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An Optical Method for Producing Structure-Factor Graphs

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Structure-factor graphs (Bragg & Lipson, 1936) may be very informative at certain stages of a structure determination but the labour involved in their preparation is sometimes considered to be too great for profitable use. A simple extension of optical transform theory shows that they can be prepared easily and with sufficient accuracy for most purposes by the methods available for preparing optical transforms. Some examples are given, together with calculated graphs for comparison.

Introduction

In the course of a study of the projection on the basal plane of a hexagonal inorganic crystal optical-transform methods were tried but were found to be of limited use. The projection under consideration has the probable two-dimensional space group $p6m$ and hence general positions of twelve-fold multiplicity. It is therefore difficult to consider first the transform of a single asymmetric unit and later the combined transform of all the related asymmetric units as suggested by Hanson, Lipson & Taylor (1953). The transform is, in fact, more obviously affected by the patterns produced by the symmetrical repetition of each atom than by the arrangement of the atoms within the asymmetric unit. This suggests that it may be better to consider the problem atom by atom rather than in terms of the whole asymmetric unit. Since the number of independent observable reflexions is small (nine for this structure) it seemed likely that structure-factor graphs (Bragg & Lipson, 1936) would provide a useful method of approach and attention was turned to the possibility of reducing labour by preparing them optically. The technique proves to be quite simple for this two-dimensional space group and

is applicable to all the other 16 groups, although for some it is a little more troublesome.

Use of structure-factor graphs

Structure-factor graphs are contoured maps showing the combined contribution of an atom and its symmetry-related counterparts to a particular reflexion as a function of the position of the atom in the unit cell. They are probably most useful in semi-quantitative work in the earlier stages of structure determinations and can give rapid indications of the general plausibility of an atomic arrangement in terms of the agreement with selected reflexions. At a later stage the direction of probable atomic movements may be deduced and a useful feature is the possibility of assessing the 'sensitivity' of various atomic positions; where the slope of the structure-factor graph is steep, small movements make significant changes in the total structure amplitude but atoms lying on plateau-like regions may be moved a considerable distance without affecting that particular reflexion. Since structure-factor graphs are rarely used when accurate quantitative measurements are needed it seems probable that

optically-produced representations will give all the information normally required.

Extension of optical-transform theory

If a mask containing holes punched at positions representing atomic sites in a single unit cell is placed in the parallel beam of an optical diffractometer the intensity at a point in the observed diffraction pattern is proportional to the square of the Fourier transform of the unit cell contents. Thus, if the pattern is sampled at reciprocal-lattice points, the amplitude at these points is proportional to the structure amplitude which would be associated with the reciprocal-lattice points in the X-ray diffraction pattern for the structure (e.g. Hanson, Lipson & Taylor, 1953).

The optical transform may thus be regarded as a graph of the structure factor as a function of the indices h and k treated not as integral numbers but as continuous variables

$$F(h, k) = \sum_n f_n \exp 2\pi i(hx_n + ky_n).$$

x_n and y_n in this equation have specific values and f_n is the scattering factor for the n th atom.

Remembering that x and y are coordinates in real space and h and k in reciprocal space, and that the Fourier-transform relationship is entirely reciprocal, we could interchange the variables and write

$$F(x, y) = \sum_n f \exp 2\pi i(xh_n + yk_n).$$

F is now a function of x and y as continuous variables for given values of h_n and k_n ; in other words, it is the structure-factor graph. Since only one atom is now under consideration, the value of f is constant.

Thus, if holes are punched to represent the reciprocal-lattice points $h_n k_n$, the resulting optical transform will be, in effect, the structure-factor graph for the corresponding reflexion.

The principle becomes clearer if we consider a simple example. Let us consider the two-dimensional space group $pm\bar{m}$.

The coordinates of the equivalent positions are

$$x, y; \bar{x}, y; \bar{x}, \bar{y}; x, \bar{y}.$$

The complete structure-factor expression for a single atom and its space-group related counterparts is:

$$F(h, k) = f \exp 2\pi i(hx + ky) + f \exp 2\pi i(h\bar{x} + ky) \\ + f \exp 2\pi i(h\bar{x} + k\bar{y}) + f \exp 2\pi i(hx + k\bar{y})$$

which may be re-written

$$F(x, y) = f \exp 2\pi i(xh + yk) + f \exp 2\pi i(x\bar{h} + yk) \\ + f \exp 2\pi i(x\bar{h} + y\bar{k}) + f \exp 2\pi i(xh + y\bar{k}).$$

If a mask is punched with holes at points corresponding to reciprocal-lattice points $h, k; \bar{h}, k; \bar{h}, \bar{k}; h, \bar{k}$ (for a specific h, k) its diffraction pattern will

then be the structure-factor graph for the reflexion having those indices.

