Diffraction Symmetries of Complicated Structures

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Diffraction symmetries and extinctions of diffracted spots of complicated crystals are discussed by means of space group theoretical treatment. The complicated crystals mean: (*a*) Crystals are composed of several substructures and (*b*) unit cells of crystals can be divided into several subcells which have higher symmetry than that of the unit cells. Laue symmetries of crystals (*a*) were discussed by Iwasaki [Acta Cryst. (1972). A**28**, 253–260]. Diffraction symmetries and extinctions of the crystals belonging to the *types* 1 and 2 of Iwasaki's classification are studied more detail, and it is shown that enhancement of diffraction symmetries does not occur for the crystals belonging to the *type* 2, contrary to Iwasaki's result. Symmetries and extinctions of crystals (*b*) are discussed in connection with symmetries of subcells and symmetries between the subcells. The symmetries of subcells are shown that they can not be determined uniquely from the diffraction symmetries and extinctions

1. Introduction

Laue symmetry and extinctions of diffraction spots are symmetrical informations from the X-ray diffraction pattern of a crystal for the crystal structure. In the case of complicated crystal structures, the orders of Laue symmetries may become higher ones than those deduced from the crystal symmetries, and also extraordinary extinctions which can not be interpreted by the space groups of the crystals may appear.

Enhancement of Laue symmetries of crystals which are composed of several substructures was discussed by Iwasaki (1972). His discussion can be reduced very simple by considering that Laue symmetry is that which transforms invariantly the absolute value of structure factor. The symmetries and extinctions of the composite crystals of *types* 1 and 2 of Iwasaki's classification are discussed in this article. Since there is no remark to his discussion for crystals of *types* 3 and 4, and there is no extraordinary extinction, the crystals of *types* 3 and 4 are not discussed.

It is advantageous to analyze crystal structures by dividing the unit cells into several subcells in following cases, (1) the positions of strong intensities in reciprocal lattice space form a sublattice of the reciprocal lattice and (2) there are non-space-group extinctions, and the extraordinary extinctions can be interpreted as ordinary ones with respect to a sublattice of the

reciprocal lattice. Interpretations of the extraordinary extinctions were practically carried out by many investigators in the processes of structure analyses. The best of them is that of Kasper, Lucht and Harker (1950). However, the studies on systematization of the interpretation are very few. We can find only a reasonable one discussed by Niggli (1959). The author discusses the symmetries and extinctions in the above cases.

2. Preliminary

It is necessary to distinguish between vectors or operations and their representations. In ordinary theoretical treatment, we postulate that

$$\boldsymbol{k}S^{-1}=S\boldsymbol{k}, \tag{1}$$

where S is a rotation operation in real space and $\boldsymbol{k}$ is a vector in reciprocal lattice space. Furthermore, base vectors in real or reciprocal lattice are assumed that they are orthogonal to one another, respectively, in many cases. If the base vectors are orthogonal unit vectors, the representation of a rotation by matrix becomes an orthogonal matrix of three dimensions. It is convenient to adopt unit cell vectors as the base vectors in the field of crystallography. If the base vectors are unit cell vectors, the representation of a rotation becomes a unimodular matrix that the elements of the matrix are ± 1 or 0. We must notice that if rotations are represented by square matrices the vectors must be represented by row or column matrices. In this article, vectors in real space are represented by column matrices and vectors in reciprocal lattice space are represented by row matrices. We should notice that eq. (1) becomes meaningless if $\boldsymbol{k}$ and S are represented by matrices.

In ordinary treatment, an operation with R on a scalar function $f(\boldsymbol{r})$ results in

$$Rf(\boldsymbol{r})=f(R^{-1}\boldsymbol{r}). \tag{2}$$

If eq. (1) becomes meaningless, eq. (2) becomes no more advantageous. In this article, rotations do not mean that those of co-ordinate axes of crystals but those of crystal bodies, then we can express as

$$Rf(\boldsymbol{r})=f(R\boldsymbol{r}). \tag{3}$$

A space group symmetry operation is represented by the form as

$$R=(A|\boldsymbol{t}), \tag{4}$$

where A is the representation of a proper or improper rotation and $\boldsymbol{t}$ is that of a translation which is given by a sum of a lattice translation and its fractional one. Operation with R on $\boldsymbol{r}$ is defined by

$$R\boldsymbol{r}=A\boldsymbol{r}+\boldsymbol{t}. \tag{5}$$

Product of two operations of a space group is defined by

$$(A|\boldsymbol{t}_a+\boldsymbol{t}_m)(B|\boldsymbol{t}_b+\boldsymbol{t}_n)=(AB|A\boldsymbol{t}_b+\boldsymbol{t}_a+\boldsymbol{t}_{m'}). \tag{6}$$

where $\boldsymbol{t}_a$ is the fractional translation which follows after A and $\boldsymbol{t}_m$ is a lattice translation. The product must be equivalent with one of symmetry operations of the space group,

$$(AB|A\boldsymbol{t}_b+\boldsymbol{t}_a+\boldsymbol{t}_{m'})\equiv(AB|A\boldsymbol{t}_b+\boldsymbol{t}_a)\equiv(C|\boldsymbol{t}_c) \pmod{T}, \tag{7}$$

where T is the translation group of the space group.

