

Optical Methods in X-ray Analysis.

II. Fourier Transforms and Crystal-Structure Determination

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The optical apparatus described in Part I of this series can be used to determine experimentally the Fourier transforms of two-dimensional projections of atomic arrangements. Methods of using these transforms to determine crystal structures are surveyed, and examples of their application to certain known structures are described; since no calculation is involved, trial-and-error methods can be carried through very rapidly, and under certain circumstances direct crystal-structure determination is possible. Ways of extending this process of direct crystal-structure determination are discussed.

1. Basic principles

The application of Fourier transforms to the determination of crystal structures has been advocated by several authors (Knott, 1940; Wrinch, 1946; Klug, 1950*a*), and Klug (1950*b*) has determined the structure of triphenylene in this way. The theoretical advantages of the method are great, but they are offset by certain practical disadvantages, the most important of which is the large amount of calculation involved; the calculation of a section of a Fourier transform, for example, is much more laborious than the calculation of a zone of structure factors, since, in effect, the Fourier transform is the structure-factor function for non-integral as well as integral values of indices. In other words, the Fourier transform must be evaluated throughout reciprocal space and not only at the reciprocal-lattice points.

Some method of eliminating these computational difficulties is therefore desirable, and, acting on the suggestion of Bragg (1944), we have attempted to use the optical apparatus described in Part I of this series (Taylor, Hinde & Lipson, 1951). Optical methods also provide an elegant way of explaining the basis of the Fourier-transform method, since this is essentially an application of the physical principles underlying the process of diffraction in general.

The apparatus gives the Fraunhofer diffraction pattern of any chosen object. If the object is periodic, the diffraction pattern consists of a set of discrete beams (grating spectra); but if it is non-periodic—for example, an irregular array of holes—the diffraction pattern (Fig. 2(*a*)) is continuous, although it may have zero intensity at certain points. If another similar array of holes, in parallel orientation, is placed adjacent to the first, the diffraction pattern is similar, as shown in Fig. 2(*b*), except that sinusoidal fringes are superimposed (Jenkins & White, 1937). If a further pair of arrays is added, crossed fringes are superimposed (Fig. 2(*c*)), and as the number of arrays is increased the fringes become sharper until ultimately the diffracted light is appreciable only at particular points (Fig. 2(*d*)).

These points are the reciprocal-lattice points. From Fig. 2 it can be seen that the intensity associated with any particular point is related to the intensity at that point of the diffraction pattern of the single unit; where this diffraction pattern is strong, the intensity of the neighbouring reciprocal-lattice points is also strong, and vice versa. This can be clearly seen in Fig. 2(*d*), where the spacings of the grating are large compared with the dimensions of the unit; under these conditions several reciprocal-lattice points occupy each peak in the diffraction pattern; but when the spacings of the gratings are about the same size as the dimensions of the unit (Fig. 2(*e*))—as in most crystals—the correlation is not so clear because the reciprocal-lattice points tend to lie on separate peaks.

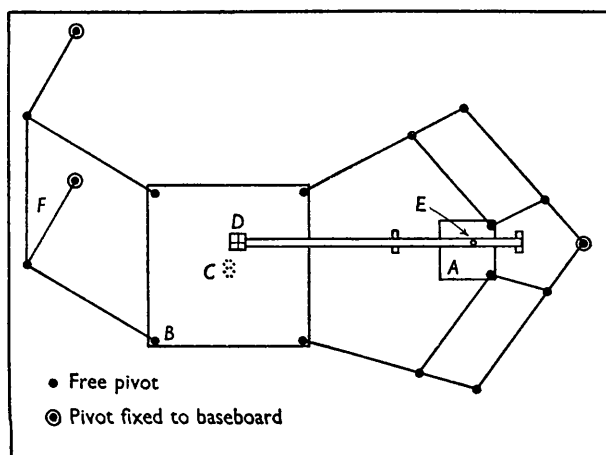


Fig. 1. Pantograph used for punching masks.

