

On the Diffraction Enhancement of Symmetry

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Diffraction symmetry is in general specified by the point group of a crystal. However, there are some exceptional cases in which the diffraction symmetry becomes, other than as a result of Friedel's law, higher than the point-group symmetry (diffraction enhancement of symmetry). Using a general expression for the square of the structure amplitude, the necessary conditions for the diffraction enhancement have been systematically investigated for the following four kinds of structures: (1) crystals composed of essentially the same substructures, (2) different substructures which have the same symmetry, (3) substructures with the same point group and different space groups, and (4) substructures with isomorphic point groups. It has been shown that symmetry enhancement like $4/m$, $4/mmm$, $\bar{3}m1$ ($\bar{3}1m$), $6/m$ or $6/mmm$ does occur in addition to $2/m$ or mmm as suggested by Sadanaga & Takeda [*Acta Cryst.* (1968) B24, 144] and by Marumo & Saito [*Acta Cryst.* (1972) B28, 867]

Introduction

The diffraction symmetry or Laue symmetry is in general, except for the addition of a centre of inversion, uniquely determined by the point group of a crystal. Let us suppose that a position \mathbf{x}' in a unit cell is generated by the operation of a 3×3 rotation matrix R on a position \mathbf{x} , followed by the addition of a translation vector \mathbf{t} :

$$\mathbf{x}' = R\mathbf{x} + \mathbf{t}. \quad (1)$$

Then it can be shown that

$$F(\mathbf{h}') = F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{t}), \quad (2)$$

$$\mathbf{h}' = \tilde{R}\mathbf{h}, \quad (3)$$

where $F(\mathbf{h})$ is the structure amplitude of the reflexion with index \mathbf{h} , and \tilde{R} is the transposed matrix of R (Waser, 1955).^{*} Equations (2) and (3) state that symmetry-equivalent reflexions are produced by the rotational part (including improper rotations) of the symmetry operation (1). Therefore, the distribution of equivalent reflexions is determined from the point group of the crystal alone. When Friedel's law holds, the Laue group becomes isomorphic with the direct product of the inherent point group and the group $\bar{1}$.

In this paper we consider the cases in which the peculiarity of the atomic arrangement causes a complete hypersymmetry in the diffraction patterns. Such a structure has been described, for example, for one of the polytypes of silicon carbide (SiC, type 10H; Ramsdell & Kohn, 1951). According to Ramsdell & Kohn, this crystal consists of two substructures, namely that composed of silicon atoms and that of carbon atoms. These substructures have the symmetry $\bar{6}m2$ and are separated by $3/40$ along the c axis. The

space group of this crystal is $P3m1$, while the apparent Laue symmetry is $6/mmm$.

Sadanaga & Takeda (1968) have shown that some triclinic crystals consisting of a stack of parallel layers of two kinds give X-ray diffraction patterns with monoclinic symmetry. They called such a phenomenon 'diffraction enhancement of symmetry'. Their theory has recently been re-examined by Marumo & Saito (1972) for similar structures. These authors have shown that some monoclinic crystals also may produce orthorhombic diffraction patterns.

The aim of the present paper is to deal with the theory of the diffraction enhancement of symmetry in a more general way and to show that symmetry enhancement like $4/m$, $4/mmm$, $\bar{3}m1$ ($\bar{3}1m$), $6/m$ or $6/mmm$ does occur in addition to $2/m$ or mmm as suggested by previous authors.

Classification of the structures

Let us consider the crystals composed of several substructures. The structure amplitude F can be written in the form:

$$F = \sum_p F_p \cdot \exp(2\pi i \mathbf{h} \cdot \mathbf{u}_p), \quad (4)$$

where F_p is the component of F from the p th substructure, and \mathbf{u}_p is the vector from the origin of the crystal to that of the p th substructure. Hence

$$I = \sum_p I_p + \frac{1}{2} \sum_{p \neq q} [F_p F_q^* \exp\{2\pi i \mathbf{h} \cdot (\mathbf{u}_p - \mathbf{u}_q)\} + F_p^* F_q \exp\{-2\pi i \mathbf{h} \cdot (\mathbf{u}_p - \mathbf{u}_q)\}], \quad (5)$$

where I and I_p denote $|F|^2$ and $|F_p|^2$ respectively. The summation in the second term is taken over all the possible combinations of p and q , except for $p = q$.

The first term of equation (5) gives diffraction patterns consistent with the lowest symmetry among the substructures. The symmetry of the crystal is generally lowered by the overlap of the substructures,

^{*} $\mathbf{x} = (xyz)$, xyz as fractions; $\mathbf{h} = (hkl)$.

and the whole diffraction symmetry is governed by the remaining part of equation (5). If this term is either zero or of the same symmetry as the first term, the Laue symmetry is specified by the point group of the substructures, irrespective of the crystal symmetry. We will examine this second term for four kinds of structures separately:

- Type 1. Crystals composed of essentially the same substructures.
 Type 2. Crystals composed of different substructures with the same symmetry.
 Type 3. Crystals composed of two substructures with the same point group and different space groups.
 Type 4. Crystals composed of two substructures with different but isomorphic point groups.

The following two conditions are assumed throughout the present paper:

(I) The lattice parameters must be consistent with the apparent Laue symmetry which might be enhanced. For example, if a triclinic crystal exhibits the Laue symmetry of $2/m$, two of the angles α , β and γ must be 90° .

