Acta Cryst. (1979). A**35**, 115–122

Basic Theorems of Vector Symmetry in Crystallography

BY R. SADANAGA AND K. OHSUMI

Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo 113, *Japan*

(*Received* 20 *April* 1978; *accepted* 7 *August* 1978)

Abstract

An attempt has been made to deduce the condition necessary for diffraction enhancement of symmetry to occur in the diffraction pattern of a structure **X**, and because the symmetry of the diffraction pattern of **X** coincides with that of its vector set **V**, the symmetric feature of **X** derived from the symmetry of **V** was studied. The symmetry with the point group $\mathbf{G}_V$ or $\mathbf{G}_V/\mathbf{G}_I$, according as **X** is inversion-symmetric or not, is defined as the vector symmetry of **X**, where $\mathbf{G}_V$ is the point group of **V** and $\mathbf{G}_I$ is the inversion group, and when the vector symmetry of **X** is $\mathbf{C}_n$, for example, **X** is specified as $\mathbf{C}_n$-vector-symmetric. When **X** is homometric with itself by a rotation of $2\pi/n$, it is specified as n-fold self-homometric. **X** being n-fold self-homometric is the necessary and sufficient condition for **X** to be n-fold vector-symmetric. Also, **X** exhibits an enhanced vector (diffraction) symmetry if it is a space-groupoid structure with the kernel whose point-group symmetry is, other than by addition of an inversion, higher than the point-group symmetry of **X**. Four examples of enhanced vector symmetry are examined.

1. Introduction

In the field of X-ray crystallography, it had long been believed that the point group $\mathbf{G}_D$ of the X-ray diffraction pattern **D** of a crystal structure **X** with a point group $\mathbf{G}_X$ is always isomorphic with either $\mathbf{G}_X$ when **X** is inversion-symmetric, or $\mathbf{G}_X \times \mathbf{G}_I$ when **X** is not inversion-symmetric and Friedel's law holds, where $\mathbf{G}_I$ is the inversion group and $\mathbf{G}_X \times \mathbf{G}_I$ the direct product of $\mathbf{G}_X$ with $\mathbf{G}_I$. However, Ramsdell & Kohn (1951) discovered that the trigonal polytype $10H$ of SiC exhibits a diffraction pattern which is strictly hexagonal, and Ross, Takeda & Wones (1966) found that the symmetry of the X-ray diffraction pattern of the triclinic modification $10Tc_3$ of mica is strictly monoclinic. Sadanaga & Takeda (1968) then theoretically dealt with the latter example, confirmed that under certain conditions the point group $\mathbf{G}_D$ of the diffraction pattern **D** can be monoclinic when the point group $\mathbf{G}_X$ of the structure **X** is triclinic, and proposed the term 'diffraction enhancement of symmetry' for the cases in which the symmetry of the diffraction pattern of a crystal becomes higher than the point-group symmetry of the crystal, other than as a result of Friedel's law.

Examples, both experimental and theoretical, of diffraction enhancement of symmetry have since been provided by Marumo & Saito (1972), Iwasaki (1972, 1974*a*,*b*, 1975), Ohsumi, Okamura & Sadanaga (1972), Sadanaga, Ohsumi & Matsumoto (1973*a*,*b*), Matsumoto, Kihara & Iwasaki (1974), Sadanaga & Ohsumi (1975), Matsumoto (1975), and Perez-Mato & Iglesias (1977). However, all these investigations were based upon structural models that produce enhanced diffraction symmetries, and accordingly dealt with only those conditions sufficient for the diffraction symmetry to be enhanced. In expectation of a better understanding of the nature of the phenomenon, therefore, we have been engaged in the search for the conditions necessary for the enhancement to occur, and now present the results of our study.

2. Basic assumption and concepts

Though some interesting types of diffraction enhancement of symmetry have been reported for structures with points of more than one kind of weight, such as that described by Iwasaki (1974*a*) and those referred to in the last section of the present paper, we assume in this paper that all the points in the structure **X** under examination are of equal weight. This is because the introduction of a variety of weight to the points in **X** will create an almost insurmountable difficulty in the derivation of conditions necessary for the enhancement to occur; the conclusions based upon this assumption prove to be sufficiently significant. As a result of this assumption Friedel's law will always hold in the diffraction pattern **D** of **X**.

If all the vectors in a structure **X** are shifted in parallel so that each may make each of its end points coincide with the origin O of a three-dimensional space, the well-known vector set **V** of **X** will be obtained. Because of the assumption that all the points in **X** are of equal weight, the vector set **V** is inversion-symmetric,

0567-7394/79/010115-08$01.00

which corresponds to Friedel's law in **D**. The symmetry of the diffraction pattern **D** of the structure **X** can then be proved to coincide with the symmetry of its vector set **V** (Ohsumi, Koyama & Tamada, 1977). Therefore, we shall henceforward replace the diffraction pattern with the corresponding vector set, and try to deduce the symmetric feature of a crystal from the symmetry assumed for its vector set.

In the kinds of structure we consider in this paper, three types of operation will appear for the superposition of a configuration of points upon itself or another. The first is a symmetry operation which is effective everywhere in a crystal space and is called a global operation. It is an ordinary space-group operation which brings the entire structure **X** to superpose upon itself. The second is a symmetry operation called a local operation which is effective only within a certain subspace of a crystal space and brings the subspace to superpose upon itself. The third type of operation will be specified as partial. It operates only on a subspace **A** of a crystal space to bring it to superposition upon another **B** and is accordingly not a symmetry operation. The most general form of the partial operation is either a partial screw or a partial rotatory inversion.