The problem of finding the orientation of a given unit, such as a chemical molecule, in a unit cell is essentially the problem of fitting the reciprocal lattice upon the diffraction pattern of the unit in such a way that the reciprocal-lattice points corresponding to strong X-ray reflexions fall upon peaks in the diffraction pattern and

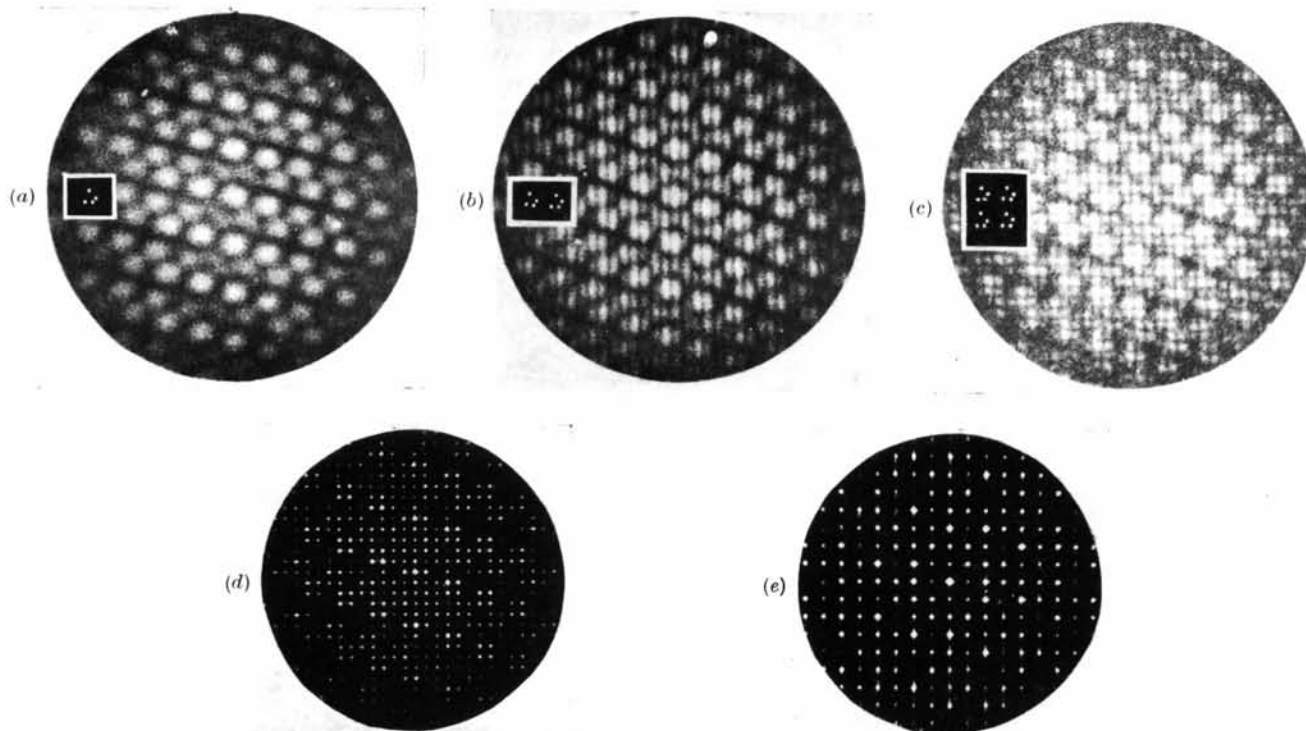


Fig. 2. (a) Diffraction pattern of array of four holes shown in inset. (b) Diffraction pattern of two arrays of holes arranged as shown in inset. (c) Diffraction pattern of four arrays of holes arranged as shown in inset to Fig. 1 (c). (d) Diffraction pattern of large number of arrays arranged relatively as shown in inset to Fig. 1 (c). (e) Diffraction pattern of large number of arrays arranged more closely than those producing Fig. 1 (d).

