

The Ambiguity Problem of Vector-Set Interpretation

BY N. M. ANDRUSHEWSKY AND B. M. SHCHEDRIN

Department of Computing Mathematics and Cybernetics, Moscow State University, Moscow 117234, USSR

AND T. J. MALINOWSKY

Institute of Applied Physics, Academy of Sciences of MSSR, Kishinev 277028, USSR

(Received 31 July 1986; accepted 20 January 1988)

Abstract

An efficient method based on the utilization of crystal symmetry for the interpretation of vector sets of crystals belonging to space groups of higher symmetry than $P1$ is described. New equality relations between atomic position vectors which are sufficient to provide the possibility of an ambiguous solution are derived. It is proved that for many space groups of the polar kind these conditions of ambiguity are necessarily satisfied. A complete list of such space groups is given.

Introduction

The principles of conventional Patterson methods are based on the fact that the Patterson function, in the point-atom approximation, can be represented as an N -fold image of an N -atom structure (Buerger, 1959). The problem of the deconvolution of N images depends first on the correct selection of a series of interatomic vectors, all of which must belong to the same image of the structure. It is well known that this problem is resolvable in principle (Wrinch, 1939). However, the process of recovery of structure is not free from ambiguity and this causes problems in the determination of crystal structures. On the other hand, information about the possibility of an ambiguous solution may be of use in the process of the correct identification of structural fragments.

The sufficient conditions for the correct interpretation of vector sets of crystals with symmetry $P1$ and $P\bar{1}$ were established by Cochran (1958). As a further development of this topic we propose a new algorithm of vector-set interpretation, which results in the uniform conditions of the ambiguous solutions caused by crystal symmetry.

1. The solution of vector sets by factor-set filtration

We shall consider crystal structures with point atoms. Their space groups are assumed to be different from $P1$.

Let the symmetry operations of the space group G relative to a fixed origin in the crystallographic basis

be represented by matrices $A_l \equiv (\mathbf{R}_l | \mathbf{t}_l)$, \mathbf{b}_k , \mathbf{n} for $l = 1, 2, \dots, L$; $k = 1, 2, \dots, K$, where \mathbf{R}_l is a rotation matrix that represents one of the symmetry operations of the crystal point group, \mathbf{t}_l is a translation vector associated with \mathbf{R}_l , \mathbf{b}_k is the Bravais-lattice centering translation vector and \mathbf{n} is a vector with integer components. L and K are the numbers of symmetry operations and centering translations, respectively. Then, relative to one arbitrary point \mathbf{r} , the infinite array of points $\{\mathbf{r}\} = \{\mathbf{R}_l \mathbf{r} + \mathbf{t}_l + \mathbf{b}_k + \mathbf{n}\}$ forms a regular set of symmetry-equivalent points. The set of points $\mathbf{S}(\mathbf{r}) = \{(\mathbf{A}_l \mathbf{r} + \mathbf{b}_k) \pmod{\mathbf{1}}\}$, for $l = 1, 2, \dots, L$; $k = 1, 2, \dots, K$, belonging to one unit cell, forms a factor set of equivalent points.

Let us consider the crystal structure $\mathbf{Q}(\mathbf{X})$ consisting of N regular sets generated from the set $\mathbf{X} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$ of non-symmetry-equivalent points. We suppose that all points of \mathbf{X} occupy general positions. The set of factor sets, $\mathbf{S}(\mathbf{X}) = \{\mathbf{S}(\mathbf{r}_i), i = 1, 2, \dots, N\}$, will be called the factor basis of the structure $\mathbf{Q}(\mathbf{X})$.

The structure $\mathbf{Q}(\mathbf{X})$ generates the vector set of interatomic distances

$$\mathbf{V}(\mathbf{X}) = \{(\mathbf{A}_l \mathbf{r}_i + \mathbf{b}_k) - (\mathbf{A}_p \mathbf{r}_j + \mathbf{b}_q) \pmod{\mathbf{1}}\} \quad (1.1)$$

for $l, p = 1, 2, \dots, L$; $k, q = 1, 2, \dots, K$; $i, j = 1, 2, \dots, N$. It follows from (1.1) that $\mathbf{V}(\mathbf{X})$ is the superposition of LKN copies of the factor basis $\mathbf{S}(\mathbf{X})$, but each copy is shifted at different positional vectors, *i.e.*

$$\mathbf{V}(\mathbf{X}) = \{\mathbf{S}(\mathbf{X}) \ominus (\mathbf{A}_l \mathbf{r}_i + \mathbf{b}_k) \pmod{\mathbf{1}}\}. \quad (1.2)$$

Alternatively, $\mathbf{V}(\mathbf{X})$ can be regarded as the shift superposition of LKN copies of the inverse factor basis $\mathbf{S}(-\mathbf{X})$, *i.e.*

$$\mathbf{V}(\mathbf{X}) = \{(\mathbf{A}_l \mathbf{r}_i + \mathbf{b}_k) \ominus \mathbf{S}(\mathbf{X}) \pmod{\mathbf{1}}\}. \quad (1.3)$$

(Here and below the signs \oplus and \ominus indicate the operations of direct sum and difference of vector sets, respectively.)