(II) Friedel's law holds. This condition is immaterial for the cases of types 1, 2 and 3, but it plays an essential role in the case of type 4.

Type 1. Crystals composed of essentially the same substructures

In the first place let us suppose that all substructures have the same symmetry. (The symmetry of some substructures may be higher than that of the others. In that case, the space group of the former must be a supergroup of those of the latter. The following discussion concerns the lowest symmetry in the substructures.) If one of the symmetry elements in the substructures is represented by the operation (R, \mathbf{t}) , we have

$$F_p(\mathbf{h}') = F_p(\mathbf{h}) \cdot \exp(-2\pi i \mathbf{h} \cdot \mathbf{t}), \quad (6)$$

where $\mathbf{h}' = \tilde{R}\mathbf{h}$. Now let us define the quantity $\varphi(\mathbf{h})$ by

$$\varphi(\mathbf{h}) = \sum_{p \neq q} F_p(\mathbf{h}) F_q^*(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{u}_{pq}) + \text{complex conjugate}, \quad (7)$$

where $\mathbf{u}_{pq} = \mathbf{u}_p - \mathbf{u}_q$. Inserting the expression

$$F_p(\mathbf{h}) = A_p + iB_p \quad (8)$$

into equation (7), we get

$$\varphi(\mathbf{h}) = \sum_{p \neq q} [2(A_p A_q + B_p B_q) \cos 2\pi \mathbf{h} \cdot \mathbf{u}_{pq} + 2(A_p B_q - B_p A_q) \sin 2\pi \mathbf{h} \cdot \mathbf{u}_{pq}]. \quad (9)$$

Similarly we have, by using equation (6),

$$\varphi(\mathbf{h}') = \sum_{p \neq q} [2(A_p A_q + B_p B_q) \cos 2\pi \mathbf{h}' \cdot \mathbf{u}_{pq} + 2(A_p B_q - B_p A_q) \sin 2\pi \mathbf{h}' \cdot \mathbf{u}_{pq}], \quad (10)$$

where A_p , B_p etc. refer to the index \mathbf{h} , not \mathbf{h}' . Therefore, if following two conditions are satisfied, $\varphi(\mathbf{h})$ and $\varphi(\mathbf{h}')$

will have the same value:

$$(I) \quad \sum_{p \neq q} (A_p B_q - B_p A_q) \sin 2\pi \mathbf{h} \cdot \mathbf{u}_{pq} = 0 \quad \text{for any } \mathbf{h}, \quad (11)$$

$$(II) \quad \cos 2\pi \mathbf{h} \cdot \mathbf{u}_{pq} = \cos 2\pi \mathbf{h}' \cdot \mathbf{u}_{pq} \quad \text{for any } p, q. \quad (12)$$

In such a case, we obtain from equation (5) that

$$I(\mathbf{h}) = I(\mathbf{h}') \quad (13)$$

and the diffraction enhancement of symmetry can occur.

The translational part of the symmetry operation does not appear in the expression (10). Accordingly, in the present case, the problem of diffraction enhancement can be discussed on the basis of the point group of the substructures. If different symmetries are introduced, a space-group consideration will become important.

Since a full analysis of equations (11) and (12) is complicated, we assume first that

$$A_p B_p - B_q A_q = 0 \quad (14)$$

or,

$$B_p/A_p = B_q/A_q \quad (14')$$

for any combination of p and q . Structures which satisfy equations (14) or (14') will be called here 'type 1'. Now equation (14') means that

(i) all F_p 's have the same or the opposite phase, or
 (ii) all F_p 's are real.

Some of them may be zero. Examples of the structures corresponding to the case (i) are:

$$(i-a) \quad F_p = F_1 \text{ for any } p, \quad (15)$$

or

$$(i-b) \quad F_p = f_p G \text{ for any } p, \text{ where } G \text{ is constant.} \quad (15')$$

The case (i-a) is that when all substructures are completely identical. The case (i-b) corresponds to the structure in which the p th substructure consists of atoms of only one kind with form factor f_p , and all substructures have the same geometrical configuration. G is the geometrical structure factor. Polytypes of ZnS, CdS or SiC may give real examples. The structures which satisfy the conditions such as

$$(i-a') \quad F_p = c_p \cdot F_1 \text{ for any } p, \quad (15'')$$

or

$$(i-b') \quad F_p = c_p f_p G \text{ for any } p \quad (15''')$$

are also classified in this category if c_p is real (including zero). The case (ii) is trivial since centrosymmetric substructures can only form composite crystals consistent with the Laue symmetry, as is seen below.

Since the condition (12) is of great importance for the occurrence of diffraction enhancement in the structures of other types as well, it will now be examined in detail for all possible symmetries of the substructures.

Three components of \mathbf{u}_p and \mathbf{u}_{pq} along the crystallographic axes are hereafter designated by u_p, v_p, w_p and u_{pq}, v_{pq}, w_{pq} respectively.

(1) *General (symmetry $\bar{1}$)*

First, let us suppose that the \mathbf{u}_{pq} 's are quite arbitrary. In this case the condition (12) is satisfied only if

$$\mathbf{h} = \pm \mathbf{h}'. \quad (16)$$

This relation merely represents the usual Friedel's law. The crystal is triclinic, and the Laue symmetry will be $\bar{1}$.