When a structure **X** consists of a finite number of substructures in such local symmetries as with space groups isomorphic with each other, the set of all operations, each of which brings each of the substructures to superpose upon itself or another, forms a groupoid defined by Brandt (1926) and introduced into crystallography by Dornberger-Schiff (1957). We call the structure **X** specified above a space-groupoid structure, a planar and finitely extended model of it being illustrated in Fig. 1. A space groupoid consists of two classes of operations of superposition: one class is composed of local symmetry operations, each bringing each of the substructures to superpose upon itself, and the other is composed of operations, each bringing each of the substructures to superpose upon another. A complete set of local symmetry operations which bring one of the substructures to superpose upon itself obviously constitutes a group. According to Loewy (1927), we shall call this group $\mathbf{K}_0$ the kernel of the groupoid, and the set **H** of all the operations of the second class the hull of the groupoid, in which partial operations are necessarily contained. The groupoid **M** can be decomposed (Loewy, 1927) as

$$
\begin{aligned}
\mathbf{M} = {} & \mathbf{K}_0 \cup \mathbf{K}_0\mathbf{h}_1 \cup \mathbf{K}_0\mathbf{h}_2 \cup \cdots \cup \mathbf{K}_0\mathbf{h}_i \cup \cdots \cup \mathbf{K}_0\mathbf{h}_n \\
& \cup \mathbf{h}_1^{-1}\mathbf{K}_0 \cup \mathbf{h}_1^{-1}\mathbf{K}_0\mathbf{h}_1 \cup \mathbf{h}_1^{-1}\mathbf{K}_0\mathbf{h}_2 \cup \cdots \cup \mathbf{h}_1^{-1}\mathbf{K}_0\mathbf{h}_i \cup \cdots \cup \mathbf{h}_1^{-1}\mathbf{K}_0\mathbf{h}_n \\
& \cup \mathbf{h}_2^{-1}\mathbf{K}_0 \cup \mathbf{h}_2^{-1}\mathbf{K}_0\mathbf{h}_1 \cup \mathbf{h}_2^{-1}\mathbf{K}_0\mathbf{h}_2 \cup \cdots \cup \mathbf{h}_2^{-1}\mathbf{K}_0\mathbf{h}_i \cup \cdots \cup \mathbf{h}_2^{-1}\mathbf{K}_0\mathbf{h}_n \\
& \quad \vdots \qquad \vdots \qquad \vdots \qquad \vdots \qquad \vdots \\
& \cup \mathbf{h}_i^{-1}\mathbf{K}_0 \cup \mathbf{h}_i^{-1}\mathbf{K}_0\mathbf{h}_1 \cup \mathbf{h}_i^{-1}\mathbf{K}_0\mathbf{h}_2 \cup \cdots \cup \mathbf{h}_i^{-1}\mathbf{K}_0\mathbf{h}_i \cup \cdots \cup \mathbf{h}_i^{-1}\mathbf{K}_0\mathbf{h}_n \\
& \quad \vdots \qquad \vdots \qquad \vdots \qquad \vdots \qquad \vdots \\
& \cup \mathbf{h}_n^{-1}\mathbf{K}_0 \cup \mathbf{h}_n^{-1}\mathbf{K}_0\mathbf{h}_1 \cup \mathbf{h}_n^{-1}\mathbf{K}_0\mathbf{h}_2 \cup \cdots \cup \mathbf{h}_n^{-1}\mathbf{K}_0\mathbf{h}_i \cup \cdots \cup \mathbf{h}_n^{-1}\mathbf{K}_0\mathbf{h}_n. \qquad (1)
\end{aligned}
$$

In (1), $\mathbf{h}_i$ indicates an element of the hull which brings the ith substructure $\mathbf{X}_i$ to superpose upon the substructure $\mathbf{X}_0$ representing the kernel $\mathbf{K}_0$. Since each of the elements of $\mathbf{K}_0$ brings $\mathbf{X}_0$ to superpose upon itself, $\mathbf{K}_0\mathbf{h}_i$ expresses the set of all the elements in the hull, each of which brings $\mathbf{X}_i$ to superpose upon $\mathbf{X}_0$, and $\mathbf{h}_j^{-1}\mathbf{K}_0\mathbf{h}_i$ the set of all the elements in the hull, each of which brings $\mathbf{X}_i$ to superpose upon $\mathbf{X}_j$. Hence, the union of all the off-diagonal terms in (1) constitutes the hull **H**. The diagonal term $\mathbf{h}_i^{-1}\mathbf{K}_0\mathbf{h}_i$ brings $\mathbf{X}_i$ to superpose upon itself and is a group isomorphic with the kernel $\mathbf{K}_0$.

Because the relation between subspaces **A** and **B** is left indeterminate in the definition of the partial operation, this operation is adapted for a far wider scope of application than those of the global and local symmetry operations. As long as the isomorphism is maintained among the space groups of the substructures in a space-groupoid structure **X**, a certain part of **X** can be transformed independently from the

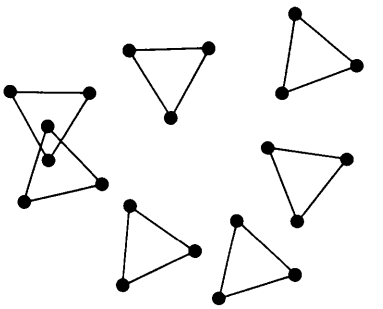

Fig. 1. Plane-groupoid structure of finite extension and composed of substructures in the form of an equilateral triangle. The substructures represent the kernel $\mathbf{K}_0$ and groups isomorphic with $\mathbf{K}_0$.

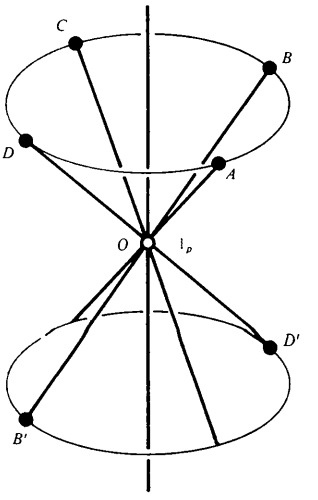

Fig. 2. Conversion of $\mathbf{C}_4$ into $\bar{\mathbf{C}}_4$ by a partial inversion. The partial inversion $\mathbf{I}_p$ is combined only with the first and third powers of the rotation $\mathbf{C}_4$; $\mathbf{I}_p$ at O operates only along BB' and DD', OA being the starting position. $\mathbf{C}_4^0(OA) = OA = \bar{\mathbf{C}}_4^0(OA)$, $\mathbf{I}_p.\mathbf{C}_4^1(OA) = OB' = \bar{\mathbf{C}}_4^1(OA)$, $\mathbf{C}_4^2(OA) = OC = \bar{\mathbf{C}}_4^2(OA)$ and $\mathbf{I}_p.\mathbf{C}_4^3(OA) = OD' = \bar{\mathbf{C}}_4^3(OA)$.

other parts in **X** by a partial operation in **H**. The partial operation is thus capable of converting the rotational part of a space group from a pure rotation to a rotatory inversion as illustrated in Fig. 2, and can also involve a similarity transformation or a change of the weight of points, or both, as demonstrated in the last section of this paper.

