The coefficients, a_1, a_2, a_3, a_4, of (12) enable us then to calculate the four transition probabilities α_i.

(2) '*Growth and deformation or transformation stacking faults' in hexagonal close-packed and cubic face centred crystals*

(*a*) *Hexagonal close-packing.*—Broadened maxima occur for $A_3 = 0$ and $A_3 = \pi$ (mod. 2π), and

$$\left.\begin{aligned} \varepsilon_0 &= \frac{1}{2\pi}\cdot\frac{(1-\alpha)-3(1-2\alpha)\gamma}{3[\alpha+(1-2\alpha)\gamma]}\,, \\ \varepsilon_\pi &= \frac{1}{2\pi}\cdot\frac{3[(1-\alpha)-(1-2\alpha)\gamma]}{\alpha+3(1-2\alpha)\gamma}\,. \end{aligned}\right\} \tag{41}$$

Thus α and β can be calculated with the aid of (41).

(*b*) *Cubic close-packing.*—Minima occur for $A_3 = 0$ and $A_3 = \pi$ (mod. 2π); (41) is still valid and can eventually be used to calculate α and β. Broadened maxima occur for

$$A_3 = \pm\theta \text{ (mod. } 2\pi)\,, \tag{42}$$

where θ is the root of (37), which will move towards $A_3 = \pm 2\pi/3$ (mod. 2π) as $\alpha \rightarrow 1$ and $\beta \rightarrow 0$ or 1.

With the aid of (42) and $\varepsilon_{\pm\theta}$, α and β can again be calculated. When $\alpha = 1$ (face centred cubic without 'growth faults'), we obtain the same equation (18), but the further calculations are different (Paterson, 1952).

(3)

For an *hk*-crystal we obtain from (38):

$$\varepsilon_0 = \frac{1}{2\pi}\cdot\frac{\frac{1}{2}-3\gamma(1-3\gamma)}{3\gamma(2-3\gamma)}\,,\quad \varepsilon_{\pm\pi/2} = \frac{1}{2\pi}\cdot\frac{\frac{1}{2}-\gamma(2-3\gamma)}{\gamma(2-3\gamma)}\,,$$
$$\varepsilon_\pi = \frac{1}{2\pi}\cdot\frac{3[\frac{1}{2}-\gamma(1-\gamma)]}{\gamma(2-3\gamma)}\,. \tag{43}$$

(4)

For an *hkk*-crystal we obtain from (39):

$$\varepsilon_0 = \frac{1}{2\pi}\cdot\frac{\gamma(4-9\gamma)}{3(1-3\gamma+3\gamma^2)}\,,$$
$$\varepsilon_{\pm 2\pi/6} = \frac{1}{2\pi}\cdot\frac{2-14\gamma+51\gamma^2-54\gamma^3}{18\gamma(1-3\gamma+3\gamma^2)}\,,$$
$$\varepsilon_\pi = \frac{1}{2\pi}\cdot\frac{4-10\gamma+30\gamma^2-27\gamma^3}{9\gamma(1-3\gamma+3\gamma^2)}\,,$$
$$\varepsilon_{\pm 2\pi/3} = \frac{1}{2\pi}\cdot\frac{2-10\gamma+23\gamma^2+18\gamma^3}{6\gamma(1-3\gamma+3\gamma^2)}\,. \tag{44}$$

With one of the formulae (43) and one of the formulae (44) we can calculate β in either case.

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A Direct Approach to the Determination of Crystal Structures

By V. Vand*

Chemistry Department, The University, Glasgow W. 2, Scotland

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A direct method of solution of the X-ray crystallographic problem is described, which consists in tabulating the complete function connecting the structure factor with the atomic positions. The successive steps of the solution can be interpreted as intersections of $(N-1)$-dimensional surfaces in N-dimensional space, where N is the number of unknown co-ordinates. A card index, graphs and tables have been prepared and published for a one-dimensional unit cell with no centre of symmetry containing up to four equal point atoms and, with centre of symmetry, up to ten equal point atoms per cell. Centrosymmetric structures with up to twenty atoms per cell can be solved by a single convolution of the above tables.

Introduction

The determination of crystal structures and the corresponding phase problem of X-ray crystallography has been attacked in the past by a variety of methods. If the direct methods applicable to special cases, such as the heavy-atom and the isomorphous-replacement methods, are not considered, the usual methods are those of trial and error, Patterson synthesis and its variants, Harker–Kasper inequalities, solution of polynomials, and statistical methods.