(2) *Apparent Laue symmetry $2/m$*

Suppose that substructures have monoclinic symmetry. For convenience, the c axis is taken to be the uni-

que axis (the first setting). Then,

$$I_p(hkl) = I_p(hk\bar{l}) = I_p(\bar{h}kl) = I_p(\bar{h}k\bar{l}). \quad (17)$$

The enhancement condition (12), therefore, becomes

$$\begin{aligned} \cos 2\pi(hu_{pq} + kv_{pq} + lw_{pq}) \\ = \cos 2\pi(hu_{pq} + kv_{pq} - lw_{pq}) \end{aligned} \quad (18)$$

for any combination of p and q . Equation (18) requires either

$$(i) \quad u_p = v_p = 0, \text{ and } w_p \neq 0 \quad (19)$$

or

$$(ii) \quad w_p = 0; \text{ and } u_p, v_p \text{ arbitrary.} \quad (20)$$

When equation (19) or equation (20) is satisfied, it follows that

$$I(hkl) = I(hk\bar{l}) \quad (21)$$

even if the whole structure is triclinic.

The case (i) is that when the substructures are shifted along the unique axis relative to one another. If the point group of the substructures, P_s , is either 2 or $2/m$, that of the crystal, P , becomes 2. If P_s is m , then P will obviously be in general 1, while the diffraction symmetry remains $2/m$. This case corresponds to the diffraction enhancement of symmetry. The case (ii) is that when the substructures are shifted perpendicular to the unique axis. If P_s is either m or $2/m$, P becomes m . If P_s is 2, then P will be 1 and the crystal will produce a monoclinic hypersymmetry in its diffraction patterns.

In Fig. 1 a simple but typical example is illustrated. The local symmetry P_s in this case is 2. The space group of the crystal is $P1$ and the Laue symmetry is $2/m$.

(3) *Laue symmetry mmm*

If the substructures have orthorhombic symmetry, we have

$$I_p(hkl) = I_p(\bar{h}kl) = I_p(h\bar{k}l) = I_p(hk\bar{l}). \quad (22)$$

Consequently, if

$$\begin{aligned} \cos 2\pi(hu_{pq} + kv_{pq} + lw_{pq}) \\ = \cos 2\pi(-hu_{pq} + kv_{pq} + lw_{pq}) \\ = \cos 2\pi(hu_{pq} - kv_{pq} + lw_{pq}) \\ = \cos 2\pi(hu_{pq} + kv_{pq} - lw_{pq}), \end{aligned} \quad (23)$$

that is, if one of the following three conditions is satisfied, the Laue symmetry will be mmm irrespective of P :

$$(i) \quad u_p \neq 0, \quad v_p = w_p = 0 \quad (24-1)$$

$$(ii) \quad v_p \neq 0, \quad u_p = w_p = 0 \quad (24-2)$$

$$(iii) \quad w_p \neq 0, \quad u_p = v_p = 0. \quad (24-3)$$

When P_s is 222 and one of equations (24) is satisfied, P becomes 2. When P_s is $mm2$ (with the polar c axis), P is m if case (i) or case (ii) holds, and $mm2$ if case (iii) holds. The first three cases correspond to the diffrac-

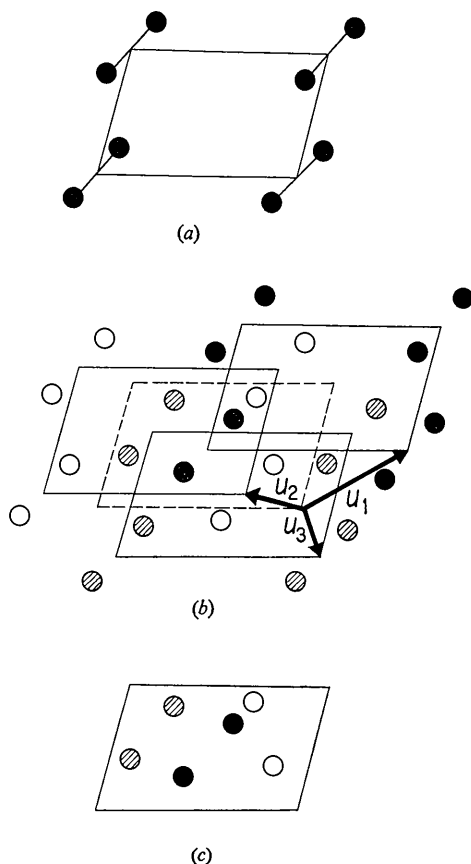


Fig. 1. A simple example of the structure with space group $P1$ which gives the diffraction symmetry of $2/m$. (a) Basic substructure with the symmetry 2. The twofold rotation axis is perpendicular to the plane of the paper. In order to remove the symmetry m , several atoms are assumed to be stacked along the twofold axis. (b) Overlap of three substructures. $\mathbf{u}_1, \mathbf{u}_2$ and \mathbf{u}_3 are perpendicular to the local twofold axes. Black, white and shaded circles compose the substructures 1, 2 and 3 respectively. If each substructure consists of only one kind of atom, those in 1, 2 and 3 may be different. Dotted lines indicate a unit cell of the composite crystal. (c) A unit cell of the composite structure. The space group is $P1$, while the Laue symmetry is $2/m$.

tion enhancement of symmetry. If P_s is mmm , P will be $2mm$, $m2m$ or $mm2$ according to (i), (ii) or (iii) respectively.