If the structure factor $F(\boldsymbol{h})$ of a crystal is operated with $(A|\boldsymbol{t}_a)$ which is not necessarily a member of the space group of the crystal, $F(\boldsymbol{h})$ is transformed into

$$(A|\boldsymbol{t}_a)F(\boldsymbol{h})=F(\boldsymbol{h}A)\exp(2\pi\mathrm{i}\boldsymbol{h}\boldsymbol{t}_a). \tag{8}$$

If $(A|\boldsymbol{t}_a)$ is a member of the space group of the crystal, then $(A|\boldsymbol{t}_a)F(\boldsymbol{h})$ should be equal to $F(\boldsymbol{h})$,

$$(A|\boldsymbol{t}_a)F(\boldsymbol{h})=F(\boldsymbol{h}). \tag{9}$$

We define basis transformation from unit cell vectors $\boldsymbol{a}$, $\boldsymbol{b}$ and $\mathbf{c}$ to new vectors $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$ by

$$\begin{pmatrix}\boldsymbol{a}\\ \boldsymbol{b}\\ \boldsymbol{c}\end{pmatrix}=\begin{pmatrix}m_{11} & m_{21} & m_{31}\\ m_{12} & m_{22} & m_{32}\\ m_{13} & m_{23} & m_{33}\end{pmatrix}\begin{pmatrix}\boldsymbol{A}\\ \boldsymbol{B}\\ \boldsymbol{C}\end{pmatrix}, \tag{10}$$

or in short,

$$\mathbf{a}=\mathbf{m}^{\mathrm{t}}\mathbf{A}, \tag{11}$$

where $\mathbf{m}^{\mathrm{t}}$ is the transposed matrix of $\mathbf{m}=(m_{ij})$ The reciprocal vectors of $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$ are given by

$$\mathbf{a}^*=\mathbf{m}^{-1}\mathbf{A}^*. \tag{12}$$

The respresentations of $\boldsymbol{r}$ and $\boldsymbol{h}$ in real and reciprocal lattice spaces are transformed to $\boldsymbol{R}$ and $\boldsymbol{H}$ under the transformation,

$$\boldsymbol{R}=\mathbf{m}\boldsymbol{r}, \tag{13}$$

$$\boldsymbol{H}=\boldsymbol{h}\mathbf{m}^{-1}. \tag{14}$$

Operations $R = (A|t_a)$ are transformed to

$$\begin{aligned} R' &= (B|t_b) \\ &= (\mathbf{m}A\mathbf{m}^{-1}|\mathbf{m}t_a) \end{aligned} \tag{15}$$

The volume of the domain spanned by $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$ is given by

$$(\boldsymbol{A}\times\boldsymbol{B})\boldsymbol{C}=\frac{1}{m}(\boldsymbol{a}\times\boldsymbol{b})\boldsymbol{c}, \tag{16}$$

where m is the determinant of matrix $\mathbf{m}$.

3. Crystals composed of several substructures

We assume that crystals are composed of several substructures which have following properties,

(1) base vectors of the substructures $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$ are equal to the unit cell vectors $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$;

(2) space groups of crystals are subgroups of those of substructures;

(3) there is no symmetry operation which transforms a substructure to the others, except the members of the space group of the substructure.

The structure factor $F(\boldsymbol{h})$ of the composite crystals is expressed as

$$F(\boldsymbol{h})=\sum_p \exp(2\pi \mathrm{i}\boldsymbol{h}\boldsymbol{u}_p)F_p(\boldsymbol{h}), \tag{17}$$

where $F_p(\boldsymbol{h})$ is the structure factor of the pth substructure and $\boldsymbol{u}_p$ is the vector from the origin of the crystal lattice to that of the pth substructure. Ordinary crystals can also be regarded to consist of substructures, for example, halite consists of two substructures, one is of Na and the other is of Cl. The space groups of all substructures of a crystal are assumed to be the same in the case that the crystal belongs to *type* 1 or 2 of Iwasaki's classification.

Operating with $(A|0)$, which is a member of the point group of substructures, on $F(\mathbf{h})$, we have

$$(A|0)F(\boldsymbol{h}) = \sum_p \exp(2\pi \mathrm{i}\boldsymbol{h}A\boldsymbol{u}_p)F_p(\boldsymbol{h}A)$$
$$= \sum_p \exp(2\pi \mathrm{i}\boldsymbol{h}A\boldsymbol{u}_p)F_p(\boldsymbol{h})\exp(-2\pi \mathrm{i}\boldsymbol{h}\boldsymbol{t}_a). \tag{18}$$

If $(A|0)F(\boldsymbol{h})$ is equal to either $F(\boldsymbol{h})\exp(\mathrm{i}\theta_1)$ or $F(\boldsymbol{h})^*\exp(\mathrm{i}\theta_2)$, the absolute value of $F(\boldsymbol{h})$ is invariant by the operation. Denoting the arguments of $F_p(\boldsymbol{h})$, $F_p(\boldsymbol{h}A)$, $\exp(2\pi \mathrm{i}\boldsymbol{h}\boldsymbol{u}_p)$ and $\exp(2\pi \mathrm{i}\boldsymbol{h}A\boldsymbol{u}_p)$ by α_p, α'_p, β_p and β'_p, respectively, we obtain a condition for the invariance of the absolute value of $F(\boldsymbol{h})$ as

$$(\alpha_p + \beta_p) - (\alpha_q + \beta_q) = \pm\{(\alpha'_p + \beta'_p) - (\alpha'_q + \beta'_q)\}, \tag{19}$$

for any p and q. If the sign of the right hand side of eq. (19) is positive and $\theta_1 = -2\pi\boldsymbol{h}\boldsymbol{t}_a$, $(A|0)$ becomes a member of the point group of the crystal, if negative $(A|0)$ becomes a member of the Laue symmetry although it is not a member of the point group of the crystal. That is to say, the enhancement of Laue symmetry arises if the sign is negative. Hereafter, we assume that $\theta_1 = -2\pi\boldsymbol{h}\boldsymbol{t}_a$.