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* Imperial Chemical Industries Research Fellow. Present address: Physics Department, Pennsylvania State University, State College, Pennsylvania, U.S.A.

In this contribution, a novel approach to the problem is sought. It consists in a fundamentally very simple idea of preparation of tables (Vand, 1953) which would contain calculated structure factors for all the possible structures. If one wishes to solve a structure, all that is necessary is to search the tables until a structure is found the structure factors of which (or their moduli) agree with the observed values. The process of solution then essentially consists of a sorting operation, which can be done by hand or by means of punched-card machines. Structures having given values of structure factors are selected and the unknown structure is contained within the selected solutions.

Although the method is quite general and straightforward, it has a severe limitation. If a function is tabulated, it is necessary to choose a finite tabulation interval. If there are n atoms per unit cell and if we let them roam independently through the full range of co-ordinate X_i from 0 to 1, subdivided by tabulation interval into m points, there will be m^n table entries. This, for reasonable values of m and n, can be a very large number. Great simplification ensues if we assume equal point atoms, to which case many organic structures can be reduced. Then we can interchange the atoms without altering the structure, and the number of entries is reduced to $(n+m)!/n!\,.\,m!$ or a similar expression, which is a much smaller number. However, even then the number of table entries is prohibitive for a three- or a two-dimensional unit cell, so that in practice the method in its present form is limited to: (1) a one-dimensional unit cell, with a comparatively coarse tabulation interval; (2) a limited number of equal point atoms per unit cell.

The practical problem is often further complicated by lack of exact knowledge of such data as the absolute scale of the intensities, the magnitude of the temperature factor, presence of not strictly equal atoms and of experimental errors. In this paper, we shall neglect these complications by assuming that the unitary 'reduced' structure factors, or their moduli, referring to 'point atoms', are known without error on an absolute scale. Only one-dimensional projections of a three-dimensional cell can be considered at the present stage.

Guided by the above considerations, tables for direct determination of one-dimensional crystal structures have been prepared for a one-dimensional unit cell with up to four equal atoms per cell and no centre of symmetry and up to ten equal atoms per cell and a centre of symmetry. The unit cell has been subdivided into $m = 16$ equal intervals. For a centrosymmetrical crystal with equal point atoms the number of entries is

$$\frac{\{\tfrac{1}{2}(n+m)\}!}{\{\tfrac{1}{2}n\}!\,\{\tfrac{1}{2}m\}!}\,;$$

this, for $n = 10$ and $m = 16$, amounts to 1287 entries, which can be easily managed by hand. Reduced structure factors, referring to point atoms, are calculated up to the eighth order.

The sorting operation is assisted by rearranging the tables on cards in order of the increasing first, second, etc., structure factor. There is, however, one complication which is common to tabular representation of any function with several variables, and which arises from the finite and constant tabulation interval of one set of variables and from the subsequent inversion of the tables. In order to elucidate the nature of the problem, it is useful to revert to the representation of the multivariable functions as vectors in multi-dimensional spaces.

The use of N-dimensional space

The N unknown co-ordinates of atoms, X_i, can be formally regarded as components of a single vector $\mathbf{X}$ in N-dimensional space and similarly the H calculated structure factors $F(h)$ can be regarded as components of a single vector $\mathbf{F}$ in H-dimensional space. The vector $\mathbf{F}$ is then a function of the vector $\mathbf{X}$ and vice versa. The two spaces differ in that the space containing vector $\mathbf{X}$ is periodic. As X_i are fractional co-ordinates, they can have any principal value $0 \leq X_i \leq 1$, so that the principal vectors $\mathbf{X}$ representing all the possible structures fill one N-dimensional cell of side 1, the principal cell. Suppose that one of the values of $|F(h)|$ is known. Then the equation connecting $|F(h)|$ with X_i imposes a constraint on the possible vectors $\mathbf{X}$, decreasing the degree of freedom by one. These vectors $\mathbf{X}$ are constrained to a $(N-1)$-dimensional surface S_h which defines the locus of all the possible structures having a given value of $|F(h)|$. If a set of values $|F(1)|$, $|F(2)|$, $\ldots$, $|F(H)|$ is given, then it is possible, in principle, to construct first the surface S_1 and then S_2 and to find their intersection. This will result generally in a $(N-2)$-dimensional space, representing all the possible structures having a given value of $|F(1)|$ and $|F(2)|$. The intersection of this space with S_3 will, in general, be a $(N-3)$-dimensional sub-space, etc., until the final intersection with S_H will have $(N-H)$ degrees of freedom and dimensions, provided the surfaces are non-parallel at the locus of intersection—a condition analogous to that of a non-vanishing determinant of a system of linear equations. If this condition is fulfilled and $H = N$, the solution, if it exists, will reduce to discrete points—the homometric structures of Patterson. If $H > N$ and the system is self-consistent, further surfaces S_h with $h > N$ must pass through the solution, if the solution exists.