(4) Laue symmetry $4/m$

The symmetry group $4/m$ is a supergroup of $2/m$. The substructures with the point groups 4 , $\bar{4}$ or $4/m$ give intensity relations of the type

$$I_p(hkl) = I_p(\bar{h}\bar{k}\bar{l}) \quad (25)$$

as well as those in equation (17). The enhancement condition (12) becomes

$$\begin{aligned} \cos 2\pi(hu_{pq} + kv_{pq} + lw_{pq}) \\ = \cos 2\pi(ku_{pq} - hv_{pq} + lw_{pq}) \end{aligned} \quad (26)$$

as well as equation (18). Therefore,

$$u_p = v_p = 0, \quad w_p \neq 0. \quad (27)$$

If P_s is either 4 , $\bar{4}$ or $4/m$ and the substructures are overlapped in such a way that the condition (27) is satisfied, P will be 4 , 2 or 4 respectively. Thus, monoclinic crystals with the local symmetry $\bar{4}$ may produce tetragonal diffraction patterns of the symmetry $4/m$.

(5) Laue symmetry $4/mmm$

The local symmetry of 422 , $4mm$, $\bar{4}2m$ ($\bar{4}m2$) or $4/mmm$ requires the diffraction symmetry of the type

$$I_p(hkl) = I_p(khl). \quad (28)$$

It can be easily shown that the enhancement condition is given again by equation (27). Conversely, if equation (27) is valid, it follows immediately that

$$I(hkl) = I(khl). \quad (29)$$

When P_s is 422 , $\bar{4}2m$, $\bar{4}m2$, $4mm$ or $4/mmm$, P will be 4 , $mm2$, $mm2$, $4mm$ or $4mm$ respectively. The first three cases correspond to the diffraction enhancement. Orthorhombic crystals with point group $mm2$ and tetragonal crystals with 4 may give the diffraction symmetry $4/mmm$.

(6) Laue symmetry $\bar{3}$

Let us consider the substructures which give an intensity relation of the type

$$I_p(hkl) = I_p(kil) = I_p(ihl) \quad (30)$$

where $i = -h - k$ (hexagonal setting of the unit cell). The enhancement condition in this case becomes as follows:

$$\begin{aligned} \cos 2\pi(hu_{pq} + kv_{pq} + lw_{pq}) \\ = \cos 2\pi(ku_{pq} + iv_{pq} + lw_{pq}) \\ = \cos 2\pi(iu_{pq} + hv_{pq} + lw_{pq}). \end{aligned} \quad (31)$$

Hence

$$u_p = v_p = 0, \quad w_p \neq 0. \quad (32)$$

However, if the local symmetry P_s is either 3 or $\bar{3}$, and if the condition (32) is satisfied, the composite crystal

will have the symmetry 3 . Therefore, this case does not correspond to the hypersymmetry in the diffraction patterns.

(7) Laue symmetry $\bar{3}m1$, $\bar{3}1m$

Again we choose a hexagonal unit cell. Since both $\bar{3}m1$ and $\bar{3}1m$ are supergroups of 3 , the condition (32) must hold if the diffraction symmetry is enhanced. The symmetry of the substructures requires

$$\text{for } \bar{3}m1: \quad I_p(hkl) = I_p(khl), \quad (33-1)$$

$$\text{for } \bar{3}1m: \quad I_p(hkl) = I_p(kh\bar{l}). \quad (33-2)$$

If the condition (32) holds, the relations

$$I(hkl) = I(khl) \quad (34-1)$$

and

$$I(hkl) = I(kh\bar{l}), \quad (34-2)$$

will be satisfied for $\bar{3}m1$ and $\bar{3}1m$ respectively. When P_s is 321 or 312 , P becomes 3 and the diffraction patterns will show a hypersymmetry. If P_s is either $3m1$, $31m$, $\bar{3}m1$ or $\bar{3}1m$, the crystal symmetry will be $3m1$, $31m$, $3m1$ or $31m$ respectively, and the diffraction symmetry will not be enhanced.

(8) Laue symmetry $6/m$

The symmetry of the substructures gives intensity relations of the type

$$I_p(hkl) = I_p(hk\bar{l}) \quad (35)$$

as well as those in equation (30). The enhancement condition is given again by condition (32). When P_s is either 6 or $6/m$, the crystal symmetry will be 6 . If P_s is $\bar{6}$, then P becomes 3 and the crystal exhibits hypersymmetry in the diffraction patterns.

(9) Laue symmetry $6/mmm$

The symmetry of the substructures requires

$$I_p(hkl) = I_p(khl) \quad (36)$$

as well as equations (30) and (35). The enhancement condition is given also by condition (32). Conversely, if condition (32) holds, the relations

$$I(hkl) = I(khl) = I(hk\bar{l}) = I(kil) \text{ etc.} \quad (37)$$

are clearly satisfied. If P_s is 622 , $\bar{6}2m$ or $\bar{6}m2$, the crystal symmetry becomes 6 , $31m$ or $3m1$ respectively. These cases correspond to diffraction enhancement. The case of $P_s = \bar{6}m2$ involves the structure of SiC type 10H described by Ramsdell & Kohn (1951). If P_s is either $6mm$ or $6/mmm$, the crystal symmetry will be $6mm$.

(10) Laue symmetry $m3$

The symmetry group $m3$ is the supergroup of both mmm and $\bar{3}$. The condition (32) can be rewritten in the form

$$u_p = v_p = w_p \neq 0 \quad (32')$$

if a rhombohedral setting is taken. Apparent Laue symmetry of $m\bar{3}$ requires that both condition (32') and one of conditions (24) hold at the same time. Such structures are impossible.

