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On Simple and Double Diffraction Enhancement of Symmetry*

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Under special circumstances, the diffraction symmetry of a crystal may be higher than that corresponding to the crystal Laue class. The phenomenon has been termed 'diffraction enhancement of symmetry'. Iwasaki [*Acta Cryst.* (1972), A**28**, 253–260] is responsible for the first systematic attempt to develop a comprehensive theory of this phenomenon. In this paper, a more general formulation has been developed which leads to enhancement conditions more compact and easier to use than Iwasaki's. By use of these conditions, several new cases of enhancement have been found, in addition to all the cases previously published. Several theorems are enunciated and proved which strongly limit the possible cases of enhancement. The formulation includes also the so-called 'double enhancement'. A set of double-enhancement cases has been found and tabulated. The extension of some of the theorems proved for simple enhancement provide limitations to the possible cases of double enhancement.

1. Introduction

The diffraction pattern of a crystal (*i.e.* diffracted intensity as a function of position in reciprocal space) is nonperiodic, and its symmetry can be consequently described with reference to some particular point group. The relation between that point group and the crystal point group is governed by von Neumann's principle, which, applied to this case, states that the diffraction pattern symmetry must correspond to a point group which is a supergroup (possibly an improper one) of the crystal point group. In the most general case (arbitrarily general structure, and different anomalous scatterers) the two groups would be isomorphous. In special cases it is possible that the point-group symmetry of the diffraction pattern is higher than the crystal point-group symmetry. A very common 'special case' is that in which anomalous dispersion can be ignored and the crystal point group is non-centrosymmetric; in such a case, the point group of the diffraction pattern is the direct product of the crystal point group with point group $\bar{1}$, and as a consequence, the diffraction pattern of such a crystal can be ascribed to one of the 11 Laue groups. This result is generally referred to as Friedel's law. Under more restrictive conditions the symmetry of the diffraction pattern of a crystal can be higher than the corresponding crystal point-group symmetry other than as a result of Friedel's law. For these cases, Sadanaga & Takeda (1968) coined the term 'diffraction enhancement of symmetry', and Iwasaki (1972) used it in his attempt to develop a systematic theory of this phenomenon.

Several cases of this type of enhancement have been encountered in actual experiment (Ramsdell & Kohn, 1951; Ross, Takeda & Wones, 1966), and it could perhaps be argued, as Iwasaki (1972) does, that the number of examples could be higher, especially among inorganic structures, if it was not for the fact that crystallographers usually expect to find a structural model in one of the space groups isogonal with those point groups obtained from the Laue group by application of Friedel's law.

In this paper we study a set of hypothetical structures which would produce this kind of effect (essentially they coincide with Iwasaki's type 1 crystals) using a modified approach which leads to enhancement conditions which are more compact and easier to work with than Iwasaki's. From these conditions we have found all the cases reported by Iwasaki (1972), and additional cases reported thereafter (Matsumoto, Kihara & Iwasaki, 1974), plus a dozen new cases previously unknown. We also prove several theorems which drastically limit the possible enhancement cases of the type we consider, and have generalized our approach to cover also the phenomenon called 'double enhancement', recently defined by Matsumoto (1975).

2. Enhancement conditions

We consider a crystal composed of several substructures and assume that the lattice parameters are consistent with the symmetry to be enhanced. Following Iwasaki (1972), we write the structure factor for reflexion **h** in the form:

$$F(\mathbf{h})=\sum_p F_p(\mathbf{h}) \exp\left[2\pi i\mathbf{h}\,.\,\mathbf{u}_p\right] \tag{1}$$

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where $F_p(\mathbf{h})$ is the structure factor corresponding to the pth substructure, and $\mathbf{u}_p$ is the radius vector of the origin of the pth substructure, drawn from the origin of the crystal. According to Iwasaki (1972) the intensity can be written as

$$|F(\mathbf{h})|^2 = \sum_p |F_p(\mathbf{h})|^2 + \tfrac{1}{2} \sum_{p\neq q} [F_p(\mathbf{h})F_q^*(\mathbf{h}) \exp(2\pi i\mathbf{h}\,.\,\mathbf{u}_{pq}) + F_p^*(\mathbf{h})F_q(\mathbf{h}) \exp(-2\pi i\mathbf{h}\,.\,\mathbf{u}_{pq})] \tag{2}$$

where $\mathbf{u}_{pq} = \mathbf{u}_p - \mathbf{u}_q$. We assume that the diffraction patterns of all substructures exhibit some rotational symmetry represented by the operator $\mathbf{R}$, *i.e.*

$$|F_p(\mathbf{h})| = |F_p(\tilde{\mathbf{R}}\mathbf{h})| \quad \forall\ p,\mathbf{h} \tag{3}$$

where $\tilde{\mathbf{R}}$ represents the transpose of $\mathbf{R}$. A sufficient (but not necessary) condition for (3) to be true would be that all substructures possessed a symmetry operation with the same rotational part $\mathbf{R}$. In this particular case, (Brown, 1971),

$$F_p(\tilde{\mathbf{R}}\mathbf{h}) = F_p(\mathbf{h}) \exp(-2\pi i\mathbf{h}\,.\,\mathbf{t}_p) \tag{4}$$

where $\mathbf{t}_p$ is the translation associated with the rotational operator $\mathbf{R}$ in the pth substructure. In a more general case,

$$F_p(\tilde{\mathbf{R}}\mathbf{h}) = F_p(\mathbf{h}) \exp[i\gamma_p(\mathbf{h})]\,, \tag{5}$$

$$\gamma_p(\mathbf{h}) = \varphi_p(\tilde{\mathbf{R}}\mathbf{h}) - \varphi_p(\mathbf{h}) \tag{6}$$

where $\varphi_p(\mathbf{h})$ is the phase angle of the reflexion of index $\mathbf{h}$ in substructure number p. If we rewrite (2) for $|F(\tilde{\mathbf{R}}\mathbf{h})|^2$ and substract (2) from the result, we obtain

$$\begin{aligned}\Delta I(\mathbf{h}) &= |F(\tilde{\mathbf{R}}\mathbf{h})|^2 - |F(\mathbf{h})|^2 \\ &= \sum_{p\neq q} t_{pq}[\cos(2\pi\tilde{\mathbf{R}}\mathbf{h}\,.\,\mathbf{u}_{pq} + \gamma_{pq}) - \cos(2\pi\mathbf{h}\,.\,\mathbf{u}_{pq})] \\ &\quad + g_{pq}[\sin(2\pi\tilde{\mathbf{R}}\mathbf{h}\,.\,\mathbf{u}_{pq} + \gamma_{pq}) - \sin(2\pi\mathbf{h}\,.\,\mathbf{u}_{pq})]\end{aligned} \tag{7}$$

where $\gamma_{pq} = \gamma_p - \gamma_q$ and

$$\begin{aligned} t_{pq} &= A_p(\mathbf{h})A_q(\mathbf{h}) + B_p(\mathbf{h})B_q(\mathbf{h}) \\ g_{pq} &= A_p(\mathbf{h})B_q(\mathbf{h}) - A_q(\mathbf{h})B_p(\mathbf{h})\,. \end{aligned} \tag{8}$$

