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Multiple Solutions of Crystal Structures by Direct Methods

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Some difficulties that may occur in crystal structure analysis by direct methods are described. The use of exclusively large E values produces an 'amplitude termination effect' in the E map. This leads to the occurrence of spurious peaks, which enhance any elements of translational symmetry present in the structural motif. There is also a danger that an analysis based on exclusively large E values will lead not to the correct structure but to a pseudo-homometric variant.

Introduction

Direct methods of crystal structure analysis make use of relationships among the observed structure amplitudes to assign or place limitations on the corresponding phase angles without any explicit assumptions concerning the atomic positions. However, at some stage or another an approximately correct set or subset of atomic positions has to be recognized in the Fourier syntheses (E maps) based on the derived phase angle or sign relationships in order for further progress to be made. Although the usefulness of direct methods has been amply demonstrated during the last few years, the difficulties that may arise at this recognition stage do not seem to have been adequately discussed. In most published accounts of successful applications the authors simply state that a chemically plausible structure was recognized in a particular synthesis and proceed to describe the further refinement of the structure.

Our own experience has indicated that while direct methods often lead in a fairly straightforward manner to the correct structure this is not always the case; in several analyses the recognition of the chemically plausible structure has been far from obvious. Sometimes so many plausible structures have been recognizable that alternative, non-direct methods have had to be invoked to settle the matter; sometimes structures have been 'recognized' and shown only later to be incorrect. These difficulties have tended to be encountered in the case of quite simple crystal structures, especially those containing structural elements with a high degree of internal regularity (benzene rings, *etc.*). They always arise because there are too many peaks in the E-Fourier synthesis, never because there are too few.

Amplitude termination effect

In any method of direct phase determination we must expect that reliable phase assignments will be possible only for the larger E values. Consequently, even if the phases assigned to the coefficients in an E-Fourier synthesis are all correct, the resulting distribution will be affected by omission of the smaller coefficients. In essence, all coefficients smaller than some limiting value are set equal to zero in the synthesis, and we may speak of an amplitude termination effect, which will operate in addition to the usual series termination effect that is implicit in E maps.

Although we are unable at present to offer a general analysis of the amplitude termination effect, it seems worthwhile to draw attention to some of its features. It will be particularly severe for structures containing several coincident or nearly coincident interatomic vectors in the asymmetric structural unit. Such structures may be described as possessing translational regularities, and their Patterson functions contain overlapping peaks. It has been shown (Hauptman & Karle, 1955, 1959; Cochran, 1958) that the simpler sign and phase determining relationships do not hold rigorously under these circumstances, but they are expected to hold approximately. We have calculated E maps for a number of centrosymmetric model structures containing translational regularities and are led to the following rule: the use of exclusively large E values (Fourier coefficients) produces an E map (Fourier synthesis) containing spurious peaks, which overemphasize any translational regularities that may be present in the actual structural motif.

Some insight into the origin of the spurious peaks may be gained by considering a very simple one-dimensional model, a set of atoms occupying most, but not all, of the finite set of points $x_i = m_i/p$ within a repeating structure of periodicity unity (m_i and p are integers, $m_i < p$; we could take $m_i = 0, 1, 2, 4, 5, 6, 8, 9$; $p = 10$). The structure factor F_H and the normalized structure factor $E_H = F_H \langle F_H^2 \rangle^{-1/2}$ of such a motif are large only for $H = np$ (n integer) *i.e.* only at the reciprocal-lattice points corresponding to a direct lattice with $a = p^{-1}$. A Fourier synthesis (or E map) calculated only with these values of F_H (or E_H) will then have maxima not only at the positions of the atoms contained in the model but also at the positions of the 'missing' atoms.

An actual one-dimensional example occurs in the structure of dimethyltriacetylene (Jeffrey & Rollett, 1952) where the carbon atoms lie on a threefold axis

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(00z) of a rhombohedral cell with $z = \pm 0{\cdot}1335$, $\pm 0{\cdot}2494$, $\pm 0{\cdot}3441$, $\pm 0{\cdot}4526$, *i.e.* approximately at $z = (2n+1)/20$ with $n = \pm 1$, ± 2, ± 3, ± 4. An E map calculated only with terms with $|E| > 2$ ($l = 0,10$) shows a spurious peak at $z = \pm 0{\cdot}05$ of height equal to that of the other atoms. Inclusion of terms with $|E| > 1{\cdot}5$ ($l = 0,9,10$) reduces the height of the spurious peak to about 90% of that of the lowest authentic peak.