3. Vector symmetry

When we try to deduce the structure **X** from its vector set **V**, we must pick up one vector for **X** from each pair of vectors inversion-symmetrically related to each other in **V**. This procedure can be expressed by a 2:1 mapping φ of **V** onto its subset **W** as

$$\varphi: \mathbf{V} \rightarrow \mathbf{W}, (\mathbf{W} \subset \mathbf{V}). \tag{2}$$

The role of this subset **W** lies in mediating between the symmetry of the vector set **V** and that of the structure **X**.

Let us first suppose that **X** is not inversion-symmetric and the point group $\mathbf{G}_V$ of **V** contains an n-fold rotation group $\mathbf{C}_n$ as its only rotational subgroup. Denote by R a matrix representing a rotation by $2\pi/n$ around the n-fold axis N in **V**. Since **V** is inversion-symmetric as assumed in the previous section, a $\mathbf{G}_V$ orbit for a vector **a** in a general direction in **V** consists of a pair of $\mathbf{C}_n$ orbits of single weight: one formed by n vectors, **a**, **Ra**, $\mathbf{R}^2\mathbf{a}$, ..., $\mathbf{R}^{n-1}\mathbf{a}$, and the other by the inversion images of these n vectors. However, when n is even and **a** lies in a plane that is perpendicular to the axis N and passes the origin O, a $\mathbf{G}_V$ orbit of single weight in the form of a $\mathbf{C}_n$ orbit can be formed by n vectors: **a**, **Ra**, $\mathbf{R}^2\mathbf{a}$, ..., $\mathbf{R}^{(n/2)-1}\mathbf{a}$ for example, together with their inversion images. The $\mathbf{G}_V$ orbits of an n-fold rotation group in **V** are therefore partitioned into two classes: one formed by $2n$ vectors, and the other by n vectors. The former orbits will be called paired orbits and the latter lone orbits.

Next, when **X** is inversion-symmetric, a $\mathbf{G}_V$ orbit is defined as a paired orbit if it consists of a pair of $\mathbf{C}_n$ orbits of double weight. A $\mathbf{G}_V$ orbit can become exactly the same lone orbit as described in the preceding paragraph, such as an orbit formed by two vectors which in **X** are the diagonals of a square perpendicular to the fourfold rotation axis in a $4/m$ symmetric configuration. A $\mathbf{G}_V$ orbit for a vector in a general direction may also be a lone orbit if it consists of a pair of $\mathbf{C}_n$ orbits of single weight, such as an orbit formed by three vectors which cross one another at the inversion point in a $\bar{3}$ symmetric configuration. However, since this type of lone orbit will not be required for the discussion to follow, the term 'lone orbit' should be understood, throughout the rest of this paper, to mean the lone orbit of the former type only.

Thus, the mapping of φ in (2) can always be so chosen as for the point group of the image $\mathbf{P}_W$ in **W** of a paired orbit $\mathbf{P}_V$ in **V** to become $\mathbf{C}_{nh}$ (n, even) or $\underline{\mathbf{C}}_{ni}$ (n, odd) when **X** is inversion-symmetric, or $\mathbf{C}_n$ or $\bar{\mathbf{C}}_n$* (n, even) or $\mathbf{C}_n$ (n, odd) when **X** is not inversion-symmetric; the symmetry of $\mathbf{P}_W$ can in any case be described by an ordinary point group. On the other hand, since a lone orbit $\mathbf{L}_V$ in **V** is a $\mathbf{C}_n$ orbit, the symmetry of its image $\mathbf{L}_W$ in **W** by φ requires special consideration as will be shown below with the example of $\mathbf{C}_4$. Because $\mathbf{L}_W$ is obviously a plane configuration, we may re-write $\mathbf{G}_I$ as $\mathbf{C}_2$. Then, in the coset decomposition of $\mathbf{C}_4$,

$$\mathbf{C}_4 = \mathsf{E}\mathbf{C}_2 \cup \mathsf{R}\mathbf{C}_2, \tag{3}$$

where E is the unit matrix and R is the matrix of rotation by $\pi/2$. Because one vector of the pair of inversion-symmetrically related vectors in each lone orbit $\mathbf{L}_V$ in **V** has been removed from **W**, the operations of superposition of $\mathbf{L}_W$ in **W** now consist of only the representatives $\{\mathsf{E},\mathsf{R}\}$ of the decomposition in (3). However, the representatives will not form a group under the law of composition defined for $\mathbf{C}_4$, because the set contains none of R^2 and R^3. On the other hand, since

$$\left.\begin{aligned} &\mathsf{R}^n \equiv \mathsf{E} \pmod{\mathbf{C}_2} \text{ for even integral } n \\ \text{and} \quad &\mathsf{R}^n \equiv \mathsf{R} \pmod{\mathbf{C}_2} \text{ for odd integral } n \end{aligned}\right\} \tag{4}$$

hold, $\{\mathsf{E},\mathsf{R}\}$ forms a group denoted by $\mathbf{C}_4 \pmod{\mathbf{C}_2}$ under the law of composition defined by (4). Then, $\mathbf{C}_4$ is expressed as

$$\mathbf{C}_4 = \mathbf{C}_4 \pmod{\mathbf{C}_2} \odot \mathbf{C}_2, \tag{5}$$

and the product in (5) is called the conditional product of $\mathbf{C}_4 \pmod{\mathbf{C}_2}$ with $\mathbf{C}_2$ (Shubnikov & Koptsik, 1972). Hence, in the case of $\mathbf{C}_4$, the group of operations of superposition of the image $\mathbf{L}_W$ in **W** of a lone orbit $\mathbf{L}_V$ in **V** is $\mathbf{C}_4 \pmod{\mathbf{C}_2}$, and the orbit in **W** consists of two vectors equal in length and perpendicular in direction to each other.