By the use of standard trigonometric identities, and the fact that

$$\tilde{\mathbf{R}}\mathbf{h}\,.\,\mathbf{u}_{pq} = \mathbf{h}\,.\,\mathbf{R}\mathbf{u}_{pq} \tag{9}$$

(7) can be rewritten in the form

$$\begin{aligned}\tfrac{1}{2}\Delta I(\mathbf{h}) = \sum_{p\neq q} &\left\{ g_{pq} \cos\left[\pi\mathbf{h}\,.\,(\mathbf{u}_{pq} + \mathbf{R}\mathbf{u}_{pq}) + \frac{\gamma_{pq}}{2}\right] \right. \\ &\left. - t_{pq} \sin\left[\pi\mathbf{h}\,.\,(\mathbf{u}_{pq} + \mathbf{R}\mathbf{u}_{pq}) + \frac{\gamma_{pq}}{2}\right]\right\} \\ &\times \sin\left[\pi\mathbf{h}\,.\,(\mathbf{R}\mathbf{u}_{pq} - \mathbf{u}_{pq}) + \frac{\gamma_{pq}}{2}\right].\end{aligned} \tag{10}$$

A sufficient condition for $\Delta I(\mathbf{h})$ to vanish (and hence, for the operator $\tilde{\mathbf{R}}$ to appear in the diffraction pattern of the crystal) can be obtained by making either of the two factors in each term of summation (10) equal zero. Since

$$\frac{g_{pq}}{t_{pq}} = \tan[\varphi_q(\mathbf{h}) - \varphi_p(\mathbf{h})]\,, \quad t_{pq} \neq 0 \tag{11}$$

we obtain

$$\left.\begin{aligned} &\mathbf{h}\,.\,(\mathbf{R}\mathbf{u}_{pq} + \mathbf{u}_{pq}) + \frac{\gamma_p(\mathbf{h}) - \gamma_q(\mathbf{h})}{2\pi} + \frac{\varphi_p(\mathbf{h}) - \varphi_q(\mathbf{h})}{\pi} = n \\ &\text{or} \qquad g_{pq} = t_{pq} = 0 \end{aligned}\right\} \tag{12}$$

and

$$\mathbf{h}\,.\,(\mathbf{R}\mathbf{u}_{pq} - \mathbf{u}_{pq}) + \frac{\gamma_p(\mathbf{h}) - \gamma_q(\mathbf{h})}{2\pi} = m \tag{13}$$

where n and m are integers.

The second form of (12) is appropriate for the case of one of the structure factors involved being equal to zero. Equations (12) and (13) will be called general enhancement conditions in what follows. Since we have found these conditions by making each term of the summation (10) vanish, we are restricting our work to those cases in which any pair of substructures would itself constitute a structure for which $\Delta I(\mathbf{h}) = 0$, $\forall\ \mathbf{h}$. This explicitly eliminates Iwasaki's (1972) type 2 crystals from any consideration here.

3. Simple enhancement

In simple-enhancement cases the substructures possess the rotation operator $\mathbf{R}$, and (4) is satisfied. Hence,

$$\gamma_{pq} = 2\pi\mathbf{h}\,.\,(\mathbf{t}_q - \mathbf{t}_p) \tag{14}$$

and the enhancement conditions (12) and (13) now read

$$\left.\begin{aligned} &\mathbf{h}\,.\,[\mathbf{R}\mathbf{u}_{pq} + \mathbf{u}_{pq} + (\mathbf{t}_q - \mathbf{t}_p)] + \frac{\varphi_p(\mathbf{h}) - \varphi_q(\mathbf{h})}{\pi} = n \\ &\text{or} \qquad g_{pq} = t_{pq} = 0 \end{aligned}\right\} \tag{15}$$

and

$$\mathbf{h}\,.\,[\mathbf{R}\mathbf{u}_{pq} - \mathbf{u}_{pq} + (\mathbf{t}_q - \mathbf{t}_p)] = m \tag{16}$$

where m and n are integer numbers.

3.1. *Type* 1 *crystals*

If $\mathbf{t}_p = \mathbf{t}_q$ for every p,q, and $\varphi_p(\mathbf{h}) = \varphi_q(\mathbf{h}) + n\pi$ for every non-zero F_p, F_q, then the structure belongs to type 1 (Iwasaki, 1972). The following are examples of physically possible type 1 crystals. (*a*) All substructures are geometrically and chemically identical; scattering can be normal or anomalous. (*b*) All substructures are geometrically identical, and all atoms of a given substructure belong to the same chemical species; normal scattering only. (*c*) All substructures are geometrically identical, and the atoms of a given substructure belong to different chemical elements. In this case we also require that the scattering factors of atoms occupying homologous positions in different substructures must be proportional, or, to say it differently, the electron density of substructure number m has to be equal to the electron density of substructure number

1 multiplied by a positive constant c_m (and, of course, shifted by the corresponding **u** vector). This case is only valid for normal scattering, and the crystal will be approximately type 1 only to the extent that proportionality between the different f curves involved can be safely assumed to hold.

For type 1 crystals, conditions (15) and (16) become

$$\mathbf{h}\,.\,(\mathbf{R}\mathbf{u}_{pq}+\mathbf{u}_{pq})=n \qquad (17)$$

$$\mathbf{h}\,.\,(\mathbf{R}\mathbf{u}_{pq}-\mathbf{u}_{pq})=m \qquad (18)$$

and, if we restrict the analysis to the case of Bragg reflexions, these conditions reduce to

$$\mathbf{R}\mathbf{u}_{pq}+\mathbf{u}_{pq}=\mathbf{L}_1 \qquad (19)$$

$$\mathbf{R}\mathbf{u}_{pq}-\mathbf{u}_{pq}=\mathbf{L}_2 \qquad (20)$$

where $\mathbf{L}_1$ and $\mathbf{L}_2$ are (direct) lattice vectors.

Either of conditions (19) or (20) is sufficient for the operation $\tilde{\mathbf{R}}$ to be present in the weighted reciprocal lattice of the crystal. However, if we are to require that symmetry enhancement occur, we need the additional condition that the total structure must not possess the operation whose rotational part is to be diffraction enhanced. In this connexion, we prove the following.

Theorem I. In a crystal composed of any number of substructures, all of them having the symmetry operation (**R**, **t**) with respect to their origins, the relation

$$\mathbf{R}\mathbf{u}_{pq}-\mathbf{u}_{pq}=\mathbf{L}_{pq}, \mathbf{L}_{pq}\in\mathscr{L} \qquad (20')$$

satisfied by all vectors $\mathbf{u}_{pq}$, is sufficient for the total structure to possess the symmetry operation (**R**,**t**). ($\mathscr{L}$ represents the set of all lattice translations).