As a second example, for the two-dimensional space group which prompted this work— $p6m$ —the equivalent positions are $\pm(x, y; \bar{y}, x-y; y-x, \bar{x}; y, x; \bar{x}, y-x; x-y, \bar{y})$ and the full structure-factor expression for a single atom is

$$F(h, k) = f \exp 2\pi i(hx + ky) + f \exp 2\pi i[h\bar{y} + k(x-y)] \\ + f \exp 2\pi i[h(y-x) + k\bar{x}] \\ + f \exp 2\pi i(hy + kx) + f \exp 2\pi i[h\bar{x} + k(y-x)] \\ + f \exp 2\pi i[h(x-y) + k\bar{y}] \\ + f \exp 2\pi i(h\bar{x} + k\bar{y}) + f \exp 2\pi i[hy + k(y-x)] \\ + f \exp 2\pi i[h(x-y) + kx] \\ + f \exp 2\pi i(h\bar{y} + k\bar{x}) + f \exp 2\pi i[hx + k(x-y)] \\ + f \exp 2\pi i[h(y-x) + ky].$$

This can be re-written

$$F(x, y) = f \exp 2\pi i(xh + yk) + f \exp 2\pi i[xk + y(\bar{h} + \bar{k})] \\ + f \exp 2\pi i[x(\bar{h} + \bar{k}) + yh] \\ + f \exp 2\pi i(xk + yh) + f \exp 2\pi i[x(\bar{h} + \bar{k}) + yk] \\ + f \exp 2\pi i[xh + y(\bar{h} + \bar{k})] \\ + f \exp 2\pi i(x\bar{h} + y\bar{k}) + f \exp 2\pi i[x\bar{k} + y(h + k)] \\ + f \exp 2\pi i[x(h + k) + y\bar{h}] \\ + f \exp 2\pi i(x\bar{k} + y\bar{h}) + f \exp 2\pi i[x(h + k) + y\bar{k}] \\ + f \exp 2\pi i[x\bar{h} + y(h + k)],$$

and the holes in the mask have to be punched at $\pm[h, k; k, (\bar{h} + \bar{k}); (\bar{h} + \bar{k}), h; k, h; (\bar{h} + \bar{k}), k; h, (\bar{h} + \bar{k})$.

Complications for certain two-dimensional space groups

The treatment becomes less straightforward when the space group is non-centrosymmetrical and also when translations of half a unit cell are involved. The group pg may be used to illustrate both points.

The equivalent positions are $x, y; \bar{x}, \frac{1}{2} + y$. Thus the combined expression for one atom is

$$F(h, k) = f \exp 2\pi i(hx + ky) + f \exp 2\pi i(h\bar{x} + ky + \frac{1}{2}k)$$

which may be re-written as before.

(1) if k is even

$$F(x, y) = f \exp 2\pi i(xh + yk) + f \exp 2\pi i(x\bar{h} + yk)$$

and

(2) if k is odd

$$F(x, y) = f \exp 2\pi i(xh + yk) + f \exp [2\pi i(x\bar{h} + yk) + i\pi].$$

The graph for a reflexion for which k is even may then be produced by punching holes at h, k and \bar{h}, k . This gives the complex amplitude of the transform. If the real and imaginary parts are required separately they may be obtained by adding or subtracting the centrosymmetrically-related set of holes to the mask. 'Subtraction' in optical terms means a change of

phase of π and this may be accomplished by using mica sheets and polarized light in the manner described by Hanson, Lipson & Taylor (1953).