(11) Laue symmetry $m\bar{3}m$

Since the group $m\bar{3}m$ is a supergroup of $m\bar{3}$, inspection of the structures with the hyper diffraction symmetry $m\bar{3}m$ is not necessary.

The above results are briefly summarized as follows. When the composed structure is of type 1, the enhancement condition is given by (12). Substructures with the point-group symmetry $2, m, 222, mm2, \bar{4}, 422, \bar{4}2m, 4m2, 321, 312, \bar{6}, 622, \bar{6}2m$ or $\bar{6}m2$ may form composite crystals with point group $1, 1, 2, m, 2, 4, mm2, mm2, 3, 3, 3, 6, 31m$ or $3m1$ respectively. In such cases the resultant Laue symmetry corresponds to the point group of the substructures, and not to that of the crystal. There is no limitation on the number of substructures. Centrosymmetrical substructures do not form any composite structures which give enhanced diffraction symmetry.

Type 2. Crystals composed of different substructures with the same symmetry

Let us suppose the crystals are composed of different kinds of substructures.

If all substructures have the same symmetry and are centrosymmetric, we obtain from equations (9) and (10) that

$$\varphi(\mathbf{h}) = \sum_{p \neq q} 2A_p A_q \cos 2\pi \mathbf{h} \cdot \mathbf{u}_{pq}, \quad (38)$$

$$\varphi(\mathbf{h}') = \sum_{p \neq q} 2A_p A_q \cos 2\pi \mathbf{h}' \cdot \mathbf{u}_{pq}. \quad (39)$$

Therefore, if $\varphi(\mathbf{h})$ is equal to $\varphi(\mathbf{h}')$ and if A_p and A_q are linearly independent, we have

$$\cos 2\pi \mathbf{h} \cdot \mathbf{u}_{pq} = \cos 2\pi \mathbf{h}' \cdot \mathbf{u}_{pq} \quad (40)$$

or

$$\mathbf{u}_{pq} = 0. \quad (41)$$

The relation (40) is of the same form as equation (12) which has been treated in the preceding section. However, according to the conclusions reached there, any centrosymmetrical substructures satisfying equation (40) form only composite structures which give their proper Laue symmetry. Equation (41) is trivial, since if $\mathbf{u}_{pq} = 0$ the whole crystal must attain the same symmetry of the substructures.

If the substructures are non-centrosymmetric and different, $\varphi(\mathbf{h})$ and $\varphi(\mathbf{h}')$ have usually different values.

However, when the number of kinds of substructure is limited to two, diffraction enhancement is still possible. Let us assume that the substructures 1 and 2 are independent, and that all others are identical with either 1 or 2. In this case $\varphi(\mathbf{h})$ and $\varphi(\mathbf{h}')$ can be written as follows:

$$\begin{aligned} \varphi(\mathbf{h}) = & 2I_1 \sum_{m \neq n} \cos 2\pi \mathbf{h} \cdot \mathbf{u}_{mn} \\ & + 2I_2 \sum_{p \neq q} \cos 2\pi \mathbf{h} \cdot \mathbf{u}_{pq} \\ & + 2(A_1 A_2 + B_1 B_2) \sum_{mp} \cos 2\pi \mathbf{h} \cdot \mathbf{u}_{mp} \\ & + 2(A_1 B_2 - B_1 A_2) \sum_{mp} \sin 2\pi \mathbf{h} \cdot \mathbf{u}_{mp} \end{aligned} \quad (42)$$

and

$$\begin{aligned} \varphi(\mathbf{h}') = & 2I_1 \sum_{m \neq n} \cos 2\pi \mathbf{h}' \cdot \mathbf{u}_{mn} \\ & + 2I_2 \sum_{p \neq q} \cos 2\pi \mathbf{h}' \cdot \mathbf{u}_{pq} \\ & + 2(A_1 A_2 + B_1 B_2) \sum_{mp} \cos 2\pi \mathbf{h}' \cdot \mathbf{u}_{mp} \\ & + 2(A_1 B_2 - B_1 A_2) \sum_{mp} \sin 2\pi \mathbf{h}' \cdot \mathbf{u}_{mp} \end{aligned} \quad (43)$$

where A_1, B_1 etc. refer to index \mathbf{h} . The subscripts m and n run through substructures of the same kind as 1, and p and q through those with the same structure as 2. In this case, if the relation

$$\sum_{mp} \sin 2\pi \mathbf{h} \cdot \mathbf{u}_{mp} = 0 \quad (44)$$

holds, the problem of diffraction enhancement is reduced to the same form as those for type 1. Structures composed of two kinds of substructures which satisfy the relation (44) will be called here 'type 2'.