If we regard substructures as points of which scattering factors are the structure factors $F_p(\boldsymbol{h})$ and which lie at $\boldsymbol{u}_p$, then eq. (19) means that every component of the structure factor $F(\boldsymbol{h})$ is rotated by the angle θ_1 or every component of the complex conjugate of $F(\boldsymbol{h})$ is rotated by the angle θ_2. We note that ordinary symmetry operations are not limited within congluent transformations. Since eq. (19) is not always necessary for the absolute value of $F(\boldsymbol{h})$ being invariant by the operation $(A|0)$ and the absolute value of $F(\boldsymbol{h})$ is invariant if eq. (19) is satisfied, eq. (19) is one of sufficient conditions for the absolute value of $F(\boldsymbol{h})$ being invariant by $(A|0)$.

3. 1. Type 1

Crystals belong to the *type* 1 of Iwasaki's classification, if the arguments of the structure factors of all the substructures are the same.

In this case, eq. (19) becomes

$$(\beta_p - \beta_q) = \pm(\beta'_p - \beta'_q). \tag{20}$$

Equation (20) is equivalent to

$$(\boldsymbol{u}_p - \boldsymbol{u}_q) \equiv \pm A(\boldsymbol{u}_p - \boldsymbol{u}_q) \pmod{T}. \tag{21}$$

If the sign in eq. (21) is negative, $(A|0)$ becomes a member of the Laue symmetry although the crystal does not have the symmetry. Equation (21) can be reduced to

$$\boldsymbol{u}_p \equiv \pm A\boldsymbol{u}_p \pmod{T} \tag{22}$$

for any p. If $\beta_p \equiv 0$ for any p, $(A|0)$ becomes always a member of the point group of the crystal in this case.

In addition to space-group extinctions of substructures, extinctions arise if

$$\sum_p \exp(2\pi i \boldsymbol{h}\boldsymbol{u}_p) = 0 \tag{23}$$

is satisfied by $\boldsymbol{h}$ in the case $F_p(\boldsymbol{h}) = F_q(\boldsymbol{h})$ for $p \neq q$. If the number of the substructures are limited within two, eq. (23) becomes equivalent to the extinction condition discussed by Niggli (1959).

One of the examples of the extinctions which can be interpreted by eq. (23) is that of $MoO_2Cl_2H_2O$ analyzed by Schulz and Schröder (1973). According to them, the following non-space-group extinctions were observed:

(1) $F(hkl)$ not present, if $k = 4n + 2$,

(2) $F(hk0)$ not present, if $k = 4n$.

The extinction (1) arises if the number of the substructures is two and $\boldsymbol{u}_1 = 0$, $\boldsymbol{u}_2 = \boldsymbol{b}/4$. If the space group of the substructures has a glide plane parallel to (001) with the fractional translation $\boldsymbol{b}/2$, the extinction (2) arises by overlapping the extinction (1). Hence, we obtain equivalent positions in the unit cell as

$$x, y, z \quad x, y+\frac{1}{4}, \bar{z} \quad x, y+\frac{1}{2}, z \quad x, y+\frac{3}{4}, \bar{z}.$$

It is obvious that the crystal which has the above equivalent positions satisfies the extinctions (1) and (2).

If all substructures can be derived from a basic substructure by symmetry, additional symmetry may appear. In this case, pth substructure can be assumed to be derived by a point group symmetry $(B_p|0)$ and to be given by

$$F_p(\boldsymbol{h}) = (B_p|0)F_1(\boldsymbol{h}). \tag{24}$$

The operations $(B_p|0)$ are assumed to form a point group and they may or may not be the members of the point group of the crystal. They should be the members of the point group of the crystal lattice of the substructures. The structure factor $F(\boldsymbol{h})$ is expressed as

$$\begin{aligned} F(\boldsymbol{h}) &= \sum_p \exp(2\pi i \boldsymbol{h}\boldsymbol{u}_p) F_1(\boldsymbol{h}B_p) \\ &= \sum_p (B_p|\boldsymbol{u}_p) F_1(\boldsymbol{h}). \end{aligned} \tag{25}$$

If a space group is generated by the set $SB = \{(B_p|\boldsymbol{u})\}$ and the translation group of the crystal lattice of the substructure, the set SB and the space group of the substructures may generate a space group. Then the crystal structure becomes an ordinary one. Diamond structure is one of the examples of the ordinary structures which consist of two substructures. Hence, we assume that the set SB and the translation group do not generate a space group.

