a twofold rotational symmetry whose axis is parallel to the layer and to a direction to be taken as the b axis of the crystal,

(3) These layers are so juxtaposed that their respective origins are arranged along a line perpendicular to the b axis. Therefore, if the c axis is taken parallel to this line and the a axis parallel to the layer and perpendicular to the b axis, a set

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of metrically monoclinic axes will be established in the structure, and

(4) The thickness of the layer of one of the kinds is an integral multiple of that of the layer of the other kind.

Condition (4) was introduced by these authors so as to treat conveniently the cases of mica polytypes they were then concerned with, but it was later revealed by Marumo and Saito (1972) that this condition is not necessary. These authors proved a theorem that if two kinds of layer A and B are stacked together with a certain periodicity, an equality holds between the number of the A–B layer-couples separated by mA and nB layers (m and n, arbitrary integers) and that of the B–A couples with the same distance of separation, provided these numbers are counted per repeat period of the layer-stacking. They showed that this theorem assures monoclinicity for the diffraction pattern of a triclinic crystal which satisfies the first three of the above conditions. This theorem will hereafter be referred to as the 'layer-couple theorem' or the 'LC-theorem' for short, and the combination of conditions (1), (2) and (3) as the 'two-layer condition' or the 'TL-condition' for short.

Iwasaki (1972) made a systematic survey on various structures which are capable of producing a diffraction pattern of enhanced symmetry and classified such structures into four types.

Through all these investigations, it has now become evident that the classical corespondence between the point-group symmetry of the crystal and its Laue symmetry no longer holds for certain polysynthetic structures, though only a very few actual examples have been known of this phenomenon. In fact, examples of this are generally difficult to obtain; a straightforward application of the usual methods of structure determination is bound to fail to achieve its purpose because of the disagreement between the diffraction symmetry and the point-group symmetry of the crystal under examination.

All the above studies of the diffraction enhancement of symmetry were carried out with the aid of the Fourier transform method. However, we believe that a clearer view will be obtained if we consider the examples, both real and imaginary, in the light of the relationship between the symmetry of the crystal structure and that of its vector set (Ohsumi *et al.*, 1972). Obviously, a triclinic crystal which gives rise to the diffraction enhancement to a monoclinic symmetry is the one that is triclinic in its structure and monoclinic in its vector set. We present in the following the interpretation of two-layer structures from this view point and a type of probable layer-stacking which requires an extension for (3) of the TL-condition.

If N couples of A–B with a certain distance of separation are found in a crystal satisfying the TL-condition, then the LC-theorem gives N couples of B–A with the same distance of separation and enables us to establish a one-to-one correspondence between such A–B and B–A couples. Because of the TL-condition, a one-to-one correspondence can also be found between interatomic vectors in one of such A–B couples and those in the corresponding B–A couple in such a way that every vector in A–B and the corresponding one in B–A are related with each other by a twofold rotation operation, and vice versa, as shown in Fig. 1. Therefore, the symmetry of the vector set of a two-layer structure satisfying the TL-condition is always monoclinic. It should also be noted that the TL-condition is to secure such twofold rotation operations in the structure, and it serves this purpose equally well if some gaps and overlappings of layers appear in the layer-stacking.

Next, let us consider an alternating stack of layers of two kinds which satisfies the TL-condition, and take an arbitrary A-B couple whose members are denoted by A_0 and B_0 as in

$$\cdots \mathbf{A}\ \ \mathbf{B}_0'\ \ \mathbf{A}\ \ \mathbf{B}_2'\ \ \mathbf{A}\ \ \mathbf{B}_1'\ \ \mathbf{A}_0\ \ \mathbf{B}_1\ \ \mathbf{A}_2'\ \ \mathbf{B}_2\ \ \mathbf{A}_1'\ \ \mathbf{B}_0\ \ \mathbf{A}_1\ \ \mathbf{B}\ \ \mathbf{A}_2\ \ \mathbf{B}\ \ \mathbf{A}_0'\ \ \mathbf{B} \cdots, \tag{I}$$

where some of other layers are also specified to meet the convenience of our subsequent identification of them. Now, suppose that A_0 and B_0 are taken off from (I) and that the removal of the A_0–B_0 couple is repeatedly carried out at certain regular intervals. It will then be easy to understand that this removal of the A_0–B_0 couples destroys

