

'Stereoscopic' Three-Dimensional Structure Analysis

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A method has been devised for deriving plane sections of three-dimensional Patterson, potential or electron-density functions by a 'stereoscopic' method from two or more two-dimensional projections corresponding to electron or X-ray diffraction patterns obtained with not very different orientations of the incident beam. The derivation of the three-dimensional Patterson function of basic lead carbonate serves as an example.

For structure analysis based on the intensities of a single-crystal electron diffraction pattern, using present-day techniques, the crystal used is ideally in the form of a thin plate, not more than a few hundred Ångströms thick and of the order of a micron in diameter (Cowley, 1953). Many substances, particularly those with a layer-lattice structure, may be made to crystallize in this form. Usually two of the principal axes of the lattice lie in the plane of the crystal plate and the third principal axis is perpendicular, or nearly perpendicular, to it. The angle which the electron beam makes with the plane of the crystal plate must exceed 30 or 45° in order that the thickness of the crystal traversed should not be too great. The usual specimen-mounting techniques limit the possible angles of incidence of the beam still further. Under these conditions it is relatively easy to obtain a pattern of spots with the beam parallel to one principal axis, but impossible to obtain a pattern with the beam parallel to either of the other principal axes.

For some substances it is possible to overcome this difficulty by applying a variety of preparation techniques to obtain suitable crystals with different lattice orientations relative to their small dimensions (Moodie, 1956). This is usually not possible for layer-lattice structures.

In X-ray diffraction work an analogous situation may occasionally arise, but rather as a result of some form of disorder in the crystal than as a result of the limitations of crystal morphology.

For convenience in discussion, we limit ourselves to the consideration of a thin crystal plate with the a and b axes lying in the plane of the plate and the c axis perpendicular to it, although all considerations apply equally well if these conditions are not satisfied. It is then possible to obtain $hk0$ spot patterns, but not the $h0l$ or $0kl$. The projection of the structure on the xy plane can be found, but information concerning the z -coordinates of atoms can be deduced only from patterns obtained with the beam making an angle of less than, say, 30° with the c axis.

If the crystal is completely ordered, it is possible to

obtain extensive spot patterns at a limited number of orientations of the beam other than that parallel to the c axis. The number of these 'tilted' patterns which are non-equivalent may be very small if the c axis is short, but the number increases with the length of the c axis. If the crystal is disordered with a more or less random stacking of the planes of atoms perpendicular to the c axis, as is usually the case with small crystals of the layer-lattice type, the c axis is effectively infinite, and an extensive spot pattern is obtained at any angle of tilt. The spot patterns represent, to a first approximation, plane sections of reciprocal-lattice space. The transforms of the intensities or amplitudes may be considered as various 'views' or projections of the three-dimensional Patterson or potential (in the case of X-rays, electron density) functions. The method which has been developed for their interpretation employs the principle of the stereoscopic viewing of photographs taken from slightly different angles.

A 'tilted' spot pattern may be indexed by assigning the h and k indices corresponding to those of the untilted $hk0$ pattern. If the intensities or amplitudes are used as coefficients of a Fourier series and the resulting Fourier (Patterson or potential) map is plotted with the a and b dimensions of the untilted pattern, the map may be considered to be a projection on the $z = 0$ plane along the direction of the electron

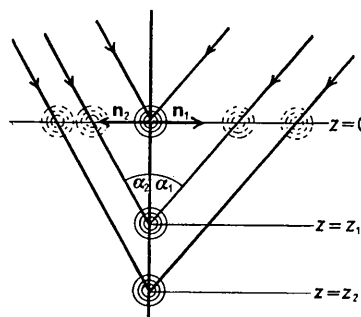


Fig. 1. Illustrating the relation of real and apparent (broken) peak positions for two angles of tilt of a crystal. Vectors \mathbf{n}_1 and \mathbf{n}_2 are coplanar in $z = 0$ but not necessarily collinear.