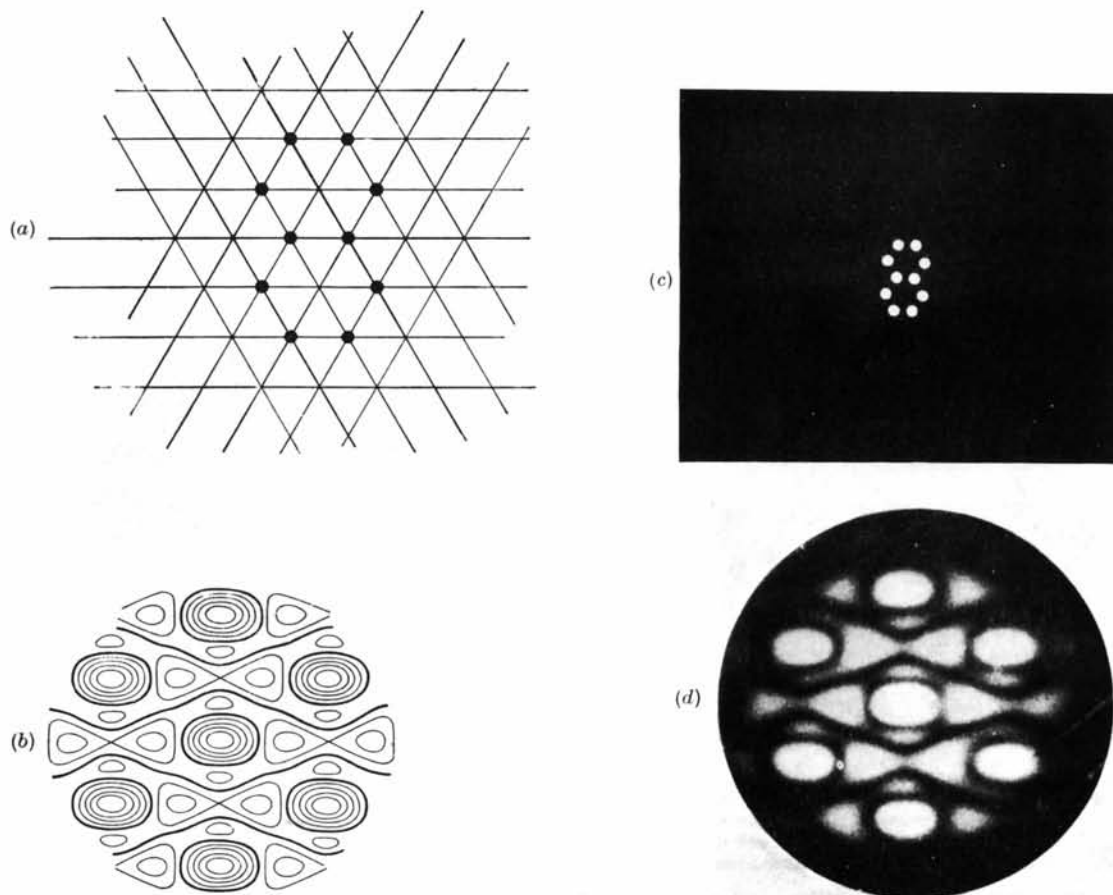


Fig. 3. (a) Diagram showing hexagonal lattice points occupied by atoms of idealized naphthalene molecule. (b) Fourier transform of idealized naphthalene molecule (after Knott). (c) Mask representing idealized naphthalene molecule. (d) Diffraction pattern of mask shown in Fig. 3 (c).

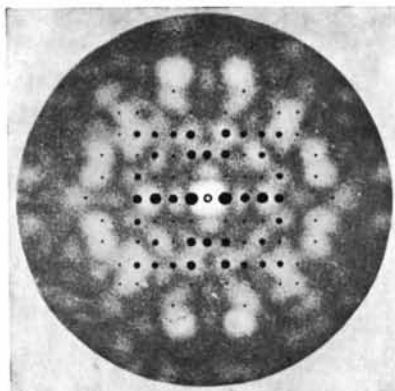
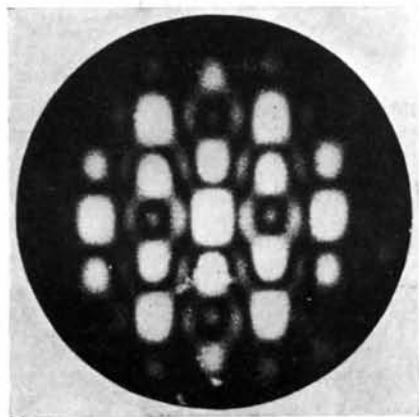
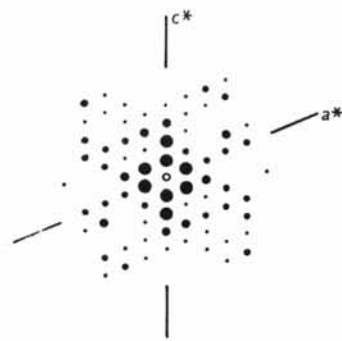