Since $\mathbf{V}(\mathbf{X})$ contains a copy of $\mathbf{S}(\mathbf{X}) \ominus \mathbf{r}_i \pmod{\mathbf{1}}$, then

$$\mathbf{S}(\mathbf{X}) \subset \mathbf{V}(\mathbf{X}) \oplus \mathbf{r}_i \pmod{\mathbf{1}},$$

i.e. the vector set $V(X)$, shifted at the positional vector r_i , contains an exact copy of the initial factor basis $S(X)$. Hence the factor basis of crystal structure $Q(X)$ can be recovered from $V(X) \oplus r^*(\text{mod } I)$, $r^* \in X$, by selection of all the factor sets associated with a given group of symmetry transformations. The algorithm will be called *S-filtration*. Fig. 1 illustrates the use of the *S-filtration* algorithm for the solution of a vector set of the model structure with symmetry *pm*.

Note that $V(X) \oplus r_i(\text{mod } I)$ can contain ghost factor sets which do not belong to $S(X)$. The appearance of ghost factor sets can be explained by accidental combinations of the interatomic vectors in $V(X)$ (Simonov, Soldatenkov & Shchedrin, 1969).

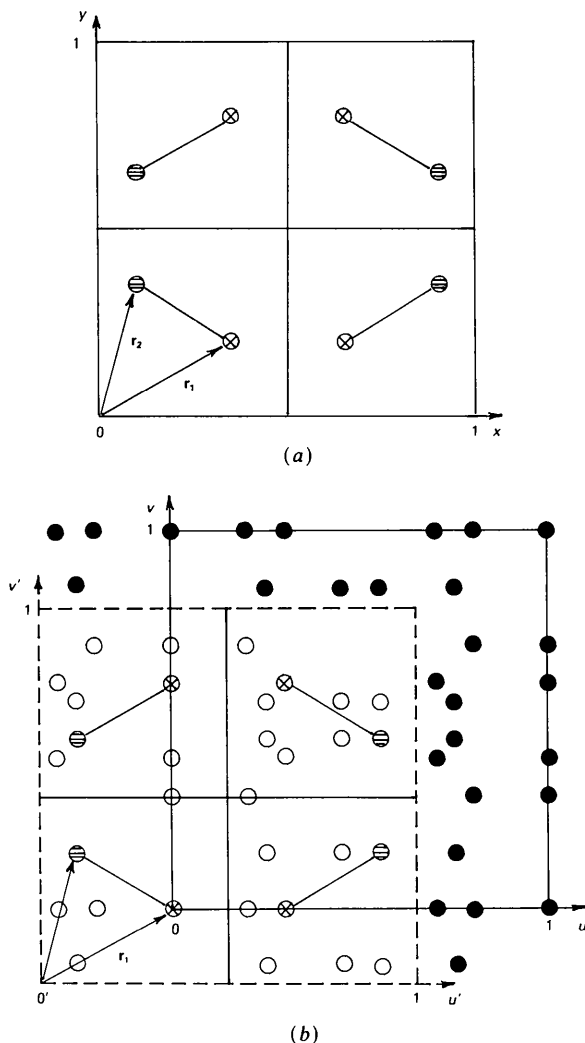


Fig. 1. Illustration of the idea of vector set interpretation by the *S-filtration* method. (a) The point atomic structure $X(r_1, r_2)$ with symmetry *pm*. \otimes and \odot denote the factor sets $S(r_1)$ and $S(r_2)$ of the symmetry-equivalent positions of two basic atoms, respectively. (b) The vector set $V(X)$ of the structure $X(r_1, r_2)$. The dashed lines restrict the vector set $V(X) \oplus r_i(\text{mod } I)$. The initial structure can be obtained by selecting from $V(X) \oplus r_i(\text{mod } I)$ the vectors which compose the factor sets with symmetry *pm*.