The structure factor $F(\boldsymbol{h})$ is given explicitly by

$$F(\boldsymbol{h}) = \sum_p \sum_i \frac{1}{m_i} f_i \exp\{2\pi \mathrm{i} \boldsymbol{h}(B_p \boldsymbol{r}_i + \boldsymbol{u}_p)\}, \tag{26}$$

where f_i is the scattering factor of the ith atom, $\boldsymbol{r}_i$ is the vector from the origin of the unit cell to the position of the ith atom in the basic substructure and m_i is the multiplicity of the position of the ith atom. Since $B_p\boldsymbol{r}_i + \boldsymbol{u}_p$ is the vector from the origin of the unit cell to the ith atom in the pth substructure, the operation with $(B_q|\boldsymbol{u}_q)$ on $F(\boldsymbol{h})$ should be given by

$$\begin{aligned}(B_q|\boldsymbol{u}_q)F(\boldsymbol{h}) &= \sum_p \sum_i \frac{1}{m_i} f_i \exp\{2\pi \mathrm{i} \boldsymbol{h}(B_q|\boldsymbol{u}_q)(B_p\boldsymbol{r}_i + \boldsymbol{u}_p)\} \\ &= \sum_p \sum_i \frac{1}{m_i} f_i \exp[2\pi \mathrm{i} \boldsymbol{h}\{B_q(B_p\boldsymbol{r}_i + \boldsymbol{u}_p) + \boldsymbol{u}_q\}] \\ &= \sum_p F_1(\boldsymbol{h}B_qB_p)\exp\{2\pi \mathrm{i} \boldsymbol{h}(B_q\boldsymbol{u}_p + \boldsymbol{u}_q)\}. \end{aligned} \tag{27}$$

Introducing vector $\boldsymbol{u}(qp) = B_q\boldsymbol{u}_p + u_q$, we rewrite eq. (27) as

$$\begin{aligned}&(B_q|\boldsymbol{u}_q)F(\boldsymbol{h}) \\ &= \exp\{2\pi \mathrm{i} \boldsymbol{h}\boldsymbol{u}(qr)\} \sum_p \exp[2\pi \mathrm{i} \boldsymbol{h}\{\boldsymbol{u}(qp) - \boldsymbol{u}(qr)\}] F_1(\boldsymbol{h}B_qB_p), \end{aligned} \tag{28}$$

where $B_qB_r = E$, the unit operation.

In case $\alpha_p = \alpha_q$ for $q \neq p$, the absolute value of $(B_q|\boldsymbol{u}_q)F(\boldsymbol{h})$ becomes equal to that of $F(\boldsymbol{h})$ if

$$\boldsymbol{u}(qp) - \boldsymbol{u}(qr) \equiv \pm \boldsymbol{u}_s \pmod{T} \tag{29}$$

is satisfied for any p and q, where $B_qB_p = B_s$. If the sign of the right hand side of eq. (29) is positive, and

$$\boldsymbol{u}(qr) \equiv 0 \pmod{T}, \tag{30}$$

$(B_q|\boldsymbol{u}_q)$ becomes a member of the space group of the crystal. Hence, if the sign of the right hand side of eq. (29) is positive and eq. (30) is not satisfied, and if the sign is negative, $(B_q|0)$ becomes a member of the Laue symmetry except the case $\beta_p = 0$ for any p. Even though eq. (29) is not

satisfied, the subset of the reciprocal lattice points, satisfying

$$\boldsymbol{h}\boldsymbol{u}_p = \text{an integer} \tag{31}$$

for any p, has the symmetry $(B_q|0)$.

If an operation $(B_p|0)$ generates a point group $K(B_p)$, additional extinction to those due to the substructures arises if

$$\sum_{K(B_p)} \exp(2\pi i \boldsymbol{h}\boldsymbol{u}_p) = 0 \tag{32}$$

is satisfied by $\boldsymbol{h}$ which is invariant by $K(B_p)$, i.e. $\boldsymbol{h}B_p = \boldsymbol{h}$. The summation in eq. (32) is over all the member of the subset of SB, of which rotations form $K(B_p)$.

One of examples of the crystal structures of this type is as follows. If a substructure with orthorhombic lattice has a two-fold rotation axis parallel to a-axis and a mirror plane perpendicular to the axis, the space group of the substructure becomes $P2/m$. If another substructure is derived by two-fold rotation of which axis is parallel to c-axis from the former substructure, the space group of the crystal formed from the two substructures becomes $Pmma$ if $\boldsymbol{u}_1 = 0$ and $\boldsymbol{u}_2 = \boldsymbol{c}/2$. If $\boldsymbol{u}_1 = 0$ and $\boldsymbol{u}_2 = \boldsymbol{c}/4$, the space group becomes Pm. In this case, the Laue symmetry becomes mmm and $00l$ reflections with $l = 4n + 2$ extinct.

3.2. Type 2

If the structure factors of substructures do not have the same arguments, i.e. $\alpha_p \neq \alpha_q$ for $p \neq q$, and if the space groups of the substructures are the same one another, the crystal belongs to the *type* 2 of Iwasaki's classification.

Since $\alpha_p - \alpha_q = \alpha'_p - \alpha'_q \neq 0$ for any p and q, the negative sign in eq. (19) should be disregarded except the case $\alpha_p + \beta_p = \alpha_q + \beta_q$ for any p and q. If $\beta_p = \beta_q$ for $p \neq q$, the point group symmetry of the substructures becomes a point group symmetry of the crystal.