Proof. Take any two substructures and let their corresponding electron densities be $\varrho_1(\mathbf{r})$ and $\varrho_2(\mathbf{r})$. Suppose the first has the operation (**R**,**t**) with respect to point $\mathbf{u}_1$ (in other words, the point of radius vector $\mathbf{u}_1$ is invariant under the rotational part of that operation), and the second has the same operation with respect to point $\mathbf{u}_2$:

$$\varrho_1(\mathbf{r})=\varrho_1[\mathbf{R}(\mathbf{r}-\mathbf{u}_1)+\mathbf{u}_1+\mathbf{t}] \qquad (21)$$

$$\varrho_2(\mathbf{r})=\varrho_2[\mathbf{R}(\mathbf{r}-\mathbf{u}_2)+\mathbf{u}_2+\mathbf{t}]\,. \qquad (22)$$

The composite electron density can thus be written

$$\varrho(\mathbf{r})=\varrho_1[\mathbf{R}\mathbf{r}-\mathbf{R}\mathbf{u}_1+\mathbf{u}_1+\mathbf{t}]+\varrho_2[\mathbf{R}\mathbf{r}-\mathbf{R}\mathbf{u}_2+\mathbf{u}_2+\mathbf{t}] \quad (23)$$

and if we substitute condition (20′) into the previous expression,

$$\begin{aligned}\varrho(\mathbf{r})&=\varrho_1[\mathbf{R}\mathbf{r}-\mathbf{R}\mathbf{u}_1+\mathbf{u}_1+\mathbf{t}]\\&\quad+\varrho_2[\mathbf{R}\mathbf{r}-\mathbf{R}\mathbf{u}_1+\mathbf{u}_1+\mathbf{t}+\mathbf{L}_{12}]\\&=\varrho[\mathbf{R}(\mathbf{r}-\mathbf{u}_1)+\mathbf{u}_1+\mathbf{t}]\end{aligned} \qquad (24)$$

which means that the composite structure has operation (**R**, **t**) around point $\mathbf{u}_1$. It is evident that the proof can be extended to any number of substructures. The converse theorem is not true, since counter-examples can be found; for instance, if two geometrically and chemically identical substructures having a twofold axis at their origins are shifted by an arbitrary vector perpendicular to that twofold axis, the resulting composite structure will have a twofold axis at the mid-point of the segment joining the origins of the substructures, but condition (20) will not, in general, be satisfied.

According to theorem I, condition (20) has to be violated in every enhancement case for type 1 crystals; consequently, our enhancement conditions for these crystals are (19) and the negation of (20), *i.e.*

$$\mathbf{R}\mathbf{u}_{pq}-\mathbf{u}_{pq}\neq\mathbf{L},\ \ \forall\,\mathbf{L}\in\mathscr{L},\ \ \text{for some } \mathbf{u}_{pq}. \qquad (25)$$

Note, however, that (19) and (25) are not sufficient conditions of enhancement, since (25) is only a necessary condition. This means that in principle, a type 1 crystal constituted of substructures which satisfy both (19) and (25) could still possess operation (**R**, **t**), and consequently, its diffraction pattern would not show symmetry enhancement. It appears that this can only occur in extremely degenerate cases (for instance, in the above-mentioned counter-example to the converse of theorem I) and for sufficiently general cases we can take (19) and (25) as a set of sufficient conditions. All cases presented in this paper have nevertheless been checked to ensure that, for a given pair of substructures, the composite structure does not possess the operation to be diffraction enhanced.

For type 1 structures, Iwasaki's enhancement condition is

$$\cos(2\pi\mathbf{h}\,.\,\mathbf{u}_{pq})=\cos(2\pi\tilde{\mathbf{R}}\mathbf{h}\,.\,\mathbf{u}_{pq}),\quad\forall\,\mathbf{h} \qquad (26)$$

which is equivalent to conditions (19) and (20). Our set of conditions is not only more restrictive than Iwasaki's, but more compact and easier to use as well.

3.2. *New cases of enhancement in type* 1 *structures*

The different cases of enhancement can be obtained by straightforward application of conditions (19) and (25). However, we prove first two theorems which limit the possible outcomes of such a search.

Theorem II. There can be no enhancement of a rotational operator **R** present in all substructures of a type 1 crystal if these are centrosymmetric.

Proof. If the substructures possess a symmetry operation with a rotational part **R** with respect to a given point, and are centrosymmetric, then they necessarily possess a symmetry operation having $-\mathbf{R}$ as its rotational part, with respect to some other point. (Note that if matrix **R** represents a n-fold rotation around some axis, then matrix $-\mathbf{R}$ represents a n-fold inversion rotation around the same axis.) If the enhancement condition (19) is satisfied for operation **R**, this can be written in the form

$$(-\mathbf{R})\mathbf{u}_{pq} - \mathbf{u}_{pq} = \mathbf{L}, \mathbf{L} \in \mathscr{L} \tag{27}$$

and, according to theorem I this is sufficient for the operation $-\mathbf{R}$ to be preserved in the total structure, and hence for the operation $-\mathbf{R}$ to appear in the diffraction pattern. On the other hand, since the substructures are centrosymmetric, and the enhancement condition (19) is satisfied by any vector $\mathbf{u}_{pq}$ for the operation of inverting through the origin, the diffraction pattern will be centrosymmetric, and the presence of operation $\mathbf{R}$ in the diffraction pattern can be considered as a byproduct of Friedel's law rather than as a result of enhancement.* This completes the proof of theorem II.

This theorem was enunciated by Iwasaki (1972), as a result of an inductive process in which he observed that none of the enhancement cases he found were based on centrosymmetric substructures. Since he failed to obtain all the cases, we consider it is pertinent to present here a general proof.

Theorem III. If the enhancement condition for the operator $\mathbf{R}$ is satisfied, then the operation $\mathbf{R}^2$ is necessarily preserved in the point group of the composite structure.

Proof. We assume that condition (19) is satisfied by a given operator $\mathbf{R}$ and a vector $\mathbf{u}$ (we drop the subscripts here for convenience). If we operate with $\mathbf{R}$ on both members of (19), we obtain

$$\mathbf{R}^2\mathbf{u} + \mathbf{R}\mathbf{u} = \mathbf{L}', \quad \mathbf{L}' \in \mathscr{L} \tag{28}$$

since the lattice must be consistent with any rotational symmetry that the substructures possess. From (19) and (28) we obtain

$$\mathbf{R}^2\mathbf{u} - \mathbf{u} = \mathbf{L}'', \quad \mathbf{L}'' \in \mathscr{L} \tag{29}$$

which, according to Theorem I, is sufficient for the composite structure to possess the operation ($\mathbf{R}^2$, 2t). (*q.e.d.*)

We now turn back to the problem of finding vector solutions to (19) subject to condition (25). Equation (19) can be put in the form

$$(\mathbf{R} + \mathbf{E})\mathbf{u} = \mathbf{L}, \quad \mathbf{L} \in \mathscr{L} \tag{30}$$

where $\mathbf{E}$ is the identity operator. It is clear that there will be an infinite number of solutions for each $\mathbf{L}$ (*i.e.* vectors depending on variable parameters) if $\det(\mathbf{R} + \mathbf{E}) = 0$. This is the case for symmetry elements 2, m, $\bar{3}$, $\bar{4}$ and $\bar{6}$. For the remaining symmetry elements 3, 4 and 6, $\det(\mathbf{R} + \mathbf{E}) \neq 0$, and there will be a unique vector $\mathbf{u}$ satisfying (30) for each lattice vector $\mathbf{L}$, *i.e.* the components of $\mathbf{u}$ will be fixed numbers. The symmetry elements 3 and $\bar{3}$ can be *a priori* excluded from any further consideration, since theorems II and III gurantee that they can never be enhanced.