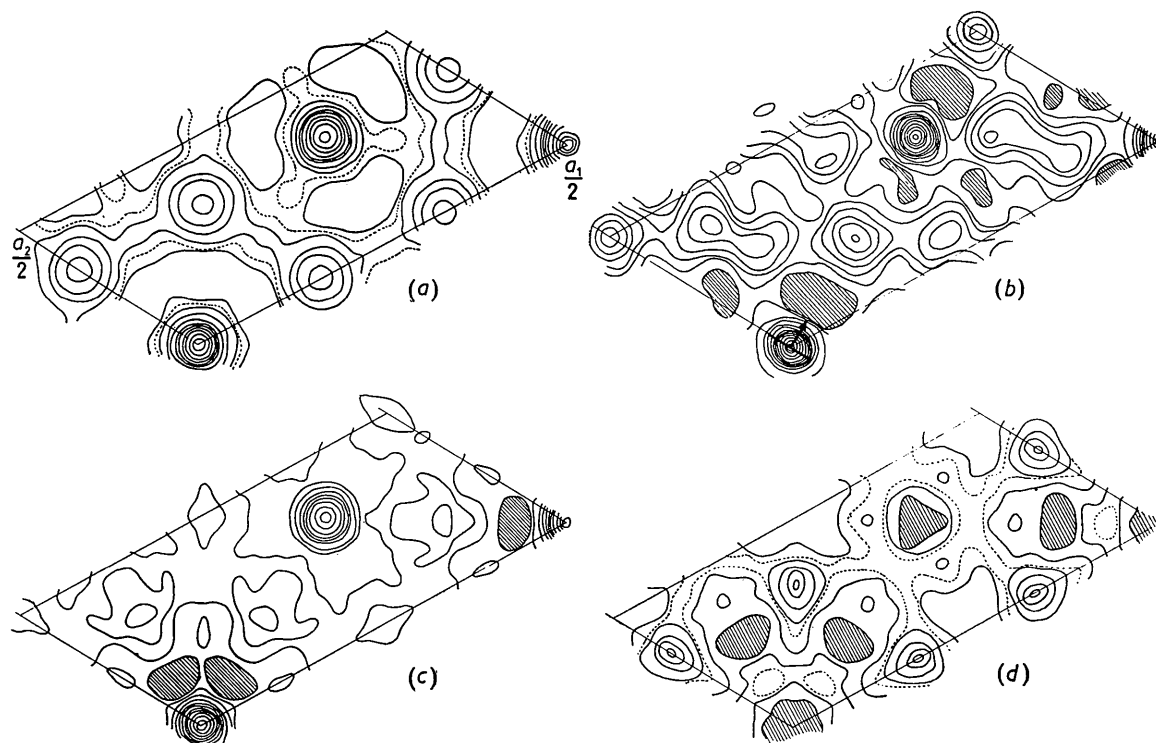


Fig. 2 (*a, b*). Projections of the modified Patterson function of basic lead carbonate: (*a*) projection down the *c* axis; (*b*) projection in a direction at an angle of $17\frac{1}{2}^\circ$ to the *c* axis. Arrow indicates tilt direction. Negative areas shaded. Broken contour at half-interval. (*c, d*). Sections of the three-dimensional Patterson function of basic lead carbonate: (*c*) $z = 0$; (*d*) $z = 0.13$. Negative areas shaded.

beam. In such a map, a peak with $z = z_i$ will be displaced by an amount $(z_i \tan \alpha_1) \mathbf{n}_1$ relative to the corresponding peak in the map obtained from an untilted pattern, α_1 being the angle of tilt and \mathbf{n}_1 being a unit vector in the $z = 0$ plane indicating the direction of tilt.

Two such maps corresponding to different tilts, but each plotted in a unit cell defined by the *a* and *b* axes, are prepared. The tilts are specified by α_1 , \mathbf{n}_1 and α_2 , \mathbf{n}_2 . Fig. 1 illustrates the geometric relationships. If these two maps are superimposed, peaks for which $z = 0$ will coincide. Peaks for which $z \neq 0$ will appear in different positions in the two maps and will overlap others only fortuitously. At each point (*x, y*) the value of the two functions is found and the minimum value is chosen. Plotting this minimum value gives a map containing all peaks for which $z = 0$, i.e. the $z = 0$ section of the three-dimensional function, plus spurious features.

Similarly, if the origin of the one map is given a displacement $-\mathbf{n}_1 z_1 \tan \alpha_1$, and the origin of the other map is given the displacement $-\mathbf{n}_2 z_2 \tan \alpha_2$, all peaks for which $z = z_i$ will coincide, and plotting the minimum of the two functions gives the $z = z_i$ section, plus spurious features.

The amount of spurious detail may be reduced by taking account of any symmetry elements in the sections. Thus if the *c* axis of the structure is a twofold

symmetry axis, the values of the function at (*x, y*) and ($-x, -y$) on both maps are minimized. Similarly, with other symmetry elements the minimum is taken of the values at all equivalent points on the two maps. For structures of low symmetry, when this procedure does not give sufficient discrimination, more than two maps, with corresponding tilts as widely different as possible, may be used.