When all the substructures are derived from a basic substructure by symmetry, the absolute value of $F(\boldsymbol{h})$ is invariant if the right hand side of eq. (29) is positive, in addition, if eq. (30) is valid, the symmetry operation $(B_q|\boldsymbol{u}_q)$ belongs to the space group of the crystal.

If there are many substructures of the same kind, the structure factor $F(\boldsymbol{h})$ is expressed as

$$F(\boldsymbol{h}) = \sum_p \sum_s \exp(2\pi i \boldsymbol{h}\boldsymbol{u}_{ps}) F_p(\boldsymbol{h}), \tag{33}$$

where $\boldsymbol{u}_{ps}$ is the vector from the origin of the crystal lattice to that of the sth substructure of the

pth kind. The condition that $(A|0)$ which is a member of the point group of the substructure belongs to the point group of the crystal can be loosened that

$$\sum_s \exp(2\pi i \boldsymbol{h}\boldsymbol{u}_{ps}) = \sum_s \exp(2\pi i \boldsymbol{h}A\boldsymbol{u}_{ps}) \tag{34}$$

is satisfied by any p. If the imaginary parts in eq. (34) are zero, the condition becomes

$$\sum_s \cos(2\pi \boldsymbol{h}\boldsymbol{u}_{ps}) = \sum_s \cos(\pm 2\pi \boldsymbol{h}A\boldsymbol{u}_{ps}). \tag{35}$$

Iwasaki's eq. (44) can be rewritten by using our notations as

$$\sum_s \sum_t \sin\{2\pi \boldsymbol{h}(\boldsymbol{u}_{ps} - \boldsymbol{u}_{qt})\} = 0. \tag{36}$$

Equation (36) can be obtained if the both arguments of $\sum_s \exp(2\pi i \boldsymbol{h}\boldsymbol{u}_{ps})$ and $\sum_t \exp(2\pi i \boldsymbol{h}\boldsymbol{u}_{qt})$ are equal to each other. If we denote the arguments of $\sum_s \exp(2\pi i \boldsymbol{h}\boldsymbol{u}_{ps})$ and $\sum_t \exp(2\pi i \boldsymbol{h}\boldsymbol{u}_{qt})$ by β_p and β_q, respectively, Iwasaki's condition for enhancement of diffraction symmetry in this case should be

$$\beta_p - \beta_q = \beta'_p - \beta'_q = 0 \tag{37}$$

in our formalization. Since $\alpha_p - \alpha_q = \alpha'_p - \alpha'_q \neq 0$ for any p and q, there is no enhancement of diffraction symmetry in this case.

Additional extinction to those due to $F_p(\boldsymbol{h}) = 0$ arises if

$$\sum_s \exp(2\pi i \boldsymbol{h}\boldsymbol{u}_{ps}) = 0 \tag{38}$$

is satisfied by $\boldsymbol{h}$ for any p.

4. Unit cells consisting of several subcells

In this section, we discuss diffraction phenomena that the lattice points where diffracted intensities are strong form a sublattice of the reciprocal lattice of a crystal and that extraordinary extinctions can be interpreted as ordinary ones if the sublattice is regarded as a reciprocal lattice. The base vectors $\boldsymbol{A}^*$, $\boldsymbol{B}^*$ and $\boldsymbol{C}^*$ of the sublattice are defined by eq. (12), where the elements of $\mathbf{m}$ are assumed to be integers. The number of the subcells in a unit cell becomes an integer m. We assume that the m subcells have the same space group. To clarify the meanings of the space group of a subcell, we introduce subcell structure. If atomic arrangement of a structure A is the same as that of the ith subcell of the other structure B, the structure A is called the subcell struc-

ture of the ith subcell of the structure B. Then the space group of a subcell means the space group of the corresponding subcell structure. Furthermore, we assume that the m subcells can be classified into p groups, and that the subcells belonging to the same group are derived symmetrically from a subcell, which is called a basic subcell of the ith group if the group is of the ith one. The symmetries which transform the p basic subcells to the equivalent ones are assumed to form a point group of the order p. Then there must be $r = m/pq$ subcells of the same kind in the unit cell.

The vector from the origin of a unit cell to that of the jth subcell of the ith kind is denoted by $\boldsymbol{t}_{ij}$. The base vectors of $\boldsymbol{t}_{ij}$ are the subcell vectors $\boldsymbol{A}$,$\boldsymbol{B}$ and $\boldsymbol{C}$, and the coefficients of the base vectors are integers. We assume that the vector $\boldsymbol{t}_{ij}$ is given by

$$\boldsymbol{t}_{ij}=\boldsymbol{t}_{i1}+\boldsymbol{t}_{1j}, \tag{39}$$

and

$$\boldsymbol{t}_{11}=0. \tag{40}$$

Simplifying $\boldsymbol{t}_{1j}$ as $\boldsymbol{t}_j$, we have.

$$\boldsymbol{t}_{ij}=\boldsymbol{t}_{i1}+\boldsymbol{t}_j. \tag{41}$$

The set $\{\boldsymbol{t}'_j=\mathbf{m}^{-1}\boldsymbol{t}_j\}$ is denoted by $\mathbf{t}$.