As pointed out in the above paragraph, when the image $\mathbf{P}_W$ of a paired orbit $\mathbf{P}_V$ is taken to be as fully symmetric as possible, its point group will become identical with $\mathbf{G}_V$ when **X** is inversion-symmetric, but two alternatives are open when **X** is not inversion-symmetric and n is even, namely $\mathbf{C}_n$ or $\bar{\mathbf{C}}_n$. However, either of these can be equally expressed as $\mathbf{G}_V/\mathbf{G}_I$. Therefore, in order to specify the orientational relation between vectors in **X** which corresponds to the symmetry of **V**, the symmetry with the point group $\mathbf{G}_V$ or $\mathbf{G}_V/\mathbf{G}_I$ will be called the vector symmetry of **X** according as **X** is inversion-symmetric or not. When the vector symmetry of **X** is $\mathbf{C}_n$, for example, **X** will be specified as $\mathbf{C}_n$-vector-symmetric. Those vectors in **X** which belong to an orbit of the point group of the vector symmetry of **X** will be said to be vector-symmetric with each other. Therefore, in a $\mathbf{C}_4$-vector-

* The n-fold rotatory inversion is denoted by $\bar{\mathbf{C}}_n$ in this paper.

symmetric structure **X**, a set of vectors vector-symmetric with a vector in a general direction will consist of four vectors which are arranged, when transferred into **W**, according to the symmetry of either $\mathbf{C}_4$ or $\bar{\mathbf{C}}_4$, but a set of vectors vector-symmetric with a vector in **X** which is perpendicular to the fourfold rotation axis in **V** will consist of either four vectors arranged in $\mathbf{C}_4$ in **W** or two vectors in $\mathbf{C}_4$ (mod $\mathbf{C}_4$) in **W** according as the corresponding orbit in **V** is paired or lone. If the point group $\mathbf{G}_X$ of **X** is known and the vector symmetry of **X** is not enhanced, it will be appropriate to take $\mathbf{G}_V/\mathbf{G}_I$ of the vector symmetry to be identical with $\mathbf{G}_X$. The case in which the vector symmetry is enhanced (*i.e.* $\mathbf{G}_V/\mathbf{G}_I > \mathbf{G}_X$) is referred to in the next section.

It will be obvious from the relation between **X** and **W** that the lattice in **X** is congruent with that found in **W**. Therefore, when **X** is $\mathbf{C}_n$- or $\bar{\mathbf{C}}_n$-vector-symmetric, the lattice in **W** is n-fold rotation-symmetric. This means that the $\mathbf{C}_n$- or $\bar{\mathbf{C}}_n$-vector-symmetric structure **X** has a lattice metrically n-fold rotation-symmetric; a $\mathbf{C}_4$-vector-symmetric **X**, for example, has a metrically tetragonal lattice, though the global symmetry of **X** may or may not be tetragonal. Thus, the crystal lattice is vector-symmetric; all the lattice-translation vectors in **X** necessarily form a class of vector-symmetric sets of vectors and are therefore vector-symmetrically self-contained. Hence, when we examine the vector symmetry of **X**, we shall always be concerned with only the vector symmetry of those position vectors from a lattice point taken as the origin O of **X** to the remaining points in a unit cell.

Then, let us suppose that all the vectors in **W** are shifted in parallel so as to reconstruct **X**. Parallel shifts preserve the angles between vectors but do not necessarily preserve the relative positions of vectors. Therefore, the model of a $\mathbf{C}_n$-vector-symmetric **X** in its most general form will consist of vector-symmetric vectors distributed asymmetrically over **X**, where one of the vectors, **a**, is brought to superposition upon another, **b**, vector-symmetric with **a**, by a partial screw or a partial rotatory inversion around an axis N_X, which is parallel to the n-fold rotation axis N in **V** when **X** and **V** are placed in parallel as usual, and whose position (and pitch as well when it is a screw) will be determined by the positions and orientations of **a** and **b**. The angle of rotation around this axis N_X is equal to one of the n-fold rotation angles. In this model of **X**, every pair of vector-symmetric vectors is associated with a partial screw or a partial rotatory inversion which is considered to belong exclusively to this pair of vectors. This situation is illustrated in Fig. 3 with a finite two-dimensional configuration which is partly $\mathbf{C}_3$-vector-symmetric only with respect to three vectors **a**, **b** and **c**.

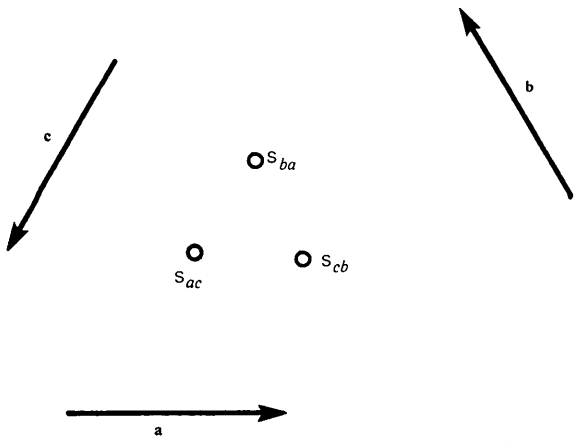

Fig. 3. Plane configuration partly $\mathbf{C}_3$-vector-symmetric with respect to three vectors **a**, **b** and **c**. $\mathbf{S}_{ji}$ indicates the axis of a partial rotation by $2\pi/3$ that brings vector **i** to superpose upon vector **j**.

4. Self-homometry, symmetry and basic theorems of vector symmetry

Suppose that between two configurations **A** and **B** there exists a 1:1 correspondence of **A** to **B** which maps each of the inter-point vectors in **A** onto a vector in **B**, say $\mathbf{a}_i$ onto $\mathbf{b}_i$, where $\mathbf{a}_i$ is equal to $\mathbf{b}_i$ in absolute value, $|\mathbf{a}_i| = |\mathbf{b}_i|$. Then, of each of the pairs of vectors, $(\mathbf{a}_1,\mathbf{b}_1)$, $(\mathbf{a}_2,\mathbf{b}_2)$, ..., $(\mathbf{a}_s,\mathbf{b}_s)$, ..., in which $\mathbf{a}_i \in \mathbf{A}$, $\mathbf{b}_i \in \mathbf{B}$ and $|\mathbf{a}_i| = |\mathbf{b}_i|$ for $i = 1, 2, \ldots, s, \ldots$, a partial operation which brings one of a pair of vectors, say $\mathbf{a}_i$, to superpose upon the other, $\mathbf{b}_i$, will be conceivable. Denote this partial operation by $\mathbf{S}_i$. If all the $\mathbf{S}_i$'s for **A** and **B** are operations around axes parallel to each other and with the same rotation angle, **A** and **B** will be homometric with each other. Further, if in a pair of homometric configurations **A** and **B** all the $\mathbf{S}_i$'s coincide with each other, **A** and **B** will then become congruent or enantiomorphic; that is, isometric with each other. Hence, isometry can be looked upon as a special case of homometry in which all the partial operations of the latter coalesce into a single operation.