For an ordered crystal, sections may be derived in this way for all values of *z*, giving a complete three-dimensional representation of the function. When the crystal is disordered the sections will not recur with the periodicity of the unit cell. By taking sections for large *z* values it may be possible to study the nature of the short-range order, if any, which exists in the stacking of the layers.

The resolution obtained in the *z* direction will necessarily be poorer than that in the *x* and *y* directions. A spherically symmetric peak will appear to have a diameter in the *z* direction which is greater by a factor of at least $\cot \alpha$, where α is the greatest angle of tilt of the patterns employed.

An example of the use of this method is provided by the derivation of the three-dimensional Patterson function of basic lead carbonate. This was an important step in the elucidation of the structure of this compound, described in an accompanying paper (Cowley, 1956*a*).

The basic lead carbonate crystals had a disordered layer-lattice-type structure and gave extensive spot patterns at all angles of tilt. The 'untilted' $hk0$ spot pattern had hexagonal symmetry. This pattern was used in conjunction with one obtained with a tilt of approximately $17\frac{1}{2}^\circ$, as deduced from the dimensions of the pattern. Instead of normal Patterson projections, modified Patterson projections (Cowley, 1956*b*) were calculated, since these contained more information on the details of the structure. The modified Patterson maps are reproduced in Fig. 2(*a*) and (*b*).

The three-dimensional Patterson function was assumed to have a sixfold symmetry about the c axis, so that six equivalent points on each of the two maps were compared. Sections for a number of values of z were derived. The section $z = 0$ is reproduced in Fig. 2(*c*), and the section $z = 0.13$ ($= 3.2 \text{ \AA}$) in Fig. 2(*d*).

The interpretation of these maps is discussed in the report of the structure analysis (Cowley, 1956*a*). However, it can be clearly seen that the major peaks of the projection, Fig. 2(*a*), have been separated into two groups with differing z coordinates. No indication was found that any of the features of the sections which were of sufficient importance to be considered in the course of a structure analysis were spurious. Comparison with the structure eventually found for the crystals showed that all the main features of the sections and most of the details were real.

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Crystallographic Study of an Arsonium Bromide, $(C_{21}H_{19}As_2)Br$

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The investigation of an arsonium bromide by X-ray crystallographic methods distinguished between three possible molecular structures. The molecule is correctly described as di-*o*-phenylene-*o*-xylylene-diarsine monomethobromide.

Introduction

The evidence from chemical work proved insufficient to distinguish between structural formulae (Fig. 1) for the compound with which this investigation was concerned. As this arsonium bromide was one of several compounds involved in a series of chemical investiga-

tions it was important to find its actual structure. In Fig. 1(*a*) the arsenic atom is common to the arsanthrene ring structure (Kalb, 1921; Chatt & Mann, 1940) and to that of *iso*-arsindoline (Lyon & Mann, 1945); hence the value of independent physical evidence for the structure of the bromide or the corresponding iodide. It was therefore decided to examine

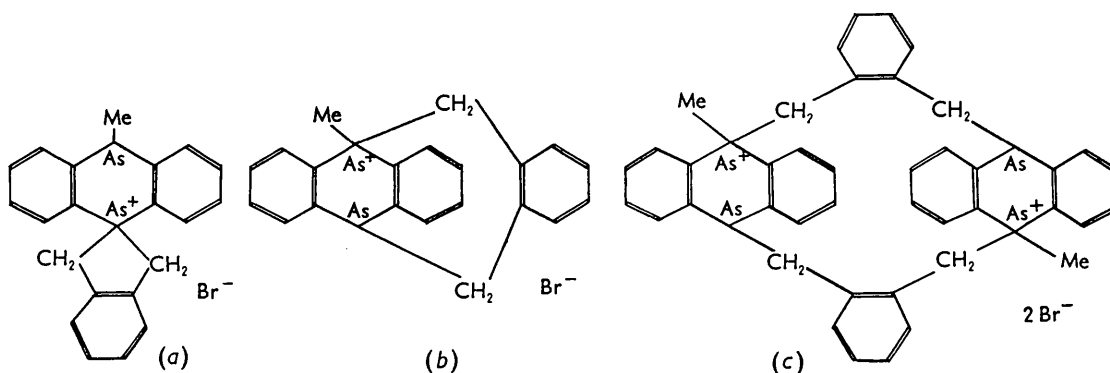


Fig. 1.