Taking all these limitations into account, we have obtained all the cases found by Iwasaki (1972), and the supplementary cases published by Matsumoto,

Table 1. *Simple enhancement cases* (*type* 1) *previously published* (*Matsumoto, Kihara & Iwasaki,* 1974)

Diffraction symmetry	Crystal symmetry (point group)	Enhancement condition	Symmetry of substructures
$2/m$ c axis unique	1	$00w, 0\frac{1}{2}w, \frac{1}{2}0w, \frac{1}{2}\frac{1}{2}w$	m
		$uv0, uv\frac{1}{2}$	2
mmm	2 a axis unique	$u00, u0\frac{1}{2}, u\frac{1}{2}0, u\frac{1}{2}\frac{1}{2}$	
	b axis unique	$0v0, 0v\frac{1}{2}, \frac{1}{2}v0, \frac{1}{2}v\frac{1}{2}$	222
	c axis unique	$00w, 0\frac{1}{2}w, \frac{1}{2}0w, \frac{1}{2}\frac{1}{2}w$	
	m a axis unique	$0v0, 0v\frac{1}{2}, \frac{1}{2}v0, \frac{1}{2}v\frac{1}{2}$	$mm2$
		$00w, 0\frac{1}{2}w, \frac{1}{2}0w, \frac{1}{2}\frac{1}{2}w$	$m2m$
	b axis unique	$u00, u0\frac{1}{2}, u\frac{1}{2}0, u\frac{1}{2}\frac{1}{2}$	$mm2$
		$00w, 0\frac{1}{2}w, \frac{1}{2}0w, \frac{1}{2}\frac{1}{2}w$	$2mm$
	c axis unique	$u00, u0\frac{1}{2}, u\frac{1}{2}0, u\frac{1}{2}\frac{1}{2}$	$m2m$
		$0v0, 0v\frac{1}{2}, \frac{1}{2}v0, \frac{1}{2}v\frac{1}{2}$	$2mm$
$4/m$	2	$00w, \frac{1}{2}\frac{1}{2}w$	$\bar{4}$
$4/mmm$	$mm2$	$00w, \frac{1}{2}\frac{1}{2}w$	$\bar{4}m2, \bar{4}2m$
	4	$00w, \frac{1}{2}\frac{1}{2}w$	422
$\bar{3}1m$	3	$00w$	312
$\bar{3}m1$	3	$00w$	321
$6/m$	3	$00w$	$\bar{6}$
$6/mmm$	$31m$	$00w$	$\bar{6}2m$
	$3m1$	$00w$	$\bar{6}m2$
	6	$00w$	622

Table 2. *New enhancement cases for type* 1 *crystals based on primitive lattices*

Diffraction symmetry	Crystal symmetry	Enhancement condition	Symmetry of substructures
$\bar{3}m$	3	$00w,$* $\frac{1}{3}\frac{2}{3}w,$† $\frac{2}{3}\frac{1}{3}w$†	321
$\bar{3}m$	3	$\frac{1}{3}\frac{2}{3}0, \frac{2}{3}\frac{1}{3}0, \frac{1}{3}\frac{2}{3}\frac{1}{2}, \frac{2}{3}\frac{1}{3}\frac{1}{2}$	$31m$
$6/m$	3	$\frac{1}{3}\frac{2}{3}0, \frac{2}{3}\frac{1}{3}0, \frac{1}{3}\frac{2}{3}\frac{1}{2}, \frac{2}{3}\frac{1}{3}\frac{1}{2}$	6
$6/mmm$	312	$\frac{1}{3}\frac{2}{3}0, \frac{2}{3}\frac{1}{3}0, \frac{1}{3}\frac{2}{3}\frac{1}{2}, \frac{2}{3}\frac{1}{3}\frac{1}{2}$	622
$6/mmm$	$3m1$	$\frac{1}{3}\frac{2}{3}0, \frac{2}{3}\frac{1}{3}0, \frac{1}{3}\frac{2}{3}\frac{1}{2}, \frac{2}{3}\frac{1}{3}\frac{1}{2}$	$6mm$
$6/mmm$	$\bar{6}$	$\frac{1}{3}\frac{2}{3}0, \frac{2}{3}\frac{1}{3}0, \frac{1}{3}\frac{2}{3}\frac{1}{2}, \frac{2}{3}\frac{1}{3}\frac{1}{2}$	$\bar{6}2m$

* This case has been previously published (Matsumoto *et al.*, 1974); included here to complete all cases for point group 321.

† $w \neq \frac{1}{3}$ if lattice is R, otherwise unrestricted.

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* Note, however, that the crystal may be non-centrosymmetric; in that case, if the substructures are of the kind described in example (*a*) above, we will have a non-centrosymmetric crystal whose diffraction pattern is centrosymmetric even with anomalous scattering. This would be a non-trivial case of enhancement of the inversion operator, and as such, ought to be included in the definition of enhancement. The statement of theorem II has to be understood in the sense that the diffraction pattern of a type 1 crystal in which the substructures are centrosymmetric would not show spurious symmetry beyond the expected addition of an inversion centre. Whether or not we consider this to be enhancement depends on the definition chosen for the phenomenon. In this paper we have chosen to follow the definition put forward by previous authors (see references), and consider as enhancement cases only those in which the diffraction symmetry is higher than expected under normal circumstances; it should however be obvious that, from a theoretical point of view, Friedel's law should be considered as a particular case, however trivial, of the more general phenomenon.

Kihara & Iwasaki (1974). For the convenience of the reader, we present their results in Table 1. In addition to these, we have found a dozen more cases which are summarized in Tables 2 and 3. In non-primitive lattices, the presence of lattice vectors with non-integral components produces several special enhancement cases, listed in Table 3. The cases presented in Table 2 are valid for all lattice types consistent with each point group.