Let us assume that the structure **X** is homometric with itself in such a way that both **A** and **B**, which are homometric with each other, come to coincide with each other and with **X**. The structure **X** will then be said to be self-homometric. When **X** is n-fold self-homometric, its vector set **V** will be n-fold symmetric, and **X** will be n-fold vector-symmetric. Thus, **X** being n-fold self-homometric is the condition sufficient for **X** to be n-fold vector-symmetric. Conversely, when **V** is n-fold symmetric, it will be superposed upon itself by a rotation of $2\pi/n$ around its n-fold rotation axis N. This means that **X** consists of vectors which correspond one-to-one in both equality in length and parallelism in direction to the vectors in **X** after a rotation by $2\pi/n$ around an axis parallel to N in **V**; that is, **X** is n-fold self-homometric. Hence, the following theorem will hold.

Theorem 1 (first basic theorem of vector symmetry): The necessary and sufficient condition for a structure **X** to be n-fold vector-symmetric is that **X** is n-fold self-homometric.

Next, let us examine the relation between vector symmetry and symmetry. The concept of self-homometry includes those of global and local symmetries. If these symmetries are excluded from self-homometry, the remainder will be called proper self-homometry. If a vector-symmetric structure **X** contains at least one such point so that every position vector from it has its vector-symmetric counterparts only by dint of proper self-homometry, **X** will be called a properly self-homometric structure. Because theorem 1 expresses the final conclusion expected from a properly self-homometric structure, in order to see if it is possible to draw any other conclusion more concrete than the theorem, it will be assumed below that the structure **X** is not properly self-homometric; that is, every point in **X** possesses among the position vectors from it at least one such vector that is given its vector-symmetric counterparts by symmetry operations. Then, each of the points in **X** must belong to an orbit of a space group whose point group is isomorphic with the point group of the vector symmetry of **X**; that is, $\mathbf{G}_V$ or $\mathbf{G}_V/\mathbf{G}_I$ according as **X** is inversion-symmetric or not. We thus arrive at the following theorem.

Theorem 2 (second basic theorem of vector symmetry): When a structure **X** is not properly self-homometric, the necessary condition for **X** to be vector-symmetric is that each of the points in **X** belongs to an orbit of such a space group $\mathbf{K}_i$ as with a point group isomorphic with the point group of the vector symmetry of **X**.

In this theorem, the symmetry which the space group $\mathbf{K}_i$ represents is either global or local.

A space group $\mathbf{G}_s$ is an extension of a lattice-translation group $\mathbf{G}_t$ by a point group $\mathbf{G}_p$; that is, $\mathbf{G}_p \simeq \mathbf{G}_s/\mathbf{G}_t$. Therefore, when $\mathbf{G}'_p \simeq \mathbf{G}'_s/\mathbf{G}'_t$, $\mathbf{G}'_p \simeq \mathbf{G}_p$ and $\mathbf{G}'_t \simeq \mathbf{G}_t$, $\mathbf{G}'_s$ is isomorphic with $\mathbf{G}_s$, $\mathbf{G}'_s \simeq \mathbf{G}_s$. Theorem 2 asserts that when **X** is vector-symmetric, all the point groups of the space groups associated with the substructures are isomorphic with each other. Therefore, if the lattice-translation groups of the space groups are also isomorphic with each other, the space groups will become isomorphic with each other, and the structure **X** will then be regarded as a space-groupoid structure. The isomorphism of lattice-translation groups in this case reduces to the matter of equal multiplicity of the lattices. When the space group $\mathbf{K}_j$ of the substructure $\mathbf{X}_j$, for example, is based upon a multiple lattice, say p-ply centred, $\mathbf{X}_j$ can then be decomposed into p components, each with a simple lattice. When **X** is partitioned in this way into such substructures, each with a simple lattice, the space groups associated with these substructures will then be isomorphic with each other, and **X** will become a space-groupoid structure, in which the p-centring translations in $\mathbf{K}_j$, for example, have since acquired their proper places in the hull of the space groupoid. This space-groupoid structure includes an ordinary space-group structure as its special case in which the kernel $\mathbf{K}_0$ comes to occupy the entire space groupoid. The following corollary will thus hold.

Corollary 1: The necessary condition for a structure **X**, which is not properly self-homometric, to exhibit an enhanced vector symmetry (enhanced diffraction symmetry) is that **X** is a space-groupoid structure with the kernel whose point-group symmetry is, other than by addition of an inversion, higher than the point-group symmetry of **X**.

If the point groups of the space groups associated with the substructures are not only isomorphic but also identical with each other, the vector symmetry of **X** may be specified by this common point group as will be done in the next section. It should be pointed out that the point groups of the space groups may not all be identical with each other, some of them being pure rotations while the rest are rotatory inversions. Even in this case, however, the corresponding space groups can coexist in the space groupoid provided such a partial inversion as illustrated in Fig. 2 is present in the hull.

Comprehensive lists of sufficient conditions for structures to exhibit enhanced vector symmetry have been published by Iwasaki (1972), Matsumoto, Kihara & Iwasaki (1974) and Perez-Mato & Iglesias (1977).

5. Examples

We will now illustrate the above theorems and corollary with four examples of enhanced vector symmetry.