The point group and the space group of the basic subcells are denoted by $G_0(S)$ and $G(S)$, respectively. We should notice that the basis of the representation of the groups is that of the sublattice of the crystal lattice. The set of the representatives of the cosets of the translation group in $G(S)$ is denoted by $\bar{G}(S) = \{(S_i|\boldsymbol{s}_i)\}$. The order of $G_0(S)$ is denoted by s. Although the space groups of all the subcells are assumed to be the same, the kinds of atoms and the atomic positions in each basic subcells of different kind are not necessarily the same one another.

The point group symmetry by which the ith subcell belonging to a group is obtained from the basic subcell in the group is denoted by $(B_i|0)$, the set of the symmetries forms a point group and is denoted by $G_0(B)$. The point group should be a subgroup of the point group of the crystal lattice of the subcell structure. If $\boldsymbol{u}_i$ is the vector from the origin of the basic subcell to that of the ith subcell, we assume that the set $\bar{G}(B) = \{(B'_i|\boldsymbol{u}'_i)\}$ becomes the set of the representatives of the cosets of the translation group of the crystal lattice in a space group $G(B)$, where $B'_1 = \mathbf{m}^{-1}B_1\mathbf{m}$ and $\boldsymbol{u}_i = \mathbf{m}^{-1}\boldsymbol{u}_i$. If $G(B)$ does not become a space group, a part of the unit cell is either

occupied by several sebcells belonging to the same group or not occupied by any subcell.

Let us obtain the structure factor $F(\boldsymbol{h})$ of the crystal satisfying the above assumptions. If the origin of the first basic subcell of the ith kind agrees with that of the unit cell, the structure factor $F_i(\boldsymbol{h})$ of the subcell is expressed as

$$\begin{aligned} F_i(\boldsymbol{h}) &= \sum_j \sum_v \frac{1}{m_v} f_v \exp\{2\pi \mathrm{i} \boldsymbol{h}(S_j'|\boldsymbol{s}_j')\boldsymbol{r}_v\} \\ &= \sum_j \sum_v \frac{1}{m_v} f_v \exp\{2\pi \mathrm{i} \boldsymbol{h}(S_j'\boldsymbol{r}_v + \boldsymbol{s}_j')\}. \end{aligned} \tag{42}$$

The structure factor of the kth subcell which is obtained by $(\boldsymbol{B}_k|0)$ from the basic subcell and lies at $\boldsymbol{u}_k$ from the origin of the basic subcell is denoted by $(\boldsymbol{B}_k'|\boldsymbol{u}_k')F_i(\boldsymbol{h})$. Then, $(\boldsymbol{B}_k'|\boldsymbol{u}_k')F_i(\boldsymbol{h})$ is expressed as

$$\begin{aligned} (\boldsymbol{B}_k'|\boldsymbol{u}_k')F_i(\boldsymbol{h}) &= \sum_j \sum_v \frac{1}{m_v} f_v exp[2\pi \mathrm{i} \boldsymbol{h}\{\boldsymbol{B}_k'(S_j'\boldsymbol{r}_v + \boldsymbol{s}_j') + \boldsymbol{u}_k'\}] \\ &= \exp(2\pi \mathrm{i} \boldsymbol{h}\boldsymbol{u}_k')F_i(\boldsymbol{h}\boldsymbol{B}_k'). \end{aligned} \tag{43}$$

Hence, the structure factor $F(\boldsymbol{h})$ of the cyrstal is exprested as

$$\begin{aligned} F(\boldsymbol{h}) &= \sum_j^p \sum_i^q \sum_k^r \exp(2\pi \mathrm{i} \boldsymbol{h}\boldsymbol{u}_j')F_i(\boldsymbol{h}\boldsymbol{B}_j')\exp\{2\pi \mathrm{i} \boldsymbol{h}(\boldsymbol{t}_{i1}' + \boldsymbol{t}_k')\} \\ &= \sum_i^p \exp(2\pi \mathrm{i} \boldsymbol{h}\boldsymbol{t}_{i1}')F_{ci}(\boldsymbol{h}), \end{aligned} \tag{44}$$

where $F_{ci}(\boldsymbol{h})$ is given by

$$F_{ci}(\boldsymbol{h}) = \sum_j^q \exp(2\pi \mathrm{i} \boldsymbol{h}\boldsymbol{u}_j')F_i(\boldsymbol{h}_j\boldsymbol{B}')\sum_k^r \exp(2\pi \mathrm{i} \boldsymbol{h}\boldsymbol{t}_k'). \tag{45}$$

If we regard $F_{ci}(\boldsymbol{h})$ as the structure factor of the ith substructure, eq. (44) becomes similar to eq. (17). Since we can not assume that the arguments of each sbustructures are the same in general, this crystal structure belongs to the *type* 2 of Iwasaki's classification. The structure of which the structure factor is given by $F_{ci}(\boldsymbol{h})$ is called the ith substructure, hereafter.

