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Abstract

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ON DETAILS OF PATTERSON SYNTHESES DIRECTLY RELATED TO SYMMETRY ELEMENTS OF THE STRUCTURE

The peaks of the Patterson function (of the vector system) are divided into linkage peaks, which fix the distances between equivalent, i.e., symmetry-related atoms, and interaction peaks, which identify vectors between atoms from different linkages. The regularities in the arrangement of the former constitute the basis of the classical implication method ([1]). S. V. Borisov developed new approaches to deciphering the Patterson function by means of interaction peaks ([2]). But already 14 years ago the joint consideration of linkage peaks for each of two nonequivalent atoms and of their interaction peaks in a centrosymmetric crystal led to the theorem on triples of peaks ([3]), which played a major role in the deciphering of a number of structures.

This theorem can also be extended to other symmetry elements and, above all, to elements of the 2nd order. It is very convenient for this purpose to represent the basic system of points in the form of a system of n segments, where n is the order of the symmetry group. The initial segment in the basic system joins two (arbitrary) atoms $x_1y_1z_1$ and $x_2y_2z_2$ from different linkages, and then we multiply it by all symmetry elements of the group. The vector system is then obtained as the totality of the images, at all points of the basic system, of the initial segment, while this segment itself connects the origin with the point $u_1 = x_2 - x_1$, $v_1 = y_2 - y_1$, $w_1 = z_2 - z_1$ (cf. ([2]))*.

Figure 1 shows the basic and vector systems for three Fedorov groups $P\bar{1}$, $P2$, and Pm (with one symmetry element of the 2nd order**). In the vector system, peaks of two types are combined by segments equal and parallel to the segments of the basic system, in addition to trivial stars around the origin, also into rhombi of peaks. In the diagram, the first atom and its linkage are denoted by triangles, the second by squares. The Patterson linkage peaks are denoted similarly. The coordinates of the interaction peaks shown by filled circles will be $u_1 = x_2 - x_1$, etc., for trivial stars, and $u_2 = x_2 + x_1$, etc., for rhombi. The center of the rhombus in the case of the group Pm is characterized by two fixed coordinates–in our example $(00u_2)$, and in the group $P2$ by one (u_2v_20). In the group $P\bar{1}$, the characteristic triple of peaks on a segment parallel to the initial

Figure 1: Basic and vector systems for the space groups $P\bar{1}$, $P2$, Pm.

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one may be regarded as a degenerate rhombus, two of whose vertices (circles of interaction peaks) have merged at the point without a fixed coordinate ($u_2v_2w_2$).

If a translational component enters into the (as yet) only symmetry element ($Pg, P2_1$), then the rhombus of peaks is displaced in the direction and by the magnitude of the glide half-translation. Thus, for the group Pb the center of the rhombus will be at ($0\frac{1}{2}w_2$), for $P2_1$ at ($u_2v_2\frac{1}{2}$), etc. The coordinates of the vertices of the rhombus change according to (^{2}).

Analogous regularities in the combination of peaks of two kinds, but with possible degeneration or particular coordinate values, occur in the cases of a special position of the required segment, when it per–

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* Having chosen some segment as the initial one, we seek and fix those of its ends which are obtained when the origin of the map is translated to all $2n$ points of the original system.
** Peaks for two, for example, the strongest atoms.

perpendicular or parallel to the symmetry element, or if one or both segments lie on the symmetry element.

A centered lattice doubles (quadruples) both the number of initial stars and the number of rhombi. If the symmetry element does not pass through the origin, for example in the group $P2_1/m$, where the mirror plane is at a distance $c/4$ from the origin, then the coordinates of the center of the rhombus determined by this m will be ($0\ 0\ \frac{1}{2} - w_2$).

In Fig. 2 the independent parts of the vector systems are reproduced for the orthorhombic groups

$$Pnma = P\ \frac{2_1}{n}\ \frac{2_1}{m}\ \frac{2_1}{a}$$

and $Pn2_1a$. Near each rhombus

Fig. 1. Basic and vector systems for the space groups $P\bar{1}$, $P2$, Pm

of peaks the symmetry element (of order 2) that generated it is indicated. Of the six rhombi (plus one degenerate into a segment) in the first group, only three remain in the second. Since for orthorhombic crystals the three-dimensional Patterson function always has three mutually perpendicular symmetry planes, for a plane we obtain not one, but two rhombi intersecting along the common "diagonal of the bond peaks" : instead of a plane rhombus–a rhombic bipyramid.

Representing the Patterson function in the form of a vector system of segments (so far for two "strong" atoms) combines peaks of two kinds into discrete rhombi

Fig. 2. Complete set of rhombi of peaks in the vector systems of the space groups Pnma, Pn2_1a

Figure 2: Fig. 2. Complete set of rhombi of peaks in the vector systems of the space groups Pnma, Pn2_1a

characterizing individual symmetry elements,

and can be used to establish the coordinates of a pair of atoms. Connecting an arbitrary Patterson peak $(u_1v_1w_1)$ with the origin, we regard it as the initial segment. The symmetric repetition of this segment near the center of the sought rhombus determined by symmetry fixes the rhombus itself, of which this image is a side. In Fig. 2 the sides for all rhombi are also shown by heavy lines. One end of such a side (the one related by symmetry to the origin) will be a bond peak, the other an interaction peak; their coordinates differ by $|u_1|\,|v_1|\,|w_1|$. Having established from the bond peaks the coordinates of the first atom, we obtain the coordinates of the second by adding $u_1v_1w_1$. The coordinates of the pair are determined with the usual k-valued ambiguity because of the arbitrariness in choosing the origin [(1)],

Fig. 2. Complete set of rhombi of peaks in the vector systems of the space groups $Pnma$, $Pn2_1a$

but the ambiguity that occurs when individual interaction peaks are used [(2)] is eliminated.

Such a "geometrical"procedure can be repeated for identifying subsequent atoms through the pairs 1–3, 2–3, 3–4, etc. The proviso concerning the k-ambiguity of the choice of origin requires mutual agreement of the results of considering segments between fixed pairs under different variants of their placement relative to the common origin*.

If an N-fold peak [(4)] is chosen as the initial one, then we arrive at N different sets of equal rhombi of peaks characteristic of the given–

* In non-centrosymmetric crystals, the possibility of an enantiomorphic solution is taken into account.

Fedorov group. Thus, with the proviso that the choice of origin is ambiguous, N pairs of atoms will be distinguished. As shown in [(4)], in this case false triplets of peaks [(4)] arise on Patterson maps of non-centrosymmetric crystals. It must not be forgotten that, for a centrosymmetric crystal, every interaction peak is at least double [(2)].

The representation of the Patterson function in the form of a vector system of segments proved very useful in deciphering the crystal structure of sodium chromate [(5)].

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REFERENCES

[1] M. Buerger, *Crystal Structure and Vector Space*, 1961.
[2] S. V. Borisov, *Crystallography*, **9**, No. 5 (1964).
[3] Kh. S. Mamedov, N. V. Belov, *Dokl. Akad. Nauk SSSR*, **106**, No. 3, 462 (1956).
[4] E. A. Kuz' min, V. V. Ilyukhin, N. V. Belov, *Crystallography*, **14**, No. 6 (1969).
[5] Yu. A. Kharitonov, E. A. Kuz' min, N. V. Belov, *Dokl. Akad. Nauk SSSR*, **186**, No. 1, 96 (1969).

Note: Figure translations are in progress. See original paper for figures.