2. Investigation of the ambiguous solutions of vector sets

Let $\Omega(G)$ be a set of shift vectors into equivalent origin (EO vectors). It is known that EO vectors ω , $\omega \in \Omega(G)$, are the solutions of the set of equations

$$(R_l - I) \cdot \omega = n + \nu b_k \tag{2.1}$$

for $l = 1, 2, \dots, L$; $k = 1, 2, \dots, K$; $\nu = 0, 1$, where I is the identity transformation. The complete list of EO vectors for all space groups is given by Giacovazzo (1974). Note that EO vectors form discrete sets except for space groups of the polar kind. In these groups they form one- or two-dimensional manifolds.

Let us prove the following statement.

Lemma:

$$S(\omega \pm r) = \omega \oplus S(r)(\text{mod } I) \tag{2.2}$$

is valid for every vector ω , $\omega \in \Omega(G)$, and every vector r .

Proof: Bearing in mind that $A_l(\omega \pm r) = R_l \omega \pm A_l r$ is true for every transformation A_l , $A_l \in G$, and taking into account (2.1), we immediately obtain (2.2). It follows from (2.2) that while, in general, the factor sets $S(r)$ and $S(r \pm \omega)$ (viewed from one fixed origin) are not isometrically equivalent, their vector sets are always homometric. We shall see that it is just the specific property of EO vectors that leads to regular ambiguities.

Theorem: If some EO vector ω , $\omega \in \Omega(G)$, connects two atomic positions r_i and $A_l r_j + b_k$ by the relation

$$r_i \mp (A_l r_j + b_k)(\text{mod } I) = \omega, \tag{2.3}$$

then $V(X) \oplus r_i(\text{mod } I)$ contains also the factor basis

$$S(\omega \oplus X) = \{S(\omega \pm r_n), n = 1, 2, \dots, N\}.$$

Proof: Since $S(X) \ominus (A_l r_j + b_k)(\text{mod } I)$ is also contained in $V(X)$, then under condition (2.3) and because of the property (2.2) we have

$$S(X) \ominus (A_l r_j + b_k) \oplus r_i(\text{mod } I) = S(\omega \oplus X).$$

Similarly, if we take the copy $(A_l r_j + b_k) \ominus S(X)(\text{mod } I)$, then we have

$$r_i \oplus (A_l r_j + b_k) \ominus S(X)(\text{mod } I) = S(\omega \ominus X).$$

According to this result the following three cases should be distinguished:

(i) The condition (2.3) can be satisfied for symmetry-equivalent points (e.g. for r_1 and $A_l r_1 + b_k$), *i.e.*

$$r_1 \mp (A_l r_1 + b_k)(\text{mod } I) = \omega. \tag{2.4}$$

In this case the solution will be obtained as a superposition of $2N - 1$ factor sets, namely

$$S(\omega + r_N), \dots, S(\omega + r_2), S(r_1), S(r_2), \dots, S(r_N)$$

and/or

$$S(\omega - r_N), \dots, S(\omega - r_2), S(r_1), S(r_2), \dots, S(r_N).$$

Thus the condition (2.4) restricts the choice of atomic position vectors for shifting the vector sets. Fig. 2 illustrates such an ambiguity of solution.

(ii) The condition (2.3) can be satisfied for non-symmetry-equivalent points (e.g. for r_1 and $A_j r_j + b_k$, $j \neq 1$). Here the ambiguous solution will also be obtained as in the previous case. However, the fact of ambiguity can be established only *a posteriori*.