For a centrosymmetrical structure, each surface S_h splits into two branches, corresponding to $F(h)$ and to $-F(h)$. If the sign is known, only the appropriate branch is used, but the argument is not affected by the lack of the knowledge of the sign of $F(h)$, the only consequence being that the number of possible solutions may be increased.

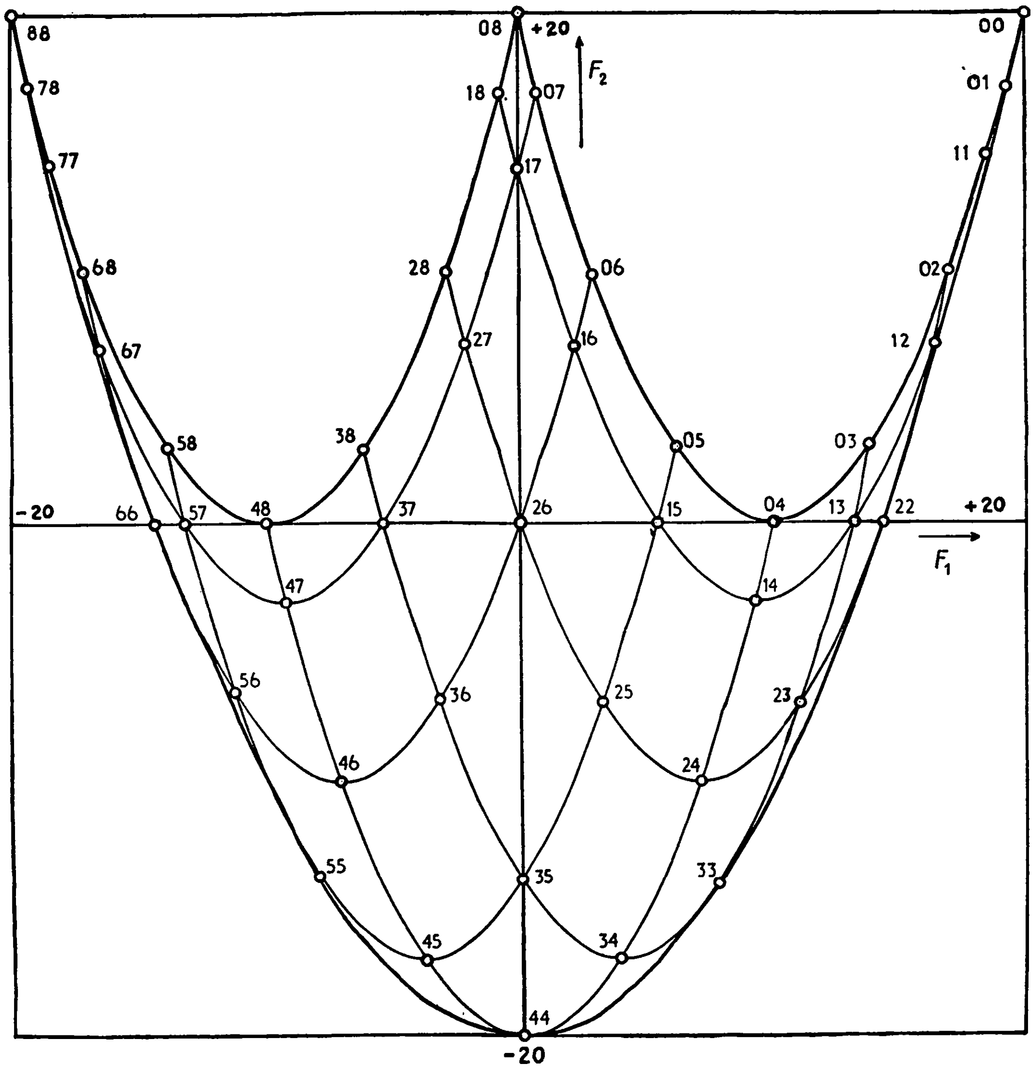

Fig. 1. Graph of $F(1)$ versus $F(2)$ for $n = 4$ (centrosymmetrical cell). Co-ordinates of atoms in 16ths of unit cell shown at each grid point. Scale: $F(0) = 20$.