The graph for a reflexion with k odd requires a phase change of π for the hole representing \bar{h}, k and again this can be achieved by using mica and polarized light. The complete set would thus be

k even – complex	$h, k; \bar{h}, k:$
k even – real part	$h, k; \bar{h}, k; \bar{h}, \bar{k}; h, \bar{k}:$
k even – imaginary	$h, k; \bar{h}, k; \bar{h}, \bar{k}_\pi; h, \bar{k}_\pi:$
k odd – complex	$h, k; \bar{h}, k_\pi:$
k odd – real part	$h, k; \bar{h}, \bar{k}; \bar{h}, k_\pi; h, \bar{k}_\pi:$
k odd – imaginary	$h, k; \bar{h}, k_\pi; \bar{h}, \bar{k}_\pi; h, \bar{k}:$

(the subscript π indicates holes for which a phase change of π relative to the others is required).

Practical details and a comparison with calculated structure-factor graphs

The examples illustrating this paper were prepared using an optical diffractometer and pantograph punch of the size described by Hughes & Taylor (1953). It was found most convenient for 1 mm. diameter holes to be used and the original drawing of the reciprocal net to be on a scale of 10 cm. = 1 reciprocal Ångström unit. The pantograph punch reduces this by a factor of 12 so that the scale on the mask is 8.33 mm. = 1 reciprocal Ångström unit. A straight row of holes with a spacing equivalent to $\frac{1}{2}$ reciprocal Ångström unit is punched at one side of the mask. Photographs of the diffraction pattern of the holes at the selected reciprocal lattice points alone and in combination with the straight row are then taken. The straight row acts as a diffraction grating giving streaks perpendicular to the row which may be used to check the orientation of the final structure-factor graph. The streaks will be spaced a distance equivalent to 2 Å apart and may be used also to set the scale in enlarging the photograph. A final scale of 2 cm. = 1 Å has been found convenient (i.e. streaks set to be 4 cm. apart).

When it is necessary to change the phase of the light passing through some of the holes *all* the holes are covered with pieces of mica cut from the same optically uniform sheet about 1–1½ thousandths of an inch thick. The mica covering the holes for which a phase change of π is required is rotated through 90° in its own plane with respect to that covering holes requiring zero phase. A polarizer is mounted above the pinhole in the diffractometer and a crossed analyser placed between the lower mirror and the camera; the mask is inserted so that both sets of mica sheets have their principal vibration directions at 45° to the plane of polarization (see Hanson & Lipson (1952) for fuller details and theory).

Signs of the regions may be deduced either by in-

spection—noting that each time a zero line is crossed the sign changes—or, if this leads to ambiguities, by the method of Pinnock & Taylor (1955). In Fig. 1(a) is shown the structure-factor graph for the reflexion $h = 1, k = 2$ of the two-dimensional space group $p6m$ and in Fig. 1(b) is the corresponding graph as given by Bragg & Lipson. The same graph could be regarded as the real part of the structure-factor graph for $p3m1$; the imaginary part is shown in Fig. 2(a) with the calculated version in Fig. 2(b). The complex form, which was not calculated by Bragg & Lipson, is shown in Fig. 3(a). Fig. 3(b) shows the zero contours of the real and imaginary parts superimposed; at the intersections the complex function has zero amplitude. In Fig. 4(a) and (b) are shown the optical and calculated graphs for $p4m$ and in Fig. 5(a) and (b) the graphs for $p4g$ with $(h+k)$ odd. In both instances the reflexion chosen is $h = 2, k = 3$.

Conclusions

The optical technique described provides a method of producing structure-factor graphs which gives certain advantages over the use of calculated graphs. The production is rapid and simple for all two-dimensional space groups except for the four involving glide planes [$pg, pmg, pgg, p4g$]. For these the use of the mica technique for phase changing brings added complications.

For non-centrosymmetrical groups the graph for the complex function is easily produced and gives useful information about sensitivity of atoms to movement. In order to make use of the graph to predict the result of changes in position it is necessary to know the phases and hence the real and imaginary parts are needed separately. Again the real part is simple but the mica technique must be used for the imaginary part. Useful indications, however, can often be obtained by the combined use of the complex graph and the real-part graph; with a little experience the general form of the imaginary part can be inferred.

By suitable choice of scale the graphs are produced for the true unit-cell shape; it is not necessary to use graphs distorted to a square unit cell. Production is so rapid that separate graphs can be prepared for multiple indices [e.g. 200, 400, 600, etc.], thereby minimizing the risk of errors which could very easily be made when using the same graph for a number of different indices, as is normally done with calculated graphs.

It is not claimed that the optically produced graphs are as accurate as those prepared by calculations; it is felt, however, that they may form a useful addition to the list of techniques available to those who have optical diffraction equipment.