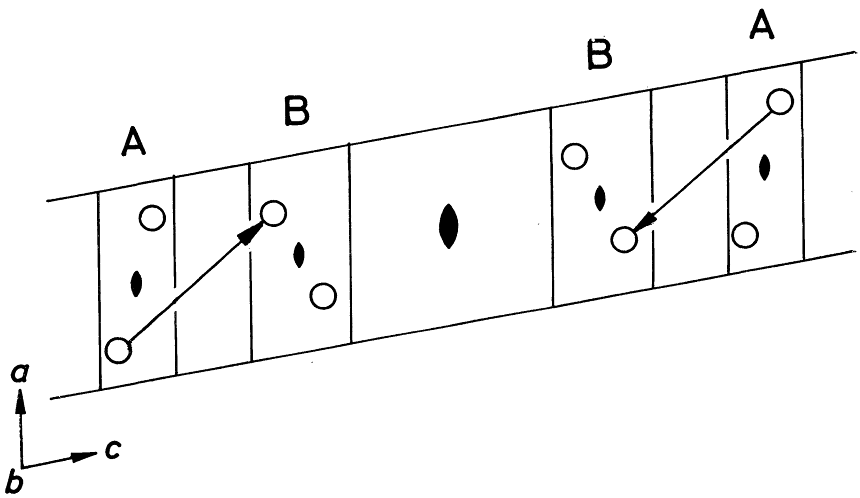

Fig. 1. Interatomic vectors related by a twofold rotation operation in a two-layer structure satisfying the TL-condition.

other couples in pairs, such as $\{A_0–B_1; B'_1–A_0\}$, $\{A_0–B_2; B'_2–A_0\}$, $\cdots$, $\{B_0–A_1; A'_1–B_0\}$, $\{B_0–A_2; A'_2–B_0\}$, $\cdots$. However, since the pairs of couples involving $A_0–B_0$, namely, $\{A_0–B_0; B'_0–A_0\}$ and $\{B_0–A'_0; A_0–B_0\}$, for example, have $A_0–B_0$ in common, the removal of one $A_0–B_0$ couple will result in the abolition of two couples of the $B–A$ type and will thus invite an unbalance between the number of $A–B$ couples with the distance of $A_0–B_0$ separation and that of the corresponding $B–A$ couples. Accordingly, the LC-theorem does not hold for

$$\cdots \mathbf{ABABAB}\times\mathbf{BABA}\times\mathbf{ABABAB}\times\mathbf{BABA}\times\mathbf{ABAB}\cdots, \quad \text{(II)}$$

where $\times$ indicates a vacant position.

Then, if we try to recover those $B–A$ couples excessively abolished, by preparing, at an arbitrary position, another layer-stack (III) which consists only of the $B–A$ couples and has its axes parallel to and its *ca* plane in coincidence with the respective ones of (II), namely as

$$\begin{array}{ll}\cdots \mathbf{ABABAB}\times\mathbf{BABA}\times\mathbf{ABABAB}\times\mathbf{BABA}\times\mathbf{ABAB}\cdots & \text{(II)}\\ \cdots\times\times\times\times\mathbf{B}\times\times\times\times\mathbf{A}\times\times\times\times\times\times\mathbf{B}\times\times\times\times\mathbf{A}\times\times\times\times\times\times\cdots, & \text{(III)}\end{array}$$

and if we add the numbers of layer-couples in (III) to the respective ones in (II), we shall realize that the LC-theorem becomes to hold for this composite system and, therefore, the union of the set of interatomic vectors in (II) and the set of those in (III) exhibits a twofold rotational symmetry about the *b* axis.