Table 3. *New cases of enhancement for type* 1 *structures based on non-primitive lattices*

	Crystal			Substructures	
Diffraction symmetry	lattice type	point group	Enhancement condition	lattice type	point group
$4/m$	B	2*	$\frac{1}{2}0\frac{1}{4}$, $0\frac{1}{2}\frac{1}{4}$	I	4
$4/mmm$	F	222†	$\frac{1}{2}0\frac{1}{4}$, $0\frac{1}{2}\frac{1}{4}$	I	422
$4/mmm$	I	$mm2$	$\frac{1}{2}0\frac{1}{4}$, $0\frac{1}{2}\frac{1}{4}$	I	$4mm$
$4/mmm$	I	$\bar{4}$	$\frac{1}{2}0\frac{1}{4}$, $0\frac{1}{2}\frac{1}{4}$	I	$\bar{4}2m$
mmm	B	2†	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$	F	$mm2$
$m3m$	F	23	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$	F	432

* *c* axis unique; *B*-lattice axes can be obtained from *I*-lattice axes by ($1\bar{1}0/010/001$).

† *F*-lattice axes can be obtained by ($1\bar{1}0/110/001$) from *I*-lattice axes.

† *B*-lattice axes are obtained by ($100/-\frac{1}{2}\frac{1}{2}0/001$) from *F*-lattice axes.

It can be seen that, besides the point group and lattice type, the orientation of the point-group symmetry elements with respect to the shortest lattice translations is important in those cases in which more orientations than one are possible. In other words, the important thing is the so-called 'arithmetic crystal class' (Niggli & Nowacki, 1935). For instance, a crystal of type 1 based on a body-centred lattice and constituted of substructures belonging to point group $\bar{4}2m$ can show diffraction enhancement of symmetry if the substructures are combined by vectors of the type $\frac{1}{2}0\frac{1}{4}$ or $0\frac{1}{2}\frac{1}{4}$ (Table 3); the $\bar{4}$ axis is preserved in the composite structure, and the rest of the symmetry elements in the substructure point group appear in the weighted reciprocal lattice, even though they are not present in the crystal point group. A similar result cannot be obtained if the point group orientation is $\bar{4}m2$, because in this case the preservation of the $\bar{4}$ axis automatically implies that the rest of the point group symmetry elements are also preserved in the composite structure. This result can be ultimately traced to the fact that in all space groups having an *I* lattice, which are isogonal with point group $\bar{4}2m$ ($I\bar{4}2m$ and $I\bar{4}2d$) there are two different kinds of equipoints with local symmetry $\bar{4}$, while in the corresponding space groups for which the point group orientation is $\bar{4}m2$ ($I\bar{4}m2$ and $I\bar{4}c2$), all equipoints which have at least local symmetry $\bar{4}$ are identical (*International Tables for X-ray Crystallography*, 1952).

3.3. *Type* 3 *crystals*

Type 3 crystals (Iwasaki, 1972) are those constituted of two substructures which belong to the same point group but to different space groups. This means that the rotational part **R** of any symmetry operation is common for both substructures, but the translational parts may be different. The enhancement conditions (15) and (16) cannot be further simplified in this case. In general, it will be extremely unlikely that two substructures satisfy the first part of (15) for all **h**. Iwasaki (1972) gives several concrete examples in which (16) is satisfied for some **h**, and the second part of (15) holds for every other **h**. All these examples were derived on the assumption that $\mathbf{u}_{12}=0$. It should be obvious, by consideration of (16), that all these examples would hold equally well for vectors in which

$$\mathbf{R}\mathbf{u}_{12}-\mathbf{u}_{12}=\mathbf{L}, \quad \mathbf{L}\in\mathscr{L} \tag{31}$$

is satisfied. The situation in which

$$\mathbf{R}\mathbf{u}_{pq}-\mathbf{u}_{pq}+\mathbf{t}_p-\mathbf{t}_q=\mathbf{L}, \quad \mathbf{L}\in\mathscr{L} \tag{32}$$

should however be avoided in constructing such examples, since a simple extension of theorem I will show that (32) is a sufficient condition for the composite structure to possess both operations, ($\mathbf{R}$, $\mathbf{t}_p$) and ($\mathbf{R}$, $\mathbf{t}_q$).

4. Double enhancement

Suppose a crystal is composed of substructures, and these are, in turn, constituted by sub-substructures. Under certain conditions, the crystal may exhibit the symmetry of the sub-substructures in its diffraction pattern, even if the substructures do not possess this symmetry; in other words, there is simple enhancement at the substructure level, and again at the structure (crystal) level (Matsumoto, 1975).

We use the general formulation developed in § 2 of this paper to analyse double enhancement. Since the diffraction symmetry of the substructures is enhanced, condition (3) is satisfied, and we can apply at once conditions (12) and (13) to the radius vectors between substructure origins. We restrict the discussion to the case that the substructures are themselves type 1 structures, and we assume that the sub-substructures corresponding to a given substructure are so arranged as to satisfy conditions (19) and (25) for a given rotational operator **R**. The condition that all substructures belong to type 1 can be expressed as

$$F_r^p(\mathbf{h})=c_r^pF_1^p(\mathbf{h}) \tag{33}$$

where $F_r^p(\mathbf{h})$ is the structure factor of index **h** of the *r*th sub-substructure belonging to the *p*th substructure, and where c_r^p is a real number for every p,r, which, in general, will depend on **h**. If we designate by $\mathbf{u}_{rs}^p$ the vector between the origins of the *r*th and *s*th sub-substructures of the *p*th substructure, then the condition for enhancement to occur at the substructure level is

$$\mathbf{R}\mathbf{u}_{rs}^p+\mathbf{u}_{rs}^p=\mathbf{L}, \quad \mathbf{L}\in\mathscr{L}, \ \forall\, \mathbf{u}_{rs}^p. \tag{34}$$

From (33) we obtain, by using an equation similar to (1),

$$F^p(\mathbf{h}) = F_1^p(\mathbf{h}) \sum c_r^p \exp\left[2\pi i\mathbf{h}\,.\,\mathbf{u}_r^p\right] \tag{35}$$

where $F^p(\mathbf{h})$ is the structure factor corresponding to the pth substructure, and $\mathbf{u}_r^p$ is the radius vector of the origin of its rth sub-substructure drawn from the origin of the pth substructure. From (35) and (4) we obtain

$$F^p(\tilde{\mathbf{R}}\mathbf{h}) = F_1^p(\mathbf{h}) \exp\left[-2\pi i\mathbf{h}\,.\,\mathbf{t}\right] \times \sum c_r^p \exp\left[2\pi i\mathbf{h}\,.\,\mathbf{R}\mathbf{u}_r^p\right], \tag{36}$$

since condition (4) applies to the structure factor of a given sub-substructure. If we define the origin of the pth substructure as coinciding with the origin of one of its sub-substructures, namely the sth sub-substructure, we can obtain from (34)

$$\mathbf{h}\,.\,\mathbf{R}\mathbf{u}_r^p = -\mathbf{h}\,.\,\mathbf{u}_r^p + n, \quad n \text{ integer}. \tag{37}$$

We define a complex number H by the expression

$$H = \sum c_r^p \exp\left[2\pi i\mathbf{h}\,.\,\mathbf{u}_r^p\right] = |H| \exp\left[i\alpha_p(\mathbf{h})\right]. \tag{38}$$