Operating with $(S_i'|\boldsymbol{s}_i')$ on $F_1(\boldsymbol{h})$, we have

$$(S_i'|\boldsymbol{s}_i')F_1(\boldsymbol{h}) = F_1(\boldsymbol{h}S_i')\exp(2\pi \mathrm{i} \boldsymbol{h}\boldsymbol{s}_i'). \tag{46}$$

If $F_1(\boldsymbol{h})$ is invariant by the operation,

$$(S_i'|\boldsymbol{s}_i')F_1(\boldsymbol{h}) = F_1(\boldsymbol{h}), \tag{47}$$

$F_1(\boldsymbol{h}\boldsymbol{B}_j')$ is also in variant. In this case, $F_1(\boldsymbol{h})$ becomes zero when $\exp(2\pi i \boldsymbol{h}\boldsymbol{s}_i') \neq 1$. The symmetries

which trasnform $F_1(\boldsymbol{h})$ invariant form a subgroup $K(S')$ of $G(S') = \{(S'_i|\boldsymbol{s}'_i)\}$. The condition that $(S'_i|0)$ belongs to the point group of the first substructure becomes:

$$\exp(2\pi i\boldsymbol{h}\boldsymbol{u}'_j)\sum_k^r \exp(2\pi i\boldsymbol{h}\boldsymbol{t}'_k) = \exp(2\pi i\boldsymbol{h}S'_i\boldsymbol{u}'_j)\sum_k^r \exp(2\pi i\boldsymbol{h}S'_i\boldsymbol{t}'_k) \tag{48}$$

is satisfied for any j.

Similarly to eq. (27), operating with $(B'_i|\boldsymbol{u}'_j)$ on $F_{c1}(\boldsymbol{h})$, we have

$$(B'_i|\boldsymbol{u}'_i)F_{c1}(\boldsymbol{h}) = \exp\{2\pi i\boldsymbol{h}(B'_i\boldsymbol{u}'_j+\boldsymbol{u}'_i)\}\sum_k^r \exp(2\pi i\boldsymbol{h}B'_i\boldsymbol{t}'_j)F_1(\boldsymbol{h}B'_1B'_j). \tag{49}$$

Since the operations $(B'_i|\boldsymbol{u}'_i)$ form a group, there is a unique operation $(B'_t|\boldsymbol{u}'_t)$ satisfying

$$(B'_i|\boldsymbol{u}'_i)(B'_j|\boldsymbol{u}'_j) = (B'_iB'_j|B'_i\boldsymbol{u}'_j+\boldsymbol{u}'_i) \equiv (B'_t|\boldsymbol{u}'_t) \pmod{T}. \tag{50}$$

Hence, if

$$\sum_k^r \exp(2\pi i\boldsymbol{h}\boldsymbol{t}'_k) = \sum_k^r \exp(2\pi i\boldsymbol{h}B'_i\boldsymbol{t}'_k) \tag{51}$$

is satisfied, $(B'_i|\boldsymbol{u}'_i)F_{c1}(\boldsymbol{h})$ becomes equal to $F_{c1}(\boldsymbol{h})$.

The set $\mathbf{t} = \{\boldsymbol{t}'_j\}$ should be invariant by B'_i, i.e. $\mathbf{t} = \{B'_i\boldsymbol{t}'_j\}$, if not, the domains occupied by the basic subcells can not be determined uniquely. In addition, $\exp(2\pi i\boldsymbol{h}\boldsymbol{t}'_{i1})$ should be invariant by the operations owing to the same reason. The Bravais lattice of the crystal is determined by the crystal lattice and the maximum subset of $\mathbf{t}$, which is invariant by the point group of the crystal lattice. The space group of the crystal is determined by the Bravais lattice, $G(B)$ and $K(S')$.

Extinction rules can be derived from $F(\boldsymbol{h}) = 0$. In eq. (44), if $F_{ci}(\boldsymbol{h}) = 0$, then $F(\boldsymbol{h}) = 0$. Since all the space groups of the subcells of different kind are the same, if $F_1(\boldsymbol{h})$ becomes zero owing to space-group extinction, then $F_i(\boldsymbol{h})$ becomes zero. The structure factors $F_{ci}(\boldsymbol{h})$ become zero, if $F_1(\boldsymbol{h})$ becomes zero and if

$$\sum_k^r \exp(2\pi i\boldsymbol{h}\boldsymbol{t}'_k) = 0. \tag{52}$$

Furthermore, for the subgroup $K(B)$ of $G(B)$, of which rotations satisfy $\boldsymbol{h}B'_j = \boldsymbol{h}$, if

$$\sum_{K(B)} \exp(2\pi i\boldsymbol{h}\boldsymbol{u}'_j) = 0, \tag{53}$$

then $F_{ci}(\boldsymbol{h})$ become zero, where the summation is over all the members of the subset $K(B)$.

By transforming the base vectors from the unit cell vectors to the subcell vectors, the structure factors $F_{c1}(\boldsymbol{h})$ become

$$F_{c1}(\boldsymbol{H})=r\sum_{j}^{q}\sum_{i}^{s}\sum_{v}\frac{1}{m_v}f_v\exp\{2\pi\mathrm{i}\boldsymbol{H}\boldsymbol{B}_j(S_i\boldsymbol{R}_v+\boldsymbol{s}_i)\}, \tag{54}$$