These structures have already been partly investigated by Sadanaga & Takeda (1968) and by Marumo & Saito (1972). According to these authors, if the crystal is composed of a stack of two kinds of parallel layers, and if the origin of each layer lies on a straight line which is not parallel to the layers, diffraction enhancement can take place. As Marumo & Saito have noticed, the condition on the thickness of the layers assumed by Sadanaga & Takeda is unnecessary. If the above-mentioned straight line is taken to be the c axis, the relation (44) becomes

$$\sum_{mp} \sin 2\pi l w_{mp} = 0. \quad (45)$$

Marumo & Saito (1972) started from equation (5) for such a structure and obtained the relation which is essentially equivalent to equation (45) for the condition for the occurrence of the hypersymmetry in the diffraction patterns [*cf.* equation (4) in their paper]. They limited their discussion to the enhanced Laue symmetry of $2/m$ and mmm . According to the present analysis, however, the diffraction enhancement like $4/m, 4/mmm, \bar{3}1m (\bar{3}m1), 6/m$ and $6/mmm$ also takes place in structures of a similar type. The enhancement conditions are given in the same form as those for the structures of type 1. In the case of the local symmetry of 2, it is necessary that all u_p 's and v_p 's are related by

$$Hu_p + Kv_p = C, \quad (20')$$

where H, K and C are some constants.

It should be added that the number of each kind of substructure in the type 2 structure must be equal to, or larger than, 3.

Type 3. Crystals composed of two substructures with the same point group and different space groups

In the following discussions on the structures of types 3 and 4, the number of substructures is limited to two. First let us consider the structures of type 3, in which the point group of each substructure is the same, while the space groups are different. (One point group may be a supergroup of the other. In this case the following discussions concern the lower point-group symmetry.) It is assumed that the point-group symmetry of the crystal is lower than that of the substructures.

Because of these assumptions, the rotational parts R of the corresponding symmetry elements in the two substructures are always the same, while the translational parts \mathbf{t} may be different. Now let us examine the case of $\mathbf{t}_1 \neq \mathbf{t}_2$.

Suppose that the reflexions \mathbf{h} and \mathbf{h}' are equivalent owing to the symmetry elements (R, \mathbf{t}_1) and (R, \mathbf{t}_2) . Then,

$$F_j(\mathbf{h}') = F_j(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{t}_j), \quad j=1,2. \quad (46)$$

Inserting equation (46) into equation (9), we obtain

$$\varphi(\mathbf{h}) = F_1^*(\mathbf{h})F_2(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{u}) + \text{complex conjugate} \quad (47)$$

$$\varphi(\mathbf{h}') = F_1^*(\mathbf{h})F_2(\mathbf{h}) \exp[2\pi i \mathbf{h} \cdot (\mathbf{t}_1 - \mathbf{t}_2)] \exp(2\pi i \mathbf{h}' \cdot \mathbf{u}) + \text{complex conjugate} \quad (48)$$

where $\mathbf{u} = \mathbf{u}_1 - \mathbf{u}_2$. In order to make discussions simpler, we assume here that $\mathbf{u} = 0$. (This is not always valid and may impose severe limitations on the following conclusion.) Now we obtain, by using equation (8),

$$\varphi(\mathbf{h}) = 2(A_1A_2 + B_1B_2), \quad (49)$$

$$\varphi(\mathbf{h}') = 2(A_1A_2 + B_1B_2) \cos 2\pi \mathbf{h} \cdot (\mathbf{t}_1 - \mathbf{t}_2) - 2(A_1B_2 - B_1A_2) \sin 2\pi \mathbf{h} \cdot (\mathbf{t}_1 - \mathbf{t}_2). \quad (50)$$

If these two quantities have the same value, the diffraction enhancement of symmetry will be observed. For example, let us suppose that

$$\cos 2\pi \mathbf{h} \cdot (\mathbf{t}_1 - \mathbf{t}_2) = 1 \quad (51)$$

for particular reflexions \mathbf{h} . Hence the sine part of (50) is zero. Reflexions which satisfy equation (51) always exist, since the three components of \mathbf{t}_j along the cell edges are generally rational numbers. Since \mathbf{t}_1 differs from \mathbf{t}_2 for several symmetry elements, equation (51) does not hold for some reflexions. Accordingly, we must postulate further that either F_1 or F_2 (or both) is zero when the relation (51) breaks down. When these conditions are satisfied, the diffraction symmetry will correspond to the point group of the substructures.

We can point out a plausible example. In tetragonal, trigonal or hexagonal systems, some substructures may have mm symmetry, in which the mirror planes are parallel to the c axis. The overlap of two substructures may cause the disappearance of this mm symmetry.

Examples of combinations of the space groups of substructures are as follows:

$P4_2mc$ and $P4_2cm$	(The point group of the substructures is $4mm$; the space group of the composite crystal is $P4_2$)
$P4_2/mmc$ and $P4_2/mcm$	$(4/mmm; P4_2/m)$
$P4_2/nmc$ and $P4_2/ncm$	$(4/mmm; P4_2/n)$
$P6_3mc$ and $P6_3cm$	$(6mm; P6_3)$
$P6_3/mmc$ and $P6_3/mcm$	$(6/mmm; P6_3/m)$

With these combinations, diffraction enhancement of the type

$$I(hkl) = I(khl) \quad (52)$$

can occur.

Several hypothetical structures which have such properties have already been described by the present author (Iwasaki, 1971). They are characterized by the special values taken by the atomic parameters and a proper interaction of the extinction rule for the reflexions from each substructure. Here we will be concerned with two typical examples.