(*A*) *Enhancement due to proper self-homometry*

The plane configuration shown in Fig. 4(*a*) represents the unit-cell content of a structure in which all the points, black and white, are of equal weight. When this configuration and those congruent with it are arranged according to a square lattice with a translation period of arbitrary length, a two-dimensional structure with $\mathbf{C}_4$ vector symmetry will be completed. The corresponding three-dimensional structure can be constructed by stacking the same plane structures together, one immediately above another. For the sake of simplicity, however, we shall deal here with this plane configuration denoted by **A*****B**.

This **A*****B** has been derived by the convolution of a plane sub-configuration **A** with another **B** as shown in Fig. 4(*b*), where **B** is homometric with **A** and so placed that one of its vectors $\mathbf{b}_i$ may be perpendicular to its homometric mate $\mathbf{a}_i$ in **A**. The actual procedure of the convolution is as follows. Take any one of the points in **B** and denote it by $\mathbf{P}_B$. Move **B** in parallel so that $\mathbf{P}_B$ may range over all the points in **A**. Whenever $\mathbf{P}_B$ meets

a point in **A**, register the positions of all the points in **B** at this instance. Then, when $\mathbf{P}_B$ has completed its travel around all the points in **A**, the union of all the registered sub-configurations will give the result of the convolution of **A** with **B**; that is, **A*****B**. The fact that **A*****B** is fourfold self-homometric can be visualized as follows.

As an arbitrarily chosen vector in **A*****B**, take $\mathbf{P}_2\mathbf{P}_3$ between $\mathbf{P}_2$ in $\mathbf{A}_i$ and $\mathbf{P}_3$ in $\mathbf{B}_h$ in Fig. 5. It will then be possible to assume that $\mathbf{P}_4\mathbf{P}_5$ is a unique vector in **A** which is equal in length and perpendicular in direction to $\mathbf{P}_1\mathbf{P}_3$ in $\mathbf{B}_h$. This means that $\mathbf{B}_j$ and $\mathbf{B}_l$ form a unique pair of sub-configurations for which the vector from a point in $\mathbf{B}_j$ to the corresponding point in $\mathbf{B}_l$ is always equal in length and parallel in direction to $\mathbf{P}_4\mathbf{P}_5$. $\mathbf{P}_6\mathbf{P}_7$ and $\mathbf{P}_8\mathbf{P}_9$ are unique vectors respectively in $\mathbf{B}_j$ and in $\mathbf{B}_l$ which are equal in length and perpendicular in direction to $\mathbf{P}_1\mathbf{P}_2$ in $\mathbf{A}_i$. Since both $\mathbf{P}_6\mathbf{P}_8$ and $\mathbf{P}_7\mathbf{P}_9$ are equal in length and parallel in direction to $\mathbf{P}_4\mathbf{P}_5$, $\mathbf{P}_6\mathbf{P}_9$ is a unique vector which is equal in length and perpendicular in direction to $\mathbf{P}_2\mathbf{P}_3$; $\mathbf{P}_6\mathbf{P}_9$ is the fourfold self-homometric mate of $\mathbf{P}_2\mathbf{P}_3$. Hence, **A*****B** forms a fourfold self-homometric configuration of finite extension.

It will then be obvious that when **A*****B** and those congruent with it are arranged according to a square lattice the resulting plane structure is fourfold self-homometric. This structure is 4 in its vector symmetry by theorem 1 while $p1$ in its global symmetry. It is to be noted that no $p4$ orbit is associated with any one of the white points in Fig. 4(*a*); the presence of such points is characteristic of the enhancement due to proper self-homometry. No actual example of this type of enhancement has yet been discovered.

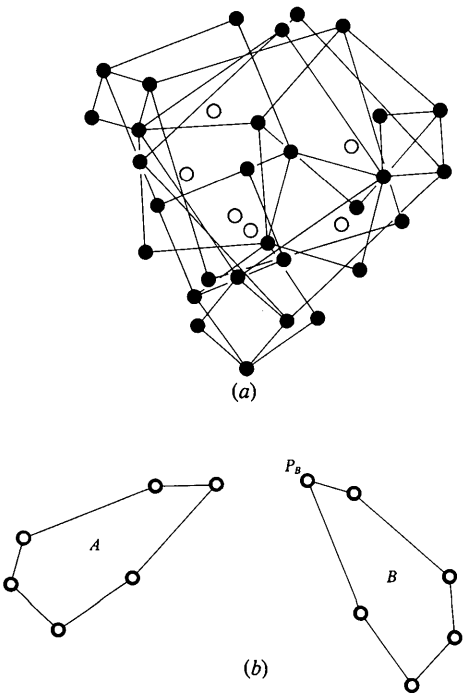

Fig. 4. Properly self-homometric plane structure with the global symmetry of $p1$ and the vector symmetry of 4. (*a*) Unit-cell content, **A*****B**. No $p4$ orbit is associated with any of the white points. (*b*) Two sub-configurations **A** and **B** used for the derivation of **A*****B**. These sub-configurations are homometric with each other, and a vector $\mathbf{a}_i$ in **A** and its homometric mate $\mathbf{b}_i$ in **B** are perpendicular to each other to form a lone orbit of the $\mathbf{C}_4$ vector symmetry.

(*B*) *Enhancement due to local symmetry*

Although some actual examples of this type of enhancement are known and more cases are expected among polytypes of mica, SiC, ZnS *etc.*, only fictitious models are chosen here to take advantage of their simple structures.

One of the typical examples will be the $\mathbf{C}_2$-vector-symmetric structure given by Iwasaki (1972). The simplest model of this type contains nine points in the unit cell of a metrically monoclinic lattice as shown in Fig. 6 in a projection along the *b* axis. The black circles in the figure lie in a plane parallel to the plane of the paper, and the white ones lie in another plane of the same description. Both kinds of circle may differ from each other in weight. Two white circles are located twofold rotation-symmetrically around an axis perpendicular to the plane of the paper and passing the black circle in the middle, and these three circles form a unit of this structure. Three such structural units are arranged in parallel with each other in a unit cell. This structure is $P1$ in its global symmetry but 2 in its vector symmetry. One of the structural units arbitrarily chosen and those lattice-translationally equivalent to it represent the kernel $P2$ of the space groupoid of this structure.