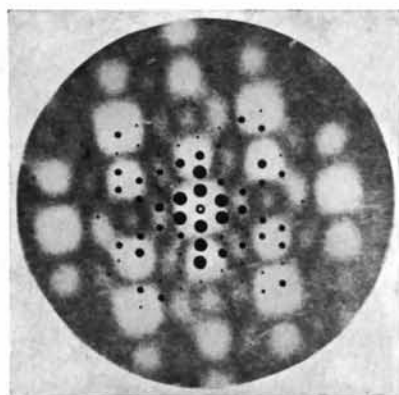
Fig. 4. $0kl$ section of weighted reciprocal lattice of naphthalene, superimposed on the diffraction pattern of the mask representing the projection of the unit-cell contents on the (100) plane.



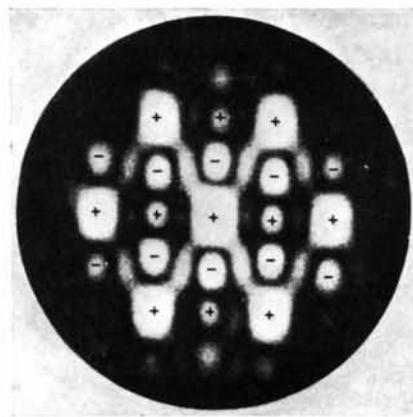
(a)



(b)



(c)



(d)

Fig. 5. (a) Diffraction pattern of mask representing idealized molecule of durene. (b) $h0l$ section of weighted reciprocal lattice of durene. (c) Diffraction pattern of mask representing correctly oriented molecule, with Fig. 5 (b) superimposed. (d) Diffraction pattern of mask similar to Fig. 5 (a), but with extra hole at centre of symmetry. Positive and negative regions are denoted.

those corresponding to weak X-ray reflexions fall near the regions of zero intensity. Ideally, this operation should be carried out in three dimensions, but for obvious reasons this is impracticable; the aim of the present work, therefore, has been to find how far two-dimensional methods are of use.

2. Experimental details

The basic optical equipment has already been described in Part I; we shall, in subsequent work, refer to it as the 'diffraction spectrometer'. Following Bragg (1939), we have in the past called it the 'X-ray microscope', its first use being to combine the X-ray diffraction data to form an image of a crystal; but the advent of the true X-ray microscope, such as that reported in the *General Electric Review* (1950), now renders this name rather deceptive, and the name 'diffraction spectrometer' emphasizes its more general function—the observation of Fraunhofer diffraction patterns.

The diffracting masks consist of thin black cardboard punched with holes to represent atoms. The holes are made with a punch attached to a specially made pantograph (Fig. 1), on which the cardboard *A* is fixed so that it follows the movement of a frame *B* with a reduction of 3:1. The frame *B* carries a scale drawing *C* representing the projected atomic positions, drawn to a scale of $\frac{1}{2}$ cm. to 1 Å.; each atomic position in turn is set at the centre of the cross-wires *D*, and the punch *E* is then operated; the result is a representation of the projection of the structure as holes of 1 mm. diameter on a scale of $\frac{1}{6}$ cm. to 1 Å. With these relative dimensions it is found that the central maximum of the diffraction pattern of a hole covers about the same range in reciprocal space as the scattering factor of the carbon atom. A typical mask is shown in Fig. 3(c).

It will be noted that the pantograph has a device *F* which keeps the frame *B* always parallel to itself. This is not strictly necessary, but this extra constraint helps to overcome some of the errors introduced by the slight flexibility of the arms.