Multiple solutions of phase problem

The enhancement, by the amplitude termination effect, of elements of translational regularity in a structural motif occurs even if the phases or signs associated with the large E coefficients are correct. There is a further difficulty in that as soon as an appreciable degree of translational regularity is present, it may be difficult, or even virtually impossible, to distinguish the correct structure from a number of 'pseudo-homometric' alternatives by direct methods alone.

Consider the two repetition patterns A and B shown in Fig. 1; B represents the superposition of A displaced by $+d/2$ and $-d/2$, each displacement having half weight. The peaks in B at 0, $\pm d$ therefore have single weight and those at $\pm 2d$ have half weight. The Fourier transform of A and B are very different but the distributions of $|E|$ for the two structures are very similar, especially in the regions of reciprocal space close to $H = nd^{-1}$, where $|E|$ is close to its maximum value. Allowing for some experimental error in the $|E|$ values, it is clear that any analysis based exclusively on the large $|E|$ values (say $|E| > 1$) can hardly distinguish between the two structures, which may be described as pseudo-homometric since their Patterson functions, although different, are virtually identical if computed exclusively with large values of E_H^2.

The essential distinction between the $E(H)$ functions corresponding to the structures A and B concerns the sign of the functions in regions close to $H = nd^{-1}$ with n odd; negative for A, positive for B. This sign cannot be determined from sign relationships involving exclusively large $|E|$ values. The sign ambiguity is analogous to that occurring for groups of reflexions with odd indices in centrosymmetric triclinic structures where one choice may lead to an essentially correct E map, the other to an E map representing a pseudo-homometric structure.

As the number of peaks in the repetition patterns A and B increases, the differences between $|E_A(H)|$ and $|E_B(H)|$ become smaller and smaller until, in the limit of infinite repetition, the $|E(H)|$ functions are identical. In this case the distinction between the two patterns depends only on the arbitrary choice of origin – at a peak in A, or midway between peaks in B.

In the course of the structure analysis of p-methyl benzylidene-p-nitroaniline (Bürgi & Dunitz, 1969; Bürgi, 1969), space group $P2_1/c$, direct methods led to an incorrect choice for one of the symbolic signs; in the resulting E map we were able to recognize two 'half-weight' molecules separated by one of the multiply occurring interatomic vectors. The correct solution proved to be the average of the two 'half-weight' molecules. A similar case has been reported by Duffin (1968), and it also seems likely that the difficulties described in the analysis of p,p'-bitolyl (Casalone, Mariani, Mugnoli & Simonetta, 1969) were of a similar nature.

Conclusion

Many organic molecules contain structural sub-units that are repeated by translational displacements *e.g.* long-chain paraffins, fatty acids, polyenes, aromatic systems containing planar hexagons, *etc.* If direct methods are used to solve the structures of crystals containing strong translational regularities, the amplitude termination effect may lead to difficulties in the interpretation of E maps based exclusively on large E values. For example, although the E map may show the orientation of a planar zigzag chain quite clearly, spurious peaks will tend to mask the terminations of the chain, which may, indeed, appear in the E map as being infinite in length. Even if the actual length of the chain is known from chemical information, its position in the unit cell may be difficult, or impossible, to deduce from the E map. In particular the E map may show a double image of the chain, the two images mutually displaced by some interatomic distance within the chain to produce a structure bearing a pseudo-homometric relation to the correct one.