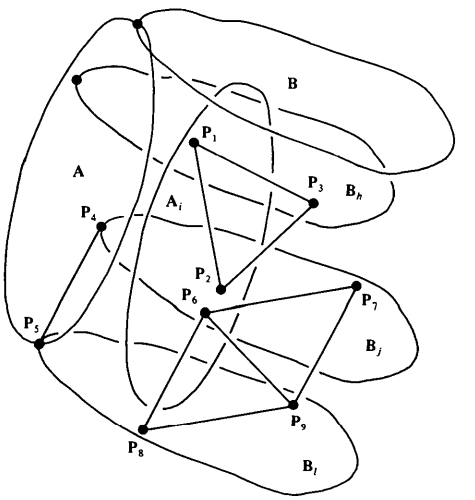

Fig. 5. Lone orbit of $\mathbf{C}_4$ vector symmetry in **A*****B** in Fig. 4(*a*). $\mathbf{A}_i$ is congruent with and parallel to **A**, and $\mathbf{B}_h$, $\mathbf{B}_j$ and $\mathbf{B}_l$ are congruent with and parallel to **B**. Points belong to sub-configurations as: $\mathbf{P}_1, \mathbf{P}_2 \in \mathbf{A}_i$; $\mathbf{P}_1, \mathbf{P}_3 \in \mathbf{B}_h$; $\mathbf{P}_4, \mathbf{P}_5 \in \mathbf{A}$; $\mathbf{P}_6, \mathbf{P}_7 \in \mathbf{B}_j$; $\mathbf{P}_8, \mathbf{P}_9 \in B_l$.

The next example is shown in Fig. 7, in which *OACB* indicates a square unit cell of a plane structure and all the points are of equal weight. Because every point in this structure **X** obviously lies in a tetragonal orbit, it is possible (theorem 2) for **X** to be $\mathbf{C}_4$-vector-symmetric. In fact, it is $\mathbf{C}_4$-vector-symmetric while its global symmetry is $p1$. One of the squares arbitrarily chosen in Fig. 7 and those lattice-translationally equivalent to it constitute the substructure representing the kernel $p4$. Consider the element $\mathbf{h}_i$ of the hull which brings $\mathbf{X}_i$ to superpose upon $\mathbf{X}_0$. This element must contain a partial translation $\mathbf{t}_i$ which brings the plane lattice $\mathbf{L}_i$ composed of the centres of the squares in $\mathbf{X}_i$ to superpose upon the corresponding lattice $\mathbf{L}_0$ in $\mathbf{X}_0$. Because the squares in $\mathbf{X}_i$ differ from those in $\mathbf{X}_0$ in both orientation and size, $\mathbf{h}_i$ must also contain a set $\mathbf{R}_i = \cup_j \mathbf{T}_j \mathbf{r}_i \mathbf{T}_j^{-1}$, where $\mathbf{r}_i$ is a partial rotation operating on the square around the origin of $\mathbf{L}_i$ to line it up in parallel with the squares in $\mathbf{X}_0$, $\mathbf{T}_j$ is a lattice translation from the origin of $\mathbf{L}_i$ to the jth lattice point in $\mathbf{L}_i$, and the union ranges over all the lattice points in $\mathbf{L}_i$, and a set $\mathbf{U}_i = \cup_j \mathbf{T}_j \mathbf{u}_i \mathbf{T}_j^{-1}$, where $\mathbf{u}_i$ is a similarity transformation operating on the above square to make it the same size as the squares in $\mathbf{X}_0$. The element $\mathbf{h}_i$ will thus be expressed as $\mathbf{h}_i = \mathbf{U}_i . \mathbf{R}_i . \mathbf{t}_i$, where $\mathbf{U}_i$, $\mathbf{R}_i$ and $\mathbf{t}_i$ commute with each other.

Finally, let us take one example from Iwasaki's (1972) type 3 and consider the case in Fig. 8 in which a tetragonal structure **X** is composed of two substructures, one with the symmetry of $P4_2cm$ and consisting of small circles in the figure, and the other with $P4_2mc$ and consisting of large circles. Though each of these substructures must be composed of points of equal weight, the weight of points in one of them may differ from that in the other. This structure is $P4_2$ in its global symmetry but $4mm$ in its vector symmetry. Though the space group $P4_2cm$ of the first substructure differs from $P4_2mc$ of the second, these are still isomorphic with each other. Hence, either of these two space groups may be taken as the kernel of the space groupoid of this structure. The element $\mathbf{h}_1$ of the hull contains, besides a bodily shift of $\mathbf{X}_1$ so as to make $z = z'$, component operations similar to $\mathbf{R}_i$ and $\mathbf{U}_i$ in the previous example, and also a change in the weight of points if the weight in one of the substructures differs from that in the other.

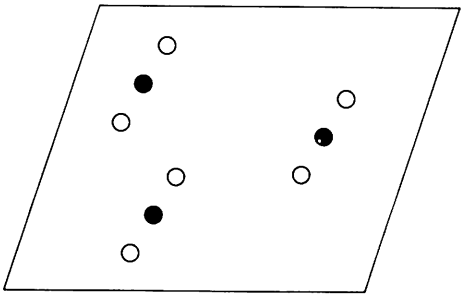

Fig. 6. $\mathbf{C}_2$-vector-symmetric space-groupoid structure. The parallelogram indicates a unit cell projected along the b axis of a metrically monoclinic lattice. This structure is $P1$ in its global symmetry and 2 in its vector symmetry.

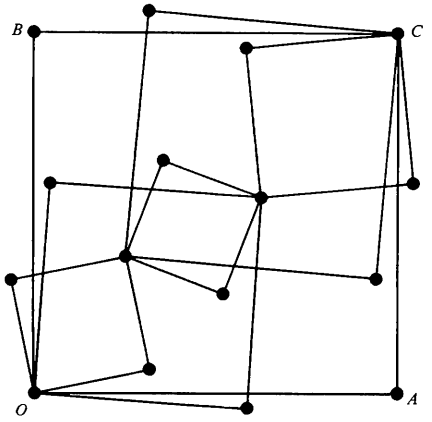

Fig. 7. $\mathbf{C}_4$-vector-symmetric plane-groupoid structure. *OACB* indicates a unit cell. This structure is $p1$ in its global symmetry and 4 in its vector symmetry.