Consider a structure composed of two substructures, one having symmetry $P4_2mc$ and the other, $P4_2cm$. The former consists of atoms in $(0, \frac{1}{4}, z; 0, \frac{3}{4}, z; \frac{1}{4}, 0, z + \frac{1}{2}; \frac{3}{4}, 0, z + \frac{1}{2})$ and the latter, atoms in $(\frac{1}{4}, \frac{1}{4}, z'; \frac{3}{4}, \frac{3}{4}, z'; \frac{1}{4}, \frac{3}{4}, z' + \frac{1}{2}; \frac{3}{4}, \frac{1}{4}, z' + \frac{1}{2})$. The parameters z and z' are arbitrary and both substructures may contain several independent atoms. The structure has neither mirror nor glide planes as a whole, and the space group is $P4_2$. On calculating structure factors, we easily obtain

$$F_1 \simeq \exp(2\pi i l z) \cdot [\cos(\pi k/2) + (-1)^l \cos(\pi h/2)], \quad (53)$$

$$F_2 \simeq \exp(2\pi i l z') \cdot \{\cos[\pi(h+k)/2] + (-1)^l \cos[\pi(h-k)/2]\}. \quad (54)$$

From these relations, we find immediately

$$I(hkl) = I(khl) \quad (55)$$

for any integral values of h , k and l . This means that the Laue symmetry is $4/mmm$, and not $4/m$.

The second example is offered by a structure with space group $P6_3$. The substructure 1 consists of atoms in $(\frac{1}{3}, 0, z)$ and its equivalent positions, and the substructure 2, atoms in $(\frac{2}{3}, \frac{1}{3}, z'; \frac{1}{3}, \frac{2}{3}, z' + \frac{1}{2})$. In this case the Laue symmetry becomes $6/mmm$. A structure of this kind exists actually, for example, in WAl_5 (Adam & Rich, 1955), and in the hexagonal modification of $BaFe_4O_7$ (Okamoto, Okamoto & Ito, 1972).

Type 4. Crystals composed of two substructures with isomorphic point groups

A slightly different but similar type of combination of substructures will also cause diffraction enhancement. In this case, the point groups of the two substructures are isomorphic, but they are distinguished by the

arrangements of the symmetry elements referred to the crystallographic axes. These local point groups must be specified without changing the origin of the unit cell. (We assume here that $\mathbf{u}=0$.) Examples of the combinations of the symmetry in the substructures are as follows:

$\bar{4}2m$ and $\bar{4}m2$;
 $\bar{3}1m$ and $\bar{3}m1$ (and also $31m$ and $3m1$; 321 and 312);
 $\bar{6}m2$ and $\bar{6}2m$.

One of the members of these pairs may be replaced by a supergroup of itself. In above examples, the point group of the crystal will be lowered to $\bar{4}$, $\bar{3}$ (or 3) and $\bar{6}$, but there are some possibilities of the diffraction symmetries $4/mmm$, $6/mmm$ and $6/mmm$ respectively occurring.

Let us consider a simple example of this type. One substructure 1 is formed by atoms in $(0, \frac{1}{4}, z; 0, \frac{3}{4}, z; \frac{1}{4}, 0, \bar{z}; \frac{3}{4}, 0, \bar{z})$ and the other, 2, by atoms in $(\frac{1}{4}, \frac{1}{4}, z'; \frac{3}{4}, \frac{3}{4}, z'; \frac{1}{4}, \frac{3}{4}, \bar{z}'; \frac{3}{4}, \frac{1}{4}, \bar{z}')$. The space group is $P\bar{4}$. For this structure we find

$$F_1 = 0 \quad (\text{if both } h \text{ and } k \text{ are odd}), \quad (56-1)$$

$$F_2 = 0 \quad (\text{if } h+k \text{ is odd}), \quad (56-2)$$

$$F_1(hkl) = F_1^*(khl) \text{ and } F_2 = \text{real} \\ (\text{if both } h \text{ and } k \text{ are even}). \quad (56-3)$$

Therefore, the relation (52) holds for any parity of h or k , and the Laue symmetry becomes $4/mmm$.

However, when Friedel's law does not hold, (56-3) breaks down. Furthermore, it can be ascertained that

$$F(hkl) \neq F(khl). \quad (57)$$

Hence the hypersymmetry does not appear in the diffraction patterns.

Partial enhancement of diffraction symmetry

When the symmetry of each constituent substructure is the same and all components of the \mathbf{u}_p vectors are expressed as rational fractions of the cell edges, the relation (11) holds for some particular reflexions irrespective of the contents of the substructures. For these reflexions, the diffraction symmetry is partly enhanced as a result of condition (12). Even if condition (12) does not hold, reflexions which satisfy relations (11) and (12) simultaneously do exist with particular kinds of indices. These cases correspond to the partial enhancement of diffraction symmetry.

Partial enhancement can also take place in structures similar to those of types 3 and 4. For example, suppose a crystal is composed of two substructures with the same point group. If F_1 and F_2 are always non-zero, then equation (51) holds only for several special reflexions. The diffraction symmetry is not enhanced for other kinds of reflexions.

Concluding remarks

When the diffraction symmetry is enhanced, it is impossible to deduce the correct point group from the symmetry of the observed diffraction patterns alone. The usual procedures for determining the space group are only applicable to the cases of ordinary diffraction symmetry. The symmetry in Patterson space is also enhanced in the case of the hypersymmetry.

There seems to be no general rule for the deduction of the correct symmetry other than the structure analysis itself. It is occasionally stated that 'no structure could be found in the space group which is in agreement with the observed intensities'. This statement is equivalent to saying that the inherent crystal symmetry is responsible for the observed diffraction symmetry.

