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Oblique projections. By P. J. BLACK,* *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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The labour of investigating a three-dimensional structural pattern is usually reduced by the use of two-dimensional projections. Two such projections may be required to determine all the parameters of a structure, but in some systems (e.g. the cubic) a single projection will suffice. Calculations in three dimensions are sometimes necessary, even when the resulting increase in accuracy is not essential, in order to resolve atoms that overlap in the projections.

A unit cell is generally chosen to have a conventional relationship to the symmetry elements of a structure, and projections are usually made parallel to the sides of the cell. This is not a necessary restriction, and one can construct a projection parallel to any direction which joins two lattice points, i.e. parallel to any direction with rational zone indices. The term 'oblique projection' will be used to denote a projection parallel to a direction which is not the edge of a conventional unit cell.

In Fig. 1(a) is shown a projection, parallel to the two-fold axis, of two pairs of atoms in a structure of space group $P2$. A new cell may be chosen as in Fig. 1(b), and projection parallel to the axis b' gives the pattern of Fig. 1(c). Whereas Fig. 1(a) has the plane group symmetry $P2$, Fig. 1(c) belongs to $P1$. Each type of atom appears twice in the projection, and from the four coordinates of this pair, all three independent atomic coordinates can be obtained. It is clear that in Fig. 1(b) other directions could have been chosen for the new direction of projection, for example, the diagonal of the A face or the body diagonal.

Similar results can be derived for the other monoclinic space groups (see Black, 1955). The monoclinic cell is effectively replaced by a triclinic cell, which will have a centre of symmetry if the monoclinic space group has one. For example, in $P2/m$ the four symmetry-related atoms (in general positions) would project parallel to an oblique axis to give two independent peaks, since the centre of

symmetry is preserved in the projection. For a non-primitive (monoclinic) lattice, the new axis can be chosen to define either a primitive or a centred triclinic cell.

The discussion can easily be extended to space groups of higher symmetry. Four atoms related by symmetry in an orthorhombic space group may give either two or four independent positions in an oblique projection. Conventional projections which are normal (e.g. in tetragonal or hexagonal) or oblique (e.g. to the triad in a cubic) to symmetry axes give independent peaks for symmetry-related atoms. Oblique projections may still be useful to resolve particular atoms which superpose accidentally in axial projections.

The discussion leads to two main conclusions which may be of use in refining structures by Fourier methods. The first is that in all space groups, except $P1$ and $P\bar{1}$, it is possible in principle to obtain all atom parameters from a single two-dimensional projection. The three-dimensional parameters will be obtained from linear combination of pairs of parameters measured in the projection (Fig. 1), so that the standard errors in them will be of the order of $\sqrt{2}$ times the normal standard error. In some cases, more than one value of each parameter is obtained because there may be more than two related atoms in the asymmetric unit; then the standard error will be reduced. Where it can be applied, the method should be more accurate and less laborious than the use of higher-layer syntheses (Cochran & Dyer, 1952).

The second conclusion is that, in a complex structure, several possible projections can be considered for refinement, and it may be possible to resolve all atomic peaks clearly by using a few selected projections and so avoid the necessity for three-dimensional refinement. Each projection requires data for only one zone which can be collected on zero-layer oscillation or Weissenberg photographs, so avoiding the uncertainties introduced by distortion of spot shapes and inter-layer correlation factors. Even in three-dimensional work, one might (for example) choose an oblique direction for a bounded pro-