Using (35), (36), (37) and (38) we obtain

$$F^p(\mathbf{h}) = F_1^p(\mathbf{h})|H| \exp\left[i\alpha_p(\mathbf{h})\right] \tag{39}$$

$$F^p(\tilde{\mathbf{R}}\mathbf{h}) = F_1^p(\mathbf{h})|H| \exp\left[-i\alpha_p(\mathbf{h}) - 2\pi i\mathbf{h}\,.\,\mathbf{t}\right], \tag{40}$$

from which [see definition of $\gamma_p(\mathbf{h})$ in (6)]:

$$\gamma_p(\mathbf{h}) - \gamma_q(\mathbf{h}) = 2[\alpha_q(\mathbf{h}) - \alpha_p(\mathbf{h})]. \tag{41}$$

We call the phase angle of $F_1^p(\mathbf{h})$ $\beta_p(\mathbf{h})$, and recall the meaning of $\varphi_p(\mathbf{h})$ in (6). Then,

$$\varphi_p(\mathbf{h}) - \varphi_q(\mathbf{h}) = [\alpha_p(\mathbf{h}) - \alpha_q(\mathbf{h})] + [\beta_p(\mathbf{h}) - \beta_q(\mathbf{h})] \tag{42}$$

so that we can write the double-enhancement conditions, starting with (12) and (13), as

$$\mathbf{h}\,.\,(\mathbf{R}\mathbf{u}_{pq} + \mathbf{u}_{pq}) + \frac{\beta_p(\mathbf{h}) - \beta_q(\mathbf{h})}{\pi} = n \tag{43}$$

$$\mathbf{h}\,.\,(\mathbf{R}\mathbf{u}_{pq} - \mathbf{u}_{pq}) + \frac{\alpha_q(\mathbf{h}) - \alpha_p(\mathbf{h})}{\pi} = m \tag{44}$$

where $\mathbf{u}_{pq}$ have the usual meaning of vectors between the origins of different substructures, and n and m are integers.

4.1. *Discussion of the conditions of double enhancement*

4.1.1. *First condition*

Suppose

$$F_1^p(\mathbf{h}) = c^{pq} F_1^q(\mathbf{h}) \quad \forall\, \mathbf{h}, \forall\, p,q \tag{45}$$

is satisfied, where c^{pq} is a real number possibly dependent on $\mathbf{h}$. Condition (45) will be satisfied, for instance, if all the sub-substructures in the crystal are geometrically identical and chemically 'proportional' in the sense of example (*c*) of § 3.1 above. From the definition of $\beta_p(\mathbf{h})$ we deduce that condition (43) can now be written, for Bragg reflexions, in the form

$$\mathbf{R}\mathbf{u}_{pq} + \mathbf{u}_{pq} = \mathbf{L}, \quad \mathbf{L} \in \mathscr{L}. \tag{46}$$

Since we are assuming that there is enhancement at the substructure level, the position vectors of the sub-substructure origins referred to the origins of the corresponding substructures satisfy equations similar to (46). Hence, the phenomenon can be described as a case of simple enhancement, in which the sub-substructures play the role of substructures.

4.1.2. *Second condition*

(*a*) We make $c_r^p = 1$, $\forall p,r$ [*cf.* equation (33)]. A possible way of satisfying this would be to have a structure in which every substructure is formed of geometrically and chemically identical sub-substructures; sub-substructures belonging to different substructures could possibly be different. In this case, the substructures will be type 1, even for anomalous scattering. Under the above assumptions, the quantity $\alpha_p(\mathbf{h})$ defined in (38) can be interpreted as the phase angle of the geometrical part of the structure factor of the 'structure' formed by the origins of the different sub-substructures of the pth substructure.

Suppose now that we partition a crystal into substructures in such a way that all atoms of the same chemical species belong to the same substructure. Within each substructure we take monatomic (and hence centrosymmetric) sub-substructures. It is clear that such a partition satisfies the condition $c_r^p = 1$, $\forall p,r$ stipulated in the previous paragraph, and also that the centre of symmetry of the sub-substructures will be enhanced at the substructure level. If we wish the inversion centre to appear in the diffraction pattern through double enhancement the condition to satisfy is

$$2\pi\mathbf{h}\,.\,\mathbf{u}_{pq} + \alpha_q(\mathbf{h}) - \alpha_p(\mathbf{h}) = n, \quad n \text{ integer} \tag{47}$$

obtained from (44). This is the same condition obtained by Iwasaki (1974) in a paper in which he studied several cases of non-centrosymmetric structures which satisfy Friedel's law even with anomalous scattering. All the cases described therein can clearly be considered as double enhancement cases of the type studied here.

(*b*) If the following conditions:

$$\mathbf{u}_r^p = \mathbf{u}_r^q, \quad \forall p,q, \quad \forall r \tag{48}$$

$$c_r^p = c_r^q, \quad \forall p,q, \quad \forall r, \tag{49}$$

are satisfied, and each substructure consists of the same number of sub-substructures, it can be seen that condition (44) simplifies to

$$\mathbf{R}\mathbf{u}_{pq} - \mathbf{u}_{pq} = \mathbf{L}, \quad \mathbf{L} \in \mathscr{L} \tag{50}$$

which is now a perfectly valid enhancement condition, because we are assuming that the substructures do not possess any symmetry operation having $\mathbf{R}$ as its rotational part.

The above conditions can be satisfied if the crystal fulfills all the following requirements. (i) All substructures are composed of the same number of geometrically identical sub-substructures, identically arranged in space. These sub-substructures are chemically 'proportional'. (ii) The ratio of the atomic scattering factors of homologous atoms in two different sub-substructures of a given substructure is the same as the corresponding ratio for the sub-substructures which occupy homologous origins in a different substructure. (iii) Sub-substructures corresponding to different substructures need not be geometrically identical. Such a crystal would approximately satisfy conditions (48) and (49) with the limitations established in example (*c*) of §3.1.

4.2. *Double-enhancement cases in type* 5 *crystals*

We define as type 5 crystals those which satisfy (45), (48) and (49), with the additional condition that all substructures have the same number of sub-substructures. A possible example would be any crystal which fulfils requirements (i) and (ii) and the contrary of (iii) in §4.1. 2(*b*) above. From the analysis in §4.1 we conclude that, for such crystals, the double-enhancement conditions (43) and (44) reduce to

$$\mathbf{R}\mathbf{u}_{pq}+\mathbf{u}_{pq}=\mathbf{L}_1 \tag{51}$$

$$\mathbf{R}\mathbf{u}_{pq}-\mathbf{u}_{pq}=\mathbf{L}_2 \tag{52}$$

for the case of Bragg reflexions, where $\mathbf{L}_1$ and $\mathbf{L}_2$ are lattice vectors.

It is to be noted that there are restrictions in the possible symmetries that a crystal exhibiting this kind of double enhancement could possibly have, similar to simple-enhancement cases. In particular, since we are assuming that there occurs simple enhancement of the operator **R** at the substructure level, theorem III guarantees that the substructures possess operation $(\mathbf{R}^2,2\mathbf{t})$. If either (51) or (52) is satisfied, an argument similar to that given for the proof of theorem III will show that this automatically entails the preservation of the operation $\mathbf{R}^2$ in the crystal point group. This means that if the point group of the sub-substructures is a cyclic one, and we arrange them in such a way that this point-group symmetry appears in the weighted reciprocal lattice by double enhancement, one could always obtain the same relation crystal symmetry/weighted reciprocal lattice symmetry by a case of simple enhancement.