If the structure is of type 1, at least two important characteristics are involved in the intensity data. The first of these is the overlap of heavy peaks in the Patterson maps. Gross peaks will be found at the position corresponding to the interatomic vector \mathbf{u}_{pq} , and also at its symmetry-related positions (here symmetry refers to those in the substructures). If the number of substructures (N_s) is 2, the height of these peaks will be about half that of the origin peak. The second characteristic is somewhat related to the general features of the intensity distribution. If $N_s=2$ and $F_1=F_2$, we obtain from equation (5)

$$I(hkl) = I_1(hkl) \cdot \cos^2(\pi \mathbf{h} \cdot \mathbf{u}_{12}). \quad (58)$$

Equation (58) means that the distribution of the intensity I is the same as that of I_1 except that it is modulated by a function $\cos^2(\pi \mathbf{h} \cdot \mathbf{u}_{12})$. If the substructures are relatively simple, the true composite structure can be deduced by a close examination of the intensity data.

The other possibility of finding the correct symmetry is mainly connected with the knowledge of the intensity distribution at off-Bragg points. If the structure is of the so-called 'OD-structure', it is possible to determine the correct symmetry by an appropriate interpretation of the disorder-type diffuse scattering (Dornberger-Schiff, 1956, 1957; Dornberger-Schiff & Grell-Niemann, 1961). The occurrence of hypersymmetry in the cases of types 3 and 4 is almost always ascribed to the fact that the indices are whole numbers. Therefore, if non-integral reciprocal points are examined, they will reveal the true crystal symmetry and will not exhibit the diffraction enhancement. If each diffraction maximum is accompanied by a spherically symmetric Laue function, the shape of the foot of the Bragg peak will perhaps show the correct point-group symmetry. This method cannot be applied to structures of types 1 and 2.

The phase relationships among the symmetry-equivalent reflexions are given by equation (2). If such a relation is lacking, the equality in the intensity must be regarded as merely accidental. The presence of a centre of inversion can be detected by a statistical treatment of intensities or by an anomalous dispersion

method. These techniques can be used for finding the correct crystal symmetry in the case of structures of type 4.

Structures of other types produce diffraction patterns with enhanced symmetry even when Friedel's law does not hold. Furthermore, in the case of type 3, the diffraction enhancement also occurs in centrosymmetric structures. For example, if a centre of inversion is added to the structure with the symmetry $P4_2$ described above, the resultant structure will belong to the space group $P4_2/m$, and the diffraction symmetry will become $4/mmm$.

The phenomena of the occurrence of hypersymmetry in diffraction patterns (diffraction enhancement of symmetry) will be encountered actually, though seldom, in crystal-structure analysis, especially in the case of inorganic compounds. The space group must not be determined by a cursory glance at the apparent

diffraction symmetry. It is, in general, dangerous to assign atomic parameters by a naive comparison of Z with the number of general positions required by such a space group. Disregard of the Laue symmetry will sometimes be necessary to attain the correct structure.

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The X-ray Structure Factors of Strontium Chloride Powder at 300° K and 80° K Analysed in Terms of Non-spherical Atoms

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The X-ray structure factors of SrCl_2 powder have been measured with $\text{Cu } K\alpha$ radiation at 300 and 80°K for 25 reflexions, including the faint ones, which in the fluorite structure obey the relation $h+k+l = 2(2n+1)$. The absolute scale was determined by comparing the intensities with those measured for a NaCl specimen. The overall agreement between the measured and calculated structure factors was good. The Debye-Waller coefficients were $B_{\text{Sr}} = 1.30 \pm 0.05$, $B_{\text{Cl}} = 1.47 \pm 0.05 \text{ \AA}^2$ at 300°K and $B_{\text{Sr}} = 0.42 \pm 0.05$, $B_{\text{Cl}} = 0.50 \pm 0.05 \text{ \AA}^2$ at 80°K. For the length of the unit-cell edge the values 6.9783 ± 0.0004 and $6.9442 \pm 0.0004 \text{ \AA}$ were obtained at 300 and 80°K respectively. An analysis based on the spherical harmonic expansion shows the electron distribution around the cation and the anion to be almost spherically symmetric. Some traces of tetrahedral deformation in Cl^- seem, however, to be present.

1. Introduction

The structure of strontium chloride has been found to be similar to the calcium fluoride structure (Mark & Tolksdorf, 1925). As the number of electrons in Sr^{2+} is twice as large as that in Cl^- , the reflexions $h+k+l = 2(2n-1)$, $n=1,2,3,\dots$, are very weak, their intensity being less than 1% relative to the intensity of the strongest (220) reflexion (Swanson, Fuyat & Ugrinic, 1955). The edge of the unit cell has been measured to be 7.01 Å (Mark & Tolksdorf, 1925), 6.979 Å (20°C; Ott, 1926) and 6.9767 Å (26°C; Swanson, Fuyat & Ugrinic, 1955).

Thermal vibrations in fluorite structures have been studied with both neutron and X-ray diffraction. Some neutron-diffraction results have been analysed by Dawson, Hurley & Maslen (1967), who report anharmonic thermal vibrations in UO_2 , ThO_2 and CaF_2 associated with the tetrahedral symmetry of the anionic sites. Cooper (1970) analysed single-crystal X-ray measurements for CaF_2 and found anharmonic components consistent with the neutron results. Calculations by Cooper & Panke (1970) based on X-ray diffraction measurements for Mg_2Si gave similar results. Non-spherical deformations of the ions in CaF_2 have been studied by Kurki-Suonio & Meisalo (1966)