We wish to express our sincere gratitude to Professor T. Ito MJA, for his interest and encouragement throughout the course of this study. One of us (RS) wishes to take this opportunity to express his warmest thanks to Professor K. Dornberger-Schiff for her kind introduction to the theory of groupoids and its application to crystallography personally given to him about twenty years ago, and to Professor V. A. Koptsik for kindly supplying him with a copy of his wonderful

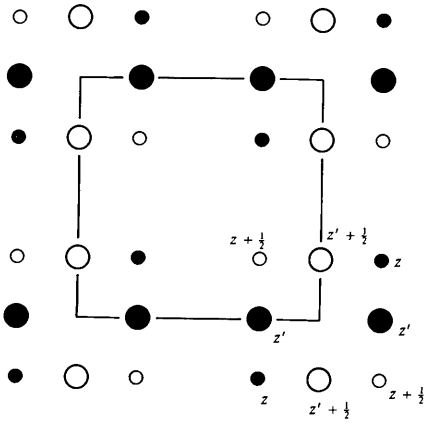

Fig. 8. Space-groupoid structure with the global symmetry of $P4_2$ and the vector symmetry of $4mm$. The square indicates a unit cell, and the heights of points are given around the lower right-hand corner. The coordinates of points in the fractions of the cell edges in the plane of projection are either $\frac{1}{4}$ or $\frac{3}{4}$.

book *Symmetry in Science and Art*, thus greatly facilitating the present work.

References

BRANDT, H. (1926). *Math. Ann.* **96**, 360–366.
DORNBERGER-SCHIFF, K. (1957). *Acta Cryst.* **10**, 820.
IWASAKI, H. (1972). *Acta Cryst.* A**28**, 253–260.
IWASAKI, H. (1974*a*). *Acta Cryst.* A**30**, 173–176.
IWASAKI, H. (1974*b*). *J. Crystallogr. Soc. Jpn*, **16**, 155–179 (in Japanese).
IWASAKI, H. (1975). *Acta Cryst.* A**31**, S6.
LOEWY, A. (1927). *J. Math.* **157**, 239–254.
MARUMO, F. & SAITO, Y. (1972). *Acta Cryst.* B**28**, 867–870.
MATSUMOTO, T. (1975). *Acta Cryst.* A**31**, S6.
MATSUMOTO, T., KIHARA, K. & IWASAKI, H. (1974). *Acta Cryst.* A**30**, 107–108.
OHSUMI, K., KOYAMA, K. & TAMADA, O. (1977). Private communication.
OHSUMI, K., OKAMURA, F. P. & SADANAGA, R. (1972). *Acta Cryst.* A**28**, S121.
PEREZ-MATO, J. M. & IGLESIAS, J. E. (1977). *Acta Cryst.* A**33**, 466–474.
RAMSDELL, L. S. & KOHN, J. A. (1951). *Acta Cryst.* **4**, 111–113.
ROSS, M., TAKEDA, H. & WONES, D. R. (1966). *Science*, **151**, 191–193.
SADANAGA, R. & OHSUMI, K. (1975). *Proc. Jpn Acad.* **51**, 179–183.
SADANAGA, R., OHSUMI, K. & MATSUMOTO, T. (1973*a*). *Proc. Jpn Acad.* **49**, 609–614.
SADANAGA, R., OHSUMI, K. & MATSUMOTO, T. (1973*b*). *Proc. Jpn Acad.* **49**, 816–819.
SADANAGA, R. & TAKEDA, H. (1968). *Acta Cryst.* B**24**, 144–149.
SHUBNIKOV, A. V. & KOPTSIK, V. A. (1972). *Symmetry in Science and Art*, p. 209 (in Russian). Moscow: Nauka.

Acta Cryst. (1979). A**35**, 122–130

Problems of Resolution and Bias in the Experimental Determination of the Distribution of Electron Density and Other Densities in Crystals

BY A. J. C. WILSON

Department of Physics, University of Birmingham, Birmingham B15 2TT, England

(*Received* 13 *June* 1978; *accepted* 27 *July* 1978)

Abstract

The limited 'window' in reciprocal space through which it is possible to observe diffraction phenomena sets a reciprocal limit to the resolution of detail in density distributions. The limit of resolution depends on whether the detail is one-, two-, or three-dimensional, and to some extent it is possible to choose between (i) lack of resolution associated with a large central maximum representing a point-object and (ii) false details associated with a smaller central maximum and more pronounced diffraction troughs. In any case, however, the limit of resolution is about one-quarter to one-half of the wavelength of the radiation used. Intensities measured by photon or particle counting are unbiased estimates of the true intensities, but their square roots are not unbiased estimates of the structure factors, and this bias may carry over into parameters based on structure factors rather than intensities. A satisfactory correction can be made for the strong reflexions, but weak reflexions (which are required if the theoretical limit of resolution is to be reached) remain a problem.

1. Introduction

1.1. The positional parameters of atoms in crystals can be determined with considerable accuracy, and in general they are remarkably little affected by systematic errors and statistical fluctuations (Wilson, 1976*b*, 1977*a*,*b*). The scaling factor and the thermal parameters, on the other hand, are sensitive to systematic errors and are biased by statistical fluctuations unless special precautions are taken (Wilson, 1975, 1976*b*, 1977*a*,*b*, 1978*b*; Lomer & Wilson, 1975). The measurement of the distribution of electron density is even more sensitive to systematic errors and statistical bias, and there is a fundamental limitation of resolving power: only reflexions with spacings greater than $\frac{1}{2}\lambda$ can be measured, where λ is the wavelength of the radiation employed, and sometimes the geometrical design of the apparatus imposes a higher limit $\lambda/2 \sin \theta_{max}$, where θ_{max} is the largest Bragg angle that can be attained. One cannot expect, therefore, to be able to resolve details of the charge distribution on a scale much less than $\frac{1}{2}\lambda$. Naturally it is possible to fit models to the observed intensities of reflexion that imply detail on a smaller scale, but the measurements would give no criterion for deciding between rival models giving approximately the same goodness of fit. These remarks apply equally, *mutatis mutandis*, to measurements of the distribution of momentum density, of spin density, and of atomic-centre distribution in imperfect structures, and to diffraction measurements with electrons, neutrons *etc.* as well as to measurements with X-rays.

0567-7394/79/010122-09$01.00