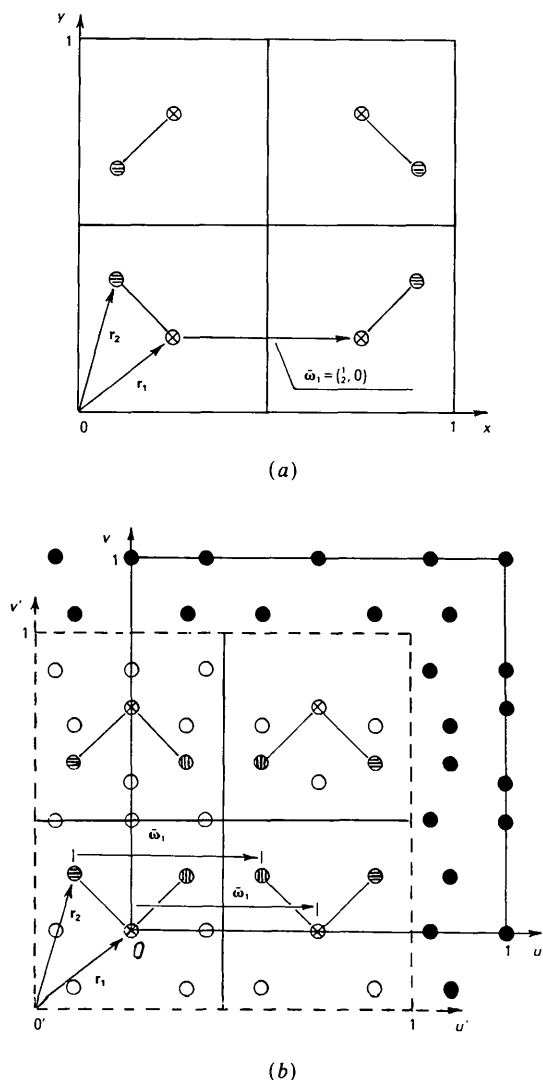


Fig. 2. The ambiguous solution of the vector set due to the special position of one basic atom. (a) Two factor sets $S(r_1)$ and $S(r_2)$ of the point atomic structure $X(r_1, r_2)$ with symmetry pmm . The shift vector into the equivalent origin, $\omega_1 = (\frac{1}{2}, 0)$, connects two symmetry-equivalent positions. (b) The vector set $V(X)$ of the structure $X(r_1, r_2)$. The vector set $V(X) \oplus r_1 \pmod{1}$ contains three factor sets with symmetry pmm . \otimes and \odot denote the points of the original factor sets $S(r_1)$ and $S(r_2)$, respectively. \oplus denotes the points of the additional factor set $S(\omega_1 + r_2)$.

(iii) There are groups G_a among the polar space groups (with continuous sets of EO vectors) for which the sum of the identity operator I and some operator $A_j \equiv (R_j | t_j)$, $A_j \in G_a$, is the projection operator onto $\Omega(G_a)$, i.e.

$$(I + R_j)r + t_j \pmod{1} = \omega_r, \omega_r \in \Omega(G_a).$$

In this case the equality

$$r \oplus A_j r \ominus S(X) \pmod{1} = S(\omega_r \ominus X)$$

is valid for any positional vector. Therefore, two homometric factor bases, namely $S(X)$ and its shift-antiomorphic copy $S(\omega_r \ominus X)$ will be systematically recovered from the vector sets of structures with this kind of symmetry. A complete list of these groups is given in Table 1. An example of the enantiomorphic ambiguity is shown in Fig. 3.

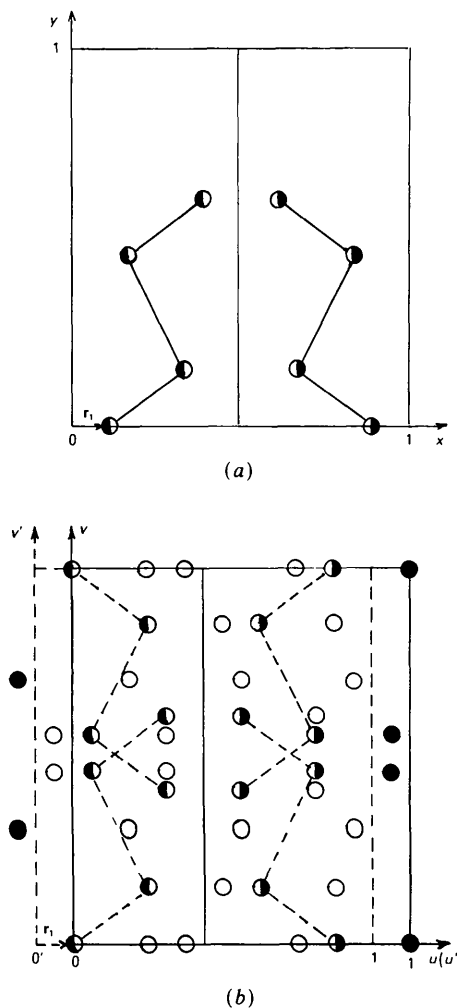


Fig. 3. Illustration of the enantiomorphic ambiguity due to crystal symmetry of the polar kind. (a) The point atomic structure $X(r_1, r_2, r_3, r_4)$ with symmetry pm . (b) The vector set $V(X)$ of the structure $X(r_1, r_2, r_3, r_4)$. The vector set $V(X) \oplus r_1 \pmod{1}$ contains the twofold image of the initial structure.