Moreover, if we look upon the combination of (III) with (II) as making up one structure, we shall recognize that the vector subset of all such interatomic vectors as between (II) and (III) also displays a twofold rotational symmetry, because every couple of the B (II)–A (III) type is related with one of the A (II)–B (III) type by a twofold rotation operation, every couple of the A (II)–A (III) type is related with itself by a twofold rotation operation, and every couple of the $\times$ (II)–A (III) type is digonally symmetric due to the digonal symmetry of A and B themselves. It is also to be noted that the digonal symmetry of the above vector subset also holds if every twofold rotation referred to above is replaced by a screw operation, that is, if the *ca* plane of (III) is above that of (II) by $\boldsymbol{b}/2$ (Cf. Matsumoto *et al.*, 1973). Though a lateral shift of (III) with respect to (II) does not interfere with the symmetry of the vector subset, the resulting structure is in general highly improbable because of the superimpositions of layers at some positions and vacancies at other positions. The only reasonable models of structure to be derived will be those without shift as shown in Fig. 2 (a) in which

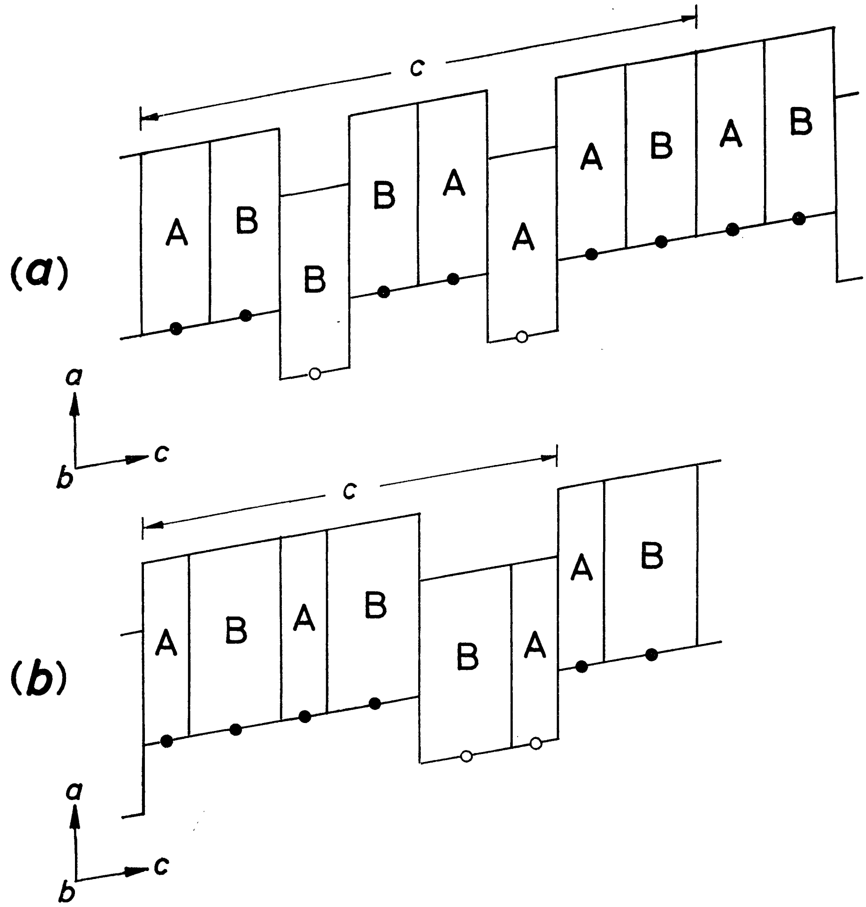

Fig. 2. Example of the two-layer triclinic structures derived from an alternating layer-stack and giving a monoclinic diffraction pattern. All the origins of layers represented by an open circle lie either in the *ac* plane in which all those origins represented by a black circle lie, or on a level above the plane by $b/2$. (a) A and B are in equal thickness ($ABBBAAAB$). (b) A is adjacent to B in the A–B couple ($ABABBA$).

A and B are in equal thickness, and in Fig. 2 (b) in which the A–B couple is a pair of AB adjacent to each other.

Thus, we conclude that (3) of the TL-condition must be augmented with:

(3′) If a structure is such as derived from an alternating layer-stack by reversing an A–B couple into B–A, where A and B are in equal thickness or A and B in the couple are adjacent to each other, and by repeating this reversal at certain regular intervals, all the reversed couples may be shifted *en bloc* by an arbitrary distance along the a axis in one direction and by 0 or $\boldsymbol{b}/2$ along the b axis.

The structures thus arrived at will in general be triclinic, but their X-ray diffraction patterns are always completely monoclinic in symmetry.

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