Suppose, for example, that a crystal has sub-substructures based on an *I* lattice, with point-group symmetry $\bar{4}$. According to Matsumoto *et al.* (1974), (see Table 1) these sub-substructures can be combined by vectors $00w$ to produce substructures belonging to point group 2. If we combine these substructures by vectors of the type $\frac{1}{2}0\frac{1}{4}$ we will satisfy condition (52) for the fourfold inversion operator, and we will end up with a monoclinic crystal (*c* axis unique), based on a *B* lattice, and belonging to point group 2. Note that we have not tried to satisfy condition (51) for the second step, because then the case would have reduced to a case of simple enhancement. Our final result cannot be explained in terms of any simple enhancement case, but the gain in symmetry $2 \rightarrow \bar{4}$ (or to $4/m$, if Friedel's law holds) is one which could be achieved by simple enhancement.

More interesting are those cases of double enhancement in which the corresponding symmetry gain could not possibly be obtained by simple enhancement. Let us consider, for example, sub-substructures belonging to point group 222. According to Matsumoto *et al.* (Table 1) we can build with them substructures belonging to point group 2 (*b* axis unique) by vectors of the type $0v0$. We can now combine such substructures in a way such that the twofold axis operation is destroyed but enhanced; this can be accomplished by vectors of the type $u0w$ or $u\frac{1}{2}w$. However, we want to have the other two twofold axes present simultaneously in the diffraction symmetry group of the crystal by double enhancement; we can obtain that result by specializing u or w to zero value. For instance, if we take $u00$, we simultaneously satisfy: (*a*) simple-enhancement* condition (51) for $2\|y$, (*b*) double-enhancement condition (52) for $2\|x$, (*c*) double-enhancement condition (51) for $2\|z$. The final point group of the crystal is 1, while its diffraction symmetry is *mmm* (or 222, where Friedel's law does not hold).

We have made no attempt to derive and tabulate all possible double-enhancement cases for type 5 crystals. The cases presented in Table 4 are the ones we have found that satisfy the condition that the gain in symmetry, in going from the crystal point group to the point group of the weighted reciprocal lattice, cannot be achieved by any of the simple enhancement cases known to date. According to the extension of theorem III (see § 4.2), if we have sub-substructures having a certain point-group symmetry we can only construct with them double enhancement cases in which the final crystal has a minimum symmetry, which will correspond to the group formed by the squares of all the operations in the point group of the sub-substructures. This means, for example, that if the sub-substructures have a fourfold axis, the minimum symmetry of a crystal built from them which shows double enhancement will correspond to point group 2. Consequently, if we disregard those cases in which the maximum lowering of symmetry can be obtained in a simple enhancement case, we will have to consider only point groups *mm*2, 222, 422, 4*mm*, $\bar{4}m2$, 622, 6*mm* and $\bar{6}m2$ as possible symmetries for the sub-substructures. We have found possible double-enhancement cases for all these, with the exception of point groups 4*mm* and 6*mm*. The last eight cases listed in Table 4 can be grouped in pairs to form only four essentially

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* The enhancement is simple because the substructures do possess a twofold axis parallel to *y*.

different cases. The distinction between the two members of a given pair is purely formal and depends on how the substructures are defined. A similar statement can be made about the first nine cases, which can be reduced to essentially three different possibilities.

5. Concluding considerations

The theory presented here covers in a single formulation the enhancement of diffraction symmetry for crystals belonging to types 1 and 3, and the double enhancement of diffraction symmetry for certain crystals which we have called type 5 crystals, as well as the double enhancement of the inversion operation in crystals which would normally violate Friedel's law under conditions of anomalous dispersion. The general equations follow loosely Iwasaki's (1972) formulation, but we have modified it by introducing condition (3) early in the derivation, instead of the more restrictive condition (4) that Iwasaki uses. Moreover the use of identity (9) permits us to obtain the final enhancement conditions for the different types of crystals in the form of vector equations, many of whose solutions can be readily found by geometrical arguments. The proofs of theorems I through III (and their extensions) definitely help in the process of finding enhancement cases, by establishing limits to the possible range of the solutions. The use of condition (3) gives generality to the treatment so that equations (12) and (13) can be used for simple as well as for double enhancement cases. By the use of this formulation we have: (*a*) considerably enlarged the catalogue of known simple enhancement cases for crystals of type 1; (*b*) Classified all cases described by Iwasaki (1974), as special double-enhancement cases; (*c*) Derived and tabulated a set of possible double-enhancement cases for type 5 crystals.

Very recently Iwasaki (1975) announced the derivation of more cases of simple enhancement for type 1 crystals. A tabulation of these new cases has not appeared in print as yet, but we find that our results appear to be irreconcilable with Iwasaki's contention that in crystals formed by equal substructures an enhancement case is possible in which a rombohedral crystal may show a cubic diffraction pattern. In our theory such a case is impossible, since theorem III precludes the possibility of a threefold rotation being diffraction enhanced. Our theory appears to be incompatible as well with Matsumoto's (1975) statement that a triclinic crystal could give a cubic diffraction pattern by a process of double enhancement. In our theory, a triclinic crystal cannot even give a tetragonal pattern, since the minimum point symmetry of a crystal which shows double enhancement is given by the group formed by the squares of all the operations present in the diffraction group. In this case, however, it is difficult to compare our results with Matsumoto's, because his abstract is not very explicit as to the conditions that his sub-substructures and substructures satisfy; our conclusions about symmetry relations in double enhancement cases (see § 4.2 above) are, of course, limited to type 5 crystals.

It should be borne in mind that the results of our analysis only apply to kinematic diffraction situations; we thank our referee for pointing this out to us. Finally, it must be emphasized that the conditions tabulated in this paper are not necessary conditions of enhancement; they are only sufficient, with the limitations established in § 2.