Table 1. List of crystal space groups with the enantiomorphous ambiguity

Crystal system	Space groups
Monoclinic	$P2, B2, C2, P2_1, Pm, Bm, Cm, Pb, Pc, Bb, Cc$
Orthorhombic	$Pmm2, Amm2, Cmm2, Fmm2, Imm2, Pmc2_1, Cmc2_1, Pcc2, Ccc2, Pma2, Ama2, Ima2, Pca2_1, Pnc2, Pmn2_1, Pba2, Aba2, Pna2_1, Iba2, Pnn2, Abm2, Fdd2$
Tetragonal	$P4, I4, P4_1, I4_1, P4_2, P4_3, P4mm, I4mm, P4bm, P4_2cm, P4_2nm, P4cc, P4nc, P4_2mc, P4_2bc, I4cm, I4_1md, I4_1cd$
Hexagonal	$P6, P6_1, P6_2, P6_3, P6_4, P6_5, P6mm, P6cc, P6_3cm, P6_3mc$

Concluding remarks

For the practical application of the proposed method it is necessary to know at least one atomic position. This problem can be solved by the trial-and-error method

$$\mathbf{r}_i \rightarrow \mathbf{S}(\mathbf{r}_i) \rightarrow \mathbf{V}[\mathbf{S}(\mathbf{r}_i)]$$

and if $\mathbf{V}[\mathbf{S}(\mathbf{r}_i)] \subset \mathbf{V}(\mathbf{X})$, then $\mathbf{r}_i \in \mathbf{X}$. Note that the vector sets of the factor sets $\mathbf{S}(\mathbf{r})$ and $\mathbf{S}(\boldsymbol{\omega} - \mathbf{r})$, as we have already mentioned, are always homometric. Therefore the scanning area for the trial vectors \mathbf{r}_i should cover, in general, only the $1/(LKM)$ th part

of the unit cell, where L is the number of symmetry operations, K is the number of centering translations, and M is the number of EO vectors.

The application of the S -filtration method is especially effective for crystals with heavy atoms and high-order symmetries. Serious problems arise for so-called difficult structures, when the crystal symmetry belongs to polar space groups (except for the trigonal system; see Table 1). In this case either Patterson or conventional direct methods would provide an ambiguous solution in which the true structure and its enantiomorph are superimposed. This obstructs the solution of the structures. Special methods have been proposed to overcome this obstacle. For a detailed discussion on this topic, the reader is referred to the paper by Fan Hai-fu (1984).

References

- BUERGER, M. J. (1959). *Vector Space and its Application in Crystal Structure Investigation*. New York: John Wiley.
 COCHRAN, W. (1958). *Acta Cryst.* **11**, 579-586.
 FAN HAI-FU (1984). *Rigaku J.* **1**, 15-21.
 GIACOVAZZO, C. (1974). *Acta Cryst.* **A30**, 390-395.
 SIMONOV, V. I., SOLDATENKOV, A. M. & SHCHEDRIN, B. M. (1969). *Kristallografiya*, **14**, 237-246.
 WRINCH, D. M. (1939). *Philos. Mag.* **27**, 98-122.

Acta Cryst. (1988). **A44**, 425-432

X-ray Diffraction by a Low-Angle Twist Boundary Perpendicular to Crystal Surface. III. The Integral Characteristics

BY D. M. VARDANYAN AND H. M. MANOUKYAN

Department of Physics, Yerevan State University, Mravyan str. 1, 375049 Yerevan, Armenia, USSR

AND H. M. PETROSYAN

Department of Physics, Yerevan Pedagogical Institute, Khandjyan str. 5, 375010 Yerevan, Armenia, USSR

(Received 28 July 1987; accepted 21 January 1988)

Abstract

For X-ray diffraction by a pure low-angle twist boundary perpendicular to a crystal surface, within the framework of the kinematic and dynamical theories, the following integral characteristics are calculated: (a) the bicrystal reflectivity in the vicinity of the l th reflection; (b) the integrated intensity of the l th reflection; (c) the bicrystal total reflectivity, i.e. the sum of the integrated intensities over all reflections. The case for even $\mathbf{h} \cdot \mathbf{b}$ (\mathbf{h} is the diffraction vector, \mathbf{b} is the Burgers vector of the boundary screw dislocations) is considered. In dynamical theory an increase of the total reflectivity of a bicrystal due to the boundary dislocation structure is obtained.

1. Introduction

Diffraction methods have been successfully used in studies of the structure of grain boundaries. A detailed presentation of the results of such studies performed by the use of X-ray and electron diffraction was given in the review paper of Sass (1980). The use of X-radiation is greatly preferable, firstly because it lacks double diffraction, which complicates the diffraction pattern, and secondly because it enables the investigation of relatively thick samples. X-ray diffraction studies of bicrystal block boundaries were carried out for the case when the boundary plane is parallel to the crystal surface. Both the high-angle and low-angle twist boundaries were investigated by Guan & Sass