The table entries represent the principal N-dimensional cell sampled at all the points of a grid in $m$ths of its cell edges. To each grid point, H values of $F(h)$ are given in the tables. The $(N-1)$-dimensional surface S_1 can thus be immediately obtained by a simple selection of all the table entries with a given value of $F(1)$. Intersections of S_1 with further surfaces S_2, S_3, ... are then obtained by further selections (or sortings, if the tables are transferred on cards). The sortings are carried out as far as desired; the extracted entries then represent the final intersection, which necessarily contains the true solution.

However, difficulty arises because the functions $F(h)$ are sampled over a finite grid and the required surfaces S_h are infinitely thin and would normally pass between the grid points. In order to ensure that there is no loss of solutions arising from the coarseness of the grid, it is necessary to take, instead of a surface S, a slab of such thickness as to enclose sufficient grid points defining the location of S.

This problem can be regarded from another point of view: The N-dimensional principal cell is subdivided by the grid used into m^N smaller cells, the grid cells, each of edges $1/m$. The true solution necessarily falls within one such grid cell, but it can be located in the tables only by means of one of the available grid points. Its distance from the nearest grid point is less than $1/2m$ in space of the vector **X**, but an unknown distance in space of vector **F**. If the slab thickness is taken so as to include all the points less than $1/2m$ distant from **S** in **X**, it will be certain that the final selection of points will contain the nearest grid point to the true solution. However, practical use of the method reveals that such a slab thickness is not economical. It is better to replace the above condition by another that the slab should contain at least one corner of the grid cell containing the true solution. This relaxation in **X** decreases considerably the slab thickness in **F** and the final volume of the intersection of slabs which contains the solution, and also it makes the slab thickness nearly independent of the number of atoms per cell.

This condition amounts to the relaxation of the localization of the solution by a factor 2 in each direction of the N-dimensional space. There are now 2^N corners to choose from, and as the sign of the error in each cosine contribution can be arbitrary, the slab thickness decreases considerably. It is a function of h which has not yet been calculated theoretically. Tables of the slab thickness were prepared from a solution of a number of random examples. Using these slab thicknesses, numerous one-dimensional examples taken with non-integral co-ordinates drawn at random were rapidly solved by this method. For 10 atoms per cell, the solution takes by hand only about a quarter of an hour. One might at first expect that as the selection is done regardless of sign of the structure factors, a large number of solutions corresponding to all the possible combinations of the signs will result. This is, however, not the case. Usually only two or three combinations of signs remain, as the tables impose the conditions of point atoms and non-negativity of electron density.

Graphical representations

The relations between any set of structure factors can be represented graphically by plotting the results from the tables on a suitable graph. These graphs can then be used for visualization of various relations, such as inequalities, etc., and statistical relations. The most useful graph is with $F(1)$ as abscissa and $F(2)$ as ordinate. As an example, one such graph for $n = 4$ is shown in Fig. 1. This graph shows that the possible solutions lie within a parabola which corresponds to the Harker–Kasper inequality. In addition, there are on the top of the graph further smaller parabolae, $n/2$ in number, which represent forbidden regions arising from the condition of point atoms. Such graphs can be produced for larger values of n by a process of convolution of the smaller graphs. Such graphs are also useful for obtaining the first two selections by describing an area round a given point $F(1)$, $F(2)$, of a radius corresponding to the relevant slab thicknesses. The grid points within that area are noted down and subjected to further selections as before.

Conclusions

It is still premature to consider the practical usefulness of the method described above for practical solution of real crystal structures. It is true that a three- or two-dimensional structure can be reduced to a number of one-dimensional projections along the cell edges and along the various diagonals. Although one can claim that the one-dimensional problem is now practically solved for structures of a moderate complexity, this method may represent a valuable aid for the solution of real structures rather than the answer to the problem.

However, the main value of the present work may lie in giving us a deeper insight into the crystallographic problem and in providing comprehensive material for testing other proposed methods for the determination of crystal structures. It has already proved valuable in testing the statistical random-walk problem, recently used by Hauptman & Karle, and it has led to a general method for constructing probability relations between the structure factors. It also brought valuable results in an investigation concerning Patterson's homometric pairs. These results will be reported in due course.

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* *Editorial note*.—See also the review of these *Tables* in this issue. The *Tables* are available either from Prof. J. Monteath Robertson, Chemistry Department, The University, Glasgow W. 2, Scotland or from the author, Physics Department, Pennsylvania State University, State College, Pa., U.S.A.