Table 4. *Cases of double enhancement in type 5 crystals*

Diffraction symmetry	Crystal symmetry	Double-enhancement conditions*	Substructure symmetry	Simple-enhancement conditions	Sub-substructure symmetry
mmm	1	$0v0, 0v\frac{1}{2}, \frac{1}{2}v0, \frac{1}{2}v\frac{1}{2}$ $00w, 0\frac{1}{2}w, \frac{1}{2}0w, \frac{1}{2}\frac{1}{2}w$	2 (*a* unique)	$u00, u0\frac{1}{2}, u\frac{1}{2}0, u\frac{1}{2}\frac{1}{2}$	222
	1	$u00, u\frac{1}{2}0, u0\frac{1}{2}, u\frac{1}{2}\frac{1}{2}$ $00w, 0\frac{1}{2}w, \frac{1}{2}0w, \frac{1}{2}\frac{1}{2}w$	2 (*b* unique)	$0v0, 0v\frac{1}{2}, \frac{1}{2}v0, \frac{1}{2}v\frac{1}{2}$	222
	1	$u00, u\frac{1}{2}0, u0\frac{1}{2}, u\frac{1}{2}\frac{1}{2}$ $0v0, 0v\frac{1}{2}, \frac{1}{2}v0, \frac{1}{2}v\frac{1}{2}$	2 (*c* unique)	$00w, 0\frac{1}{2}w, \frac{1}{2}0w, \frac{1}{2}\frac{1}{2}w$	222
	1	$u00, u\frac{1}{2}0, u0\frac{1}{2}, u\frac{1}{2}\frac{1}{2}$	*m* (*a* unique)	$0v0, 0v\frac{1}{2}, \frac{1}{2}v0, \frac{1}{2}v\frac{1}{2}$	*mm*2
	1	$0v0, 0v\frac{1}{2}, \frac{1}{2}v0, \frac{1}{2}v\frac{1}{2}$	*m* (*b* unique)	$u00, u\frac{1}{2}0, u0\frac{1}{2}, u\frac{1}{2}\frac{1}{2}$	*mm*2
	1	$u00, u\frac{1}{2}0, u0\frac{1}{2}, u\frac{1}{2}\frac{1}{2}$	*m* (*a* unique)	$00w, 0\frac{1}{2}w, \frac{1}{2}0w, \frac{1}{2}\frac{1}{2}w$	*m*2*m*
	1	$00w, \frac{1}{2}0w, 0\frac{1}{2}w, \frac{1}{2}\frac{1}{2}w$	*m* (*c* unique)	$u00, u0\frac{1}{2}, u\frac{1}{2}0, u\frac{1}{2}\frac{1}{2}$	*m*2*m*
	1	$0v0, 0v\frac{1}{2}, \frac{1}{2}v0, \frac{1}{2}v\frac{1}{2}$	*m* (*b* unique)	$00w, 0\frac{1}{2}w, \frac{1}{2}0w, \frac{1}{2}\frac{1}{2}w$	2*mm*
	1	$00w, \frac{1}{2}0w, 0\frac{1}{2}w, \frac{1}{2}\frac{1}{2}w$	*m* (*c* unique)	$0v0, 0v\frac{1}{2}, \frac{1}{2}v0, \frac{1}{2}v\frac{1}{2}$	2*mm*
4/*mmm*	(*F*)2(*c* unique)	$00w, 0\frac{1}{2}w, \frac{1}{2}0w, \frac{1}{2}\frac{1}{2}w$	(*F*)222	$\frac{1}{2}0\frac{1}{4}, 0\frac{1}{2}\frac{1}{4}$	(*I*)422
	(*B*)2(*c* unique)	$\frac{1}{2}0\frac{1}{4}, 0\frac{1}{2}\frac{1}{4}$	(*I*)4	$00w, \frac{1}{2}\frac{1}{2}w$	(*I*)422
	(*I*) 2(*c* unique)	$00w, \frac{1}{2}\frac{1}{2}w$	(*I*)$\bar{4}$	$\frac{1}{2}0\frac{1}{4}, 0\frac{1}{2}\frac{1}{4}$	(*I*)$\bar{4}2m$
	(*B*)2(*c* unique)	$\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{3}{4}\frac{3}{4}\frac{3}{4}$	(*F*)*mm*2	$00w, \frac{1}{2}\frac{1}{2}w$	(*I*)$\bar{4}2m$
6/*mmm*	3	$\frac{1}{3}\frac{2}{3}0, \frac{1}{3}\frac{2}{3}\frac{1}{2}, \frac{2}{3}\frac{1}{3}0, \frac{2}{3}\frac{1}{3}\frac{1}{2}$	6	$00w$	622
	3	$00w$	312	$\frac{1}{3}\frac{2}{3}0, \frac{1}{3}\frac{2}{3}\frac{1}{2}, \frac{2}{3}\frac{1}{3}0, \frac{2}{3}\frac{1}{3}\frac{1}{2}$	622
	3	$\frac{1}{3}\frac{2}{3}0, \frac{1}{3}\frac{2}{3}\frac{1}{2}, \frac{2}{3}\frac{1}{3}0, \frac{2}{3}\frac{1}{3}\frac{1}{2}$	31*m*	$00w$	$\bar{6}2m$
	3	$00w$	$\bar{6}$	$\frac{1}{3}\frac{2}{3}0, \frac{1}{3}\frac{2}{3}\frac{1}{2}, \frac{2}{3}\frac{1}{3}0, \frac{2}{3}\frac{1}{3}\frac{1}{2}$	$\bar{6}2m$

* When lattice type changes in going from sub-substructure to substructure these vectors are referred to the new axes imposed by the lattice type of the substructure.

Note added in proof: Dr T. Matsumoto (personal communication) has pointed out to us that some of the cases presented in Tables 2 and 3 do not hold as enhancement cases for pairs of geometrically and chemically identical substructures. It is still possible to obtain enhancement in some of those cases by combining more than two geometrically and chemically identical substructures, but, in any case, all the cases tabulated in this paper hold as enhancement cases in the more general instance of chemically different ('proportional') substructures.

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Some Information-Theory Aspects of Structure Determination

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The iterative procedure of phase determination in direct methods is considered as a filtering process. The use of different filter transforms for more effective filtering is proposed. The eigenvector transform for optimal extraction of reliable structure information from approximate densities is introduced.

1. Introduction

Since the first papers on direct methods for structure determination (Karle & Hauptman, 1950; Sayre, 1952) it was apparent that these methods were related to the *a priori* information present in the atomic arrangement and the electron density of the structure in question. The principles of positivity and atomicity together with the observed structure-factor amplitudes enabled the solution of structures of considerable complexity. Until then, the normal method of structure determination, the heavy-atom method or the more general partial-structure method, also used the atomicity principle but in a different way. The positioning of the heavy atom or partial structure and the consequent phasing of structure factors is of quite specific character and only pertains to the structure in question. However, the determination of the missing structure part by weighting the structure-factor amplitudes also relies on quite general principles and involves statistical considerations.

In contrast, the *a priori* information of direct methods is in most cases of an entirely general, statistical character. The natural way to estimate and measure the amount of information present in these principles is by information theory. In the following some information-theory aspects are used to derive results for both heavy-atom and direct methods to indicate their similarity. Furthermore the treatment is given of a special problem in structure determination as seen from information theory.

2. Structure determination as image filtering

X-ray structure determination can be considered as an imaging of an object (structure) where the Fourier transformation in the nonexistent X-ray lens is replaced by a calculated Fourier transformation to which the principles of optical image formation can be applied. Of special concern in this context is the separation of object and noise in an image.

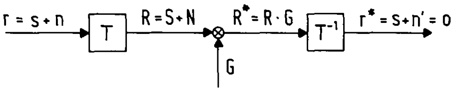

Fig. 1. Generalized Wiener filtering.