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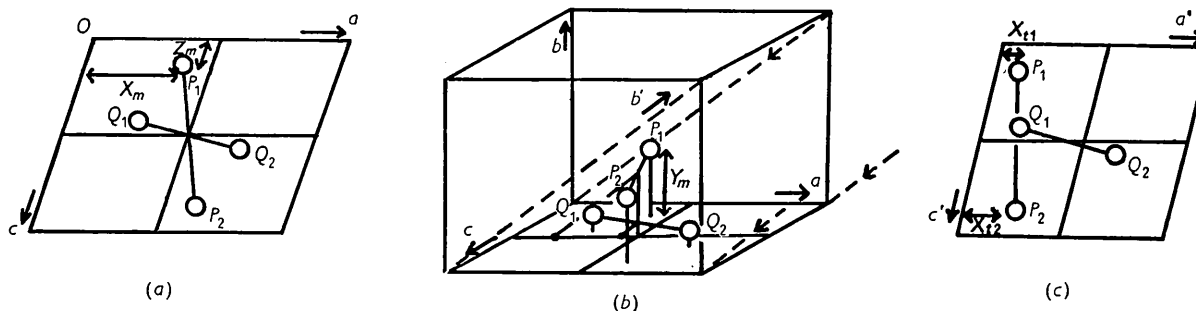


Fig. 1. (a) Projection down unique axis for space group $P2$. (b) Monoclinic cell (a, b, c) and new projection axis (b'). (c) Appearance on new projection plane of atoms of (a) and (b).

If $X_m, Y_m, Z_m, X_{t_1}, X_{t_2}$ are fractional parameters, then

$$X_m = \frac{1}{2}\{1 + X_{t_1} - X_{t_2}\}, \quad Y_m = \frac{1}{2}\{1 - (X_{t_1} + X_{t_2})\}, \quad Z_m = Z_t.$$

jection to improve resolution or to give all the atomic parameters.

An oblique projection has been used in the refinement of the FeAl_3 structure (Black, 1955). In a cell containing 100 atoms with space group $C2/m$, all three axial projections involved serious overlap. In a single oblique projection, all the peaks were fairly well resolved, and this projection served to determine all of the 40 independent parameters. This may be a particularly favourable case; it is obvious that where the change of cell involves reversion to a primitive cell there is a better chance of obtaining good resolution in projection.

Oblique projections can also be used for Patterson syntheses. Their properties can be derived by considering the relationship between the oblique projection, direct projection and three-dimensional Pattersons. One special property may be noted. Atoms related by a tetrad axis give Patterson peaks for vectors between themselves which have fourfold symmetry; in projection oblique

to the tetrad they retain this symmetry, whereas peaks due to vectors between independent atoms do not, and the two types may thus be distinguished. In general, coincidence tests between direct and oblique Patterson projections may give sufficient information about the three-dimensional Patterson without involving the labour of its calculation.

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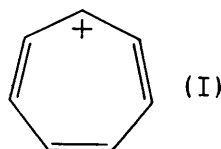
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Crystal data for tropylium chloride, $\text{C}_7\text{H}_7\text{Cl}$. By EDWIN S. GOULD, *Polytechnic Institute of Brooklyn, Brooklyn 1, N. Y., U.S.A.*

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Tropylium chloride, tropylium bromide and tropylium iodide have been described by Doering & Knox (1954). The properties of alcoholic solutions of the chloride and bromide and the spectrum of the bromide in aqueous HBr (Fately & Lippincott, 1955) suggest that these halides are dissociated in polar solvents to the halide ions and the tropylium ion. The solubility of the chloride and bromide in polar solvents, as contrasted with their insolubility in non-polar solvents, suggests that these ions might persist in the solid halides, although solids consisting of ionic networks and having at the same time



melting points below 200°C . are very rare. The tropylium ion is a seven-membered carbocyclic cation of classical formula (I), for which delocalization of the six π electrons about the ring should be possible if the ring were to assume a planar configuration. The two main points of interest in connection with the tropylium halides would then seem to be (1) the planarity of the ring, and (2) whether the halogen atoms are bonded to the rings or exist as discrete anions in the solids. We are reporting here the cell dimensions of tropylium chloride, the only one of the halides for which we were able to obtain single crystals. In view of the large number of molecules per unit cell and the low symmetry of the compound, complete structure determination will not be attempted.

Colorless, needle-like crystals of tropylium chloride, elongated in the $[110]$ direction, were obtained from anhydrous acetonitrile. Since the chloride is very deliquescent and somewhat sensitive to air oxidation, the