We wish to thank Prof. H. Lipson for his interest and for helpful discussion.

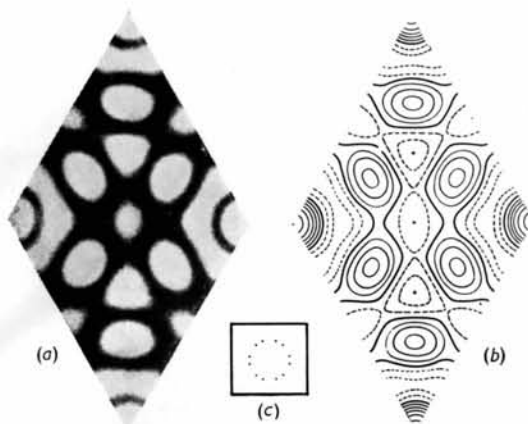


Fig. 1. (a) Optically derived structure-factor graph for the two-dimensional space group $p6m$ with $h = 1$, $k = 2$. This graph may also be regarded as the real part for the two-dimensional space group $p3m1$ with $h = 1$, $k = 2$. (b) Calculated graph (after Bragg & Lipson, 1936) corresponding to the optical graph of 1(a). (c) Contact print from mask used for 1(a).

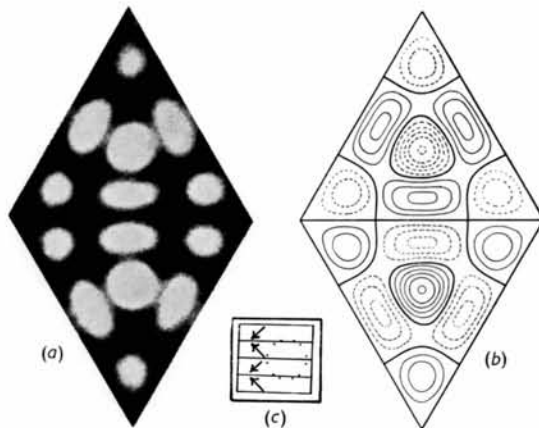


Fig. 2. (a) Optically derived structure-factor graph for the imaginary part for two-dimensional space group $p3m1$ with $h = 1$, $k = 2$. (b) Calculated graph (after Bragg & Lipson, 1936) corresponding to the optical graph of 2(a). (c) Contact print from mask used for 2(a); mica strips used for phase changing are indicated in outline with their corresponding vibration directions shown by arrows.

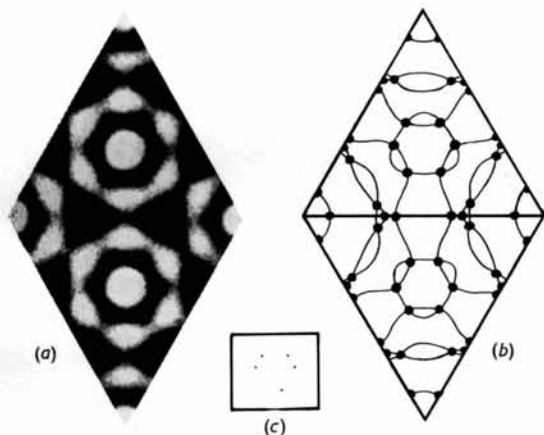


Fig. 3. (a) Optically derived complex structure-factor graph for the two-dimensional space group $p3m1$ with $h = 1$, $k = 2$. (b) Zero contours from Fig. 1(b) and Fig. 2(b) superimposed; the points of intersection, which are marked, represent zero points of the complex graph. (c) Contact print from mask used for 3(a).

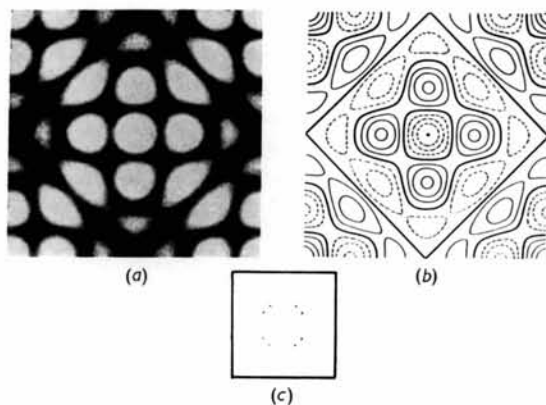


Fig. 4. (a) Optically derived structure-factor graph for the two-dimensional space group $p4m$ with $h = 2$, $k = 3$. (b) Calculated graph (after Bragg & Lipson, 1936) corresponding to the optical graph of 4(a). (c) Contact print from mask used for 4(a).