There appear to be two ways out of these difficulties. One way is to extend the use of the sign or phase determining relationships to derive signs or phase angles associated with the smaller E values. This will get rid of the amplitude termination effect. However, once an incorrect sign or phase assignment has been made for some sub-set of the stronger reflexions, there is no guarantee that the mistake will reveal itself during the extension to smaller E values. The result may be an E map in which the molecule is in correct

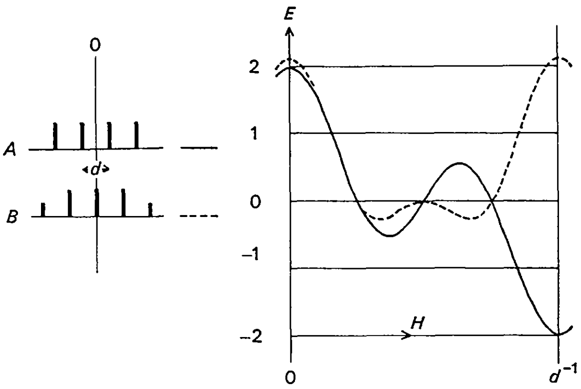

Fig. 1. Repetition patterns A and B. B represent the superposition of A displaced by $\pm d/2$, each displacement having half weight. The peaks in B at 0, $\pm d$ have single weight and those at $\pm 2d$ have half weight.

orientation but wrongly placed with respect to any symmetry elements that may be present in the unit cell. An incorrect structure of this kind may well refine reasonably satisfactorily into a false least-squares minimum; in general, however, it will correspond to unreasonable intermolecular distances. The second way is to try to establish the position of the molecule from the Patterson function calculated with the full set of reflexions. For regularly built structural motifs of known shape and in known orientation, this should not, in general, present severe difficulties.

The main danger is likely to occur from the use of fully automatized procedures for sign or phase determination, combined with automatic peak searches for trial models. These procedures may well lead not to the correct structure but to some pseudo-homometric variant, which may only be recognized as such after considerable expenditure of computer time, if at all.

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The Geometry of X-ray Multiple Diffraction in Crystals

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A derivation of the geometrical distribution of multiply diffracted X-ray beams in single crystals is presented. Included is a brief survey of the geometrical and analytical methods, with some new concepts and constructions, which are useful in the interpretation and prediction of X-ray multiple diffraction phenomena. Applications include the analysis of Kossel patterns, calculation of angles of diffraction, and precision determination of lattice parameters and wavelengths, for which appropriate formulae and procedures are given.

1. Introduction

The phenomena associated with the simultaneous diffraction of an X-ray beam by more than one Bragg plane in a crystal have long been known (Renninger, 1937; Berg, 1926). In most instances their presence constitutes an undesirable complication, as for example in the measurement of diffraction intensities from single crystals, and therefore many workers have attempted to avoid their occurrence (Coppens, 1968; Zocchi & Santoro, 1967). Several authors have found, however, that these effects have a variety of useful applications to the study of single crystals, and for this reason it is necessary to know the directions of singly- and multiply-diffracted X-ray beams in crystals. In the analysis of Kossel patterns (Kossel & Voges, 1935) the points of intersection between diffraction and deficiency conics locate the doubly-diffracted beams and their relationships are used to determine the lattice parameters of the crystal. Of particular value are those cases in which two or more doubly-diffracted beams are separated by a very small angle (Mackay, 1965). The great accuracy of absolute angular measurement possible with very small angles yields the most precise values of the lattice parameters. This principle has been used to measure the lattice parameter of diamond by Lonsdale (1947), and of silicon by Isherwood & Wallace (1966). The effect of arsenic incorporation on the germanium lattice has also been studied (Isherwood & Wallace, 1970). The theoretical basis of this method is the principal subject of the present paper.

Also of considerable interest are cases of systematic triple or multiple diffraction, the occurrence of which is independent of wavelength and is governed only by crystal symmetry. Thus if the symmetry is disturbed by a homogeneous distortion of the lattice, the resulting modifications to the geometry of the doubly-diffracted beams enable the distortion to be measured and analysed. This has been demonstrated by Isherwood (1968) in a study of the surface layers of yttrium iron garnet crystals. The theory of this method will be described in a separate paper.

2. The geometrical interpretation of multiple diffraction

In order to predict the occurrence of multiply-diffracted beams and to calculate their angular relationships to the crystal lattice, a review of the geometry of diffrac-