where $\boldsymbol{H}=\boldsymbol{h}\mathbf{m}^{-1}$ and $\boldsymbol{R}_v=\mathbf{m}\boldsymbol{r}_v$. Since $G(S)$ is the space group of the subcells, $(B_j|0)F_1(\boldsymbol{H})$ is invariant by $G(S)$. Since $(B_j|0)F_1(\boldsymbol{H})$ is $F_1(\boldsymbol{H}\boldsymbol{B}_j)$, $F_{c1}(\boldsymbol{H})$ is invariant by $G_0(B)$. Hence, the structure factor $F(\boldsymbol{H})$ is invariant by both $G(S)$ and $G_0(B)$. That is to say, the structure factor $F(\boldsymbol{H})$ of which H has integral elements has the space group which is generated by $G(S)$ and $G_0(B)$. The space group is denoted by Gs. The structure factor $F(\boldsymbol{H})$ is explicitly given by

$$\begin{aligned}F(\boldsymbol{H})\boldsymbol{H}&=r\sum_{i}^{p}\sum_{j}^{q}F_i(\boldsymbol{H}\boldsymbol{B}_j)\\&=r\sum_{i}^{p}\sum_{j}^{q}\sum_{k}^{s}\sum_{v}\frac{1}{m_v}f_v\exp\{2\pi\mathrm{i}\boldsymbol{H}\boldsymbol{B}_j(S_i\boldsymbol{R}_v+\boldsymbol{s}_i)\}.\end{aligned} \tag{55}$$

Since $F(\boldsymbol{H})$ becomes zero if $F_1(\boldsymbol{H})=0$, $F(\boldsymbol{H})$ becomes zero if

$$\sum_{K(S)}\exp(2\pi\mathrm{i}\boldsymbol{H}\boldsymbol{s}_i)=0, \tag{56}$$

where $K(S)$ is the subgroup of $G(s)$, of which rotations satisfy $HS_i=H$.

The rotations in Gs belong to the Laue symmetry of the sublattice spanned by $\boldsymbol{A}^*$, $\boldsymbol{B}^*$ and $\boldsymbol{C}^*$, and the structure obtained by Fourier transform of $F(\boldsymbol{H})$ where $\boldsymbol{H}$ has integral elements has the space group Gs. If we assume that space groups can be determined uniquely from extinctions, we can determine $G(B)$ and Gs. The space group Gs can be expressed by the right cosets of $G(S)$ or the left cosets of $G_0(B)$.

$$\begin{aligned}Gs&=G(S)+(B_2|0)G(S)+\cdots\cdots\\&=G_0(B)(E|\boldsymbol{t}_n)+G_0(B)(S_2|\boldsymbol{s}_2+\boldsymbol{t}_n)+\cdots\cdots,\end{aligned} \tag{57}$$

where $\boldsymbol{t}_n$ is the lattice translation. Since the subgroups obtained by the each representatives of the distinct left cosets of $G_0(B)$ are possible to become $G(S)$, we can not determine uniquely the space group $G(S)$. That is to say, the arrangement of atoms in a unit cell can not be determined uniquely from symmetry in a diffraction pattern in this case.

An application of the present theory to the case of $MoCl_2H_2O$ becomes as follows. The set $\mathbf{t}$ becomes $\{0, \frac{1}{4}\boldsymbol{b}\}$, $G(S)$, $G(B)$ and Gs becomes $P1$, Pb and Pm, respectively. The equivalent positions becomes the same as those described in the preceding section.

Another application to the case of decaborane analyzed by Kasper, Lucht and Harker (1950) is as follows. According to them, the extinctions were:

(1) hkl present only for $h+k=2n$,

(2) $hk0$ present only for $h=2n$, $k=2n$,

(3) $h0l$ present only for $\frac{1}{2}h+l=2n$,

(4) $0kl$ present only for $\frac{1}{2}k+l=2n$.

The extinction (1) is that due to eq. (52). The Bravais lattice is of C-centered. The extinction (2) is that due to eq, (53). $G(B)$ becomes Pa, hence $G_0(B) = m$. The extinctions (3) and (4) are those due to eq. (56). Taking into consideration that the extinctions become ordinary ones if $\boldsymbol{A}=\frac{1}{2}\boldsymbol{a}$ and $\boldsymbol{B}=\frac{1}{2}\boldsymbol{b}$, we obtain $Pnnm$ for Gs. The space group $Pnnm$ is expressed as

$$Pnnm = m(E|\boldsymbol{t}_n)+m(A|\boldsymbol{n}+\boldsymbol{t}_n)+m(B|\boldsymbol{n}\mathrm{t}+\boldsymbol{t}_n)+m(AB|\boldsymbol{t}_n)$$

where $(A|\boldsymbol{n})$ and $(B|\boldsymbol{n})$ are given by

$$A=\begin{pmatrix}\bar{1} & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix},\quad B=\begin{pmatrix}1 & 0 & 0\\ 0 & \bar{1} & 0\\ 0 & 0 & 1\end{pmatrix}\text{ and }\boldsymbol{n}=\begin{pmatrix}\frac{1}{2}\\ \frac{1}{2}\\ 0\end{pmatrix}$$

The number of the subgroups of $Pnnm$ generated by the representatives of the distinct cosets becomes four. Hence, we obtain four possible structures from the extinctions, which were discussed by Kasper *et al.*

References

Iwasaki, H. (1972). Acta Cryst. **A28**, 253–260.

Kasper, J.S. Lucht, C.M. and Harker, D. (1950). Acta Cryst. **3**, 436–455.

Niggli, A. (1959). Z. Kristallogr. **111**, 283–287.

Schulz, H. and Schröder, F.A. (1973), Acta Cryst. **A29**, 322–333.

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