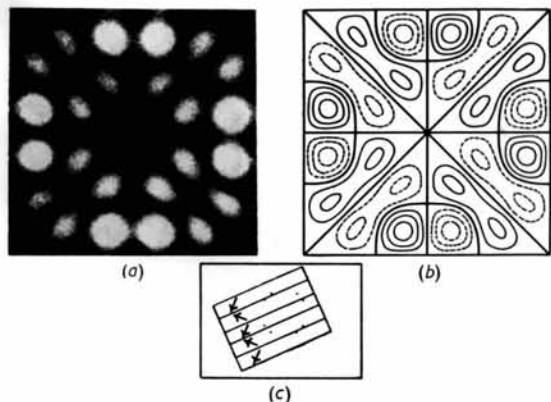


Fig. 5. (a) Optically derived structure-factor graph for the two-dimensional space group $p4g$ with $(h+k)$ odd; $h = 2$, $k = 3$. (b) Calculated graph (after Bragg & Lipson, 1936) corresponding to the optical graph of 5(a). (c) Contact print from mask used for 5(a); mica strips used for phase changing are indicated in outline with their corresponding vibration directions shown by arrows.

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Determination of the Positions of Molecules in a Unit Cell

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Taylor's method for determining the relative positions of molecules in projections with plane group *pgg* has been extended so that the choice of useful reflexions is less restricted and the final result is more precise.

Introduction

In investigating crystal structures by X-ray diffraction methods it is often possible to determine the shape and orientation of molecules by Fourier-transform methods or by interpreting the intramolecular vectors in Patterson projections. With this information available, the relative positions of the molecules in a projection with plane group *p2* may be derived by a method described by Taylor (1954), which involves setting up equations for a particular reflexion *hk* which limit the choice of the true origin to points which lie on a family of straight lines of slope $-h/k$. If the equations are set up for a second plane, a second family of straight lines is produced and the origin must lie at an intersection of the two sets of lines. By adding lines for further reflexions all but one of the intersections may be eliminated.

In theory all the reflexions can be used in applying the method, but practical considerations indicate that great care is necessary in selecting the reflexions to be used, and some general rules are given, the most important for the present discussion being:

(1) Since the scale factor is generally not accurately known in the initial stages of the analysis, it is important to use reflexions which are unobserved or have small observed values, and which lie on high parts of the transform of a single molecule.

Taylor then extends the method, with slight modifications, to plane group *pgg* with four molecules in the unit cell. An important additional condition is introduced:

(2) Reflexions must be chosen for which the contribution of one molecule of the pair of molecules related by a centre of symmetry at (0, 0) is large,

and the contribution of one molecule of the pair at $(\frac{1}{2}, \frac{1}{2})$ is zero.

This extra condition restricts the choice of useful reflexions so much that 'in order to obtain enough usable reflexions it is necessary to relax the condition and make allowance for the margin of error introduced'. The loci of possible positions for the origin are then no longer families of lines but families of bands of width depending on the deviation from zero of the contribution of the second molecule.

Recently Taylor & Morley (1959) have shown that in certain cases condition (2) cannot be satisfied, and they describe a modified method which overcomes this difficulty. While investigating the crystal structure of nitromesitylene (Trotter, 1959) we found it advantageous to apply a similar type of modification, and the method is presented here since it shows clearly how these modified methods are related to Taylor's original procedure.

Theory for plane group *pgg*

If (x_j, y_j) are the coordinates of the atoms in a molecule with respect to some fixed point within the molecule (the centre of an aromatic ring for example) and (X, Y) are the coordinates of this molecular centre with respect to the crystallographic origin, then the structure factor expressions for plane group *pgg* are

$$F = 4\sum \cos 2\pi h(x_j + X) \cdot \cos 2\pi k(y_j + Y) \\ \text{when } h+k = 2n$$

$$F = -4\sum \sin 2\pi h(x_j + X) \cdot \sin 2\pi k(y_j + Y) \\ \text{when } h+k = 2n+1$$

The expression for $(h+k)$ even can be readily expanded to

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