Each cardboard mask has four holes punched near the corners by means of a special jig; these are used to locate the masks both on the frame *B* and on the spectrometer, so that the orientation of the diffraction pattern with respect to the original drawing can be easily determined.

To compare the diffraction pattern of a proposed structure with the observed weighted reciprocal lattice, two ways are available. First, the observing microscope (Fig. 1, Part I) has been fitted with a partly silvered mirror so that both the diffraction pattern and the reciprocal lattice are simultaneously visible. Since the diffraction pattern is not very intense, however, this method is not satisfactory if fine detail is to be seen, and so it is used only in the rough preliminary stage of an investigation, where speed in accepting or rejecting proposed structures is particularly desired; accepted structures can then be more closely examined by the

second method. For this, the diffraction pattern is recorded on 35 mm. ciné film, as described in Part I, and the image, which is only about 1–2 mm. in size, is projected, by means of a micro-projector, on to a drawing of the reciprocal lattice. The magnification has been so adjusted that reciprocal-lattice drawings on the same scale—5 cm. to 1 Å.⁻¹—can be used for the direct-vision microscope also.

It is difficult to reproduce photographically the complete range of intensity in a diffraction pattern, and so the relative intensities of the various peaks are not clearly brought out. This difficulty can be overcome by taking several photographs, either with different exposures and development conditions, or on films of different contrast. For the illustrations in this paper, the negatives were overexposed and underdeveloped in order to record the general detail of the diffraction patterns, but in order to distinguish the high peaks normal exposure and development would be used.

The weighted reciprocal-lattice sections are prepared by drawing black disks, of area roughly proportional to the corresponding value of $|F|^2$, at each reciprocal-lattice point, $|F(000)|^2$ being represented symbolically. Examples are shown in Figs. 4 and 5(b).

3. Comparison of observed and calculated diffraction patterns

In order to test the performance of the apparatus, photographs have been taken of diffraction patterns that have been evaluated theoretically. If an idealized form of a molecule is assumed, the computational work may not be excessive: for example, the molecule of naphthalene may be considered to consist of two regular hexagons (Fig. 3(a)), and thus all the atoms lie on the points of a hexagonal lattice; under these conditions—and *only* under these conditions—the Fourier transform is periodic and thus only one unit cell need be evaluated. The calculations have been carried out by Knott (1940), and a representation of his results is shown in Fig. 3(b); this may be compared with the diffraction pattern (Fig. 3(d)) of the mask shown in Fig. 3(c). Close correspondence exists, and no detail in the calculated pattern is absent from the optically derived one.

It will be noted that, although the calculated transform is periodic, the diffraction pattern is not. This is so because the holes are of finite size, and, as stated in § 2, the sizes have been chosen to represent closely the diffracting power of carbon atoms.

Naphthalene does not provide a very stringent test of the apparatus, as the molecule contains only ten atoms. Larger molecules give variations on a finer scale, and we are grateful to Dr H. P. Stadler, who has allowed us access to his calculations of the Fourier transform of flavanthrone (Wilson, 1951), which contains thirty-two atoms. We find that even for molecules of this size little significant detail is lost, but it is evident that for molecules larger than this some modification of the present arrangement would be called for. Either the pin-hole

or the diffracting mask would have to be made smaller, and both processes present difficulties: pin-holes of diameter less than 0.001 cm. are difficult to make, and the pantograph is hardly accurate enough for making smaller masks. Both these considerations set a limit to the complexity of molecule that can be dealt with.

4. Crystal-structure investigations

The simplest and most direct way of using the optical-transform method is exactly analogous to the 'fly's eye' method (Bragg, 1944; Bunn, 1945): a mask is made of the contents of a single unit cell and its diffraction pattern is compared with the weighted reciprocal-lattice section. It is then possible to see immediately whether the structure gives approximately the correct X-ray intensities. An example of this type of use is given in § 5.

The method has, however, an important advantage over the 'fly's eye': if acceptable agreement is not obtained, knowledge of the complete transform can suggest how the agreement can be improved. For example, if an observed strong reflexion falls on a weak part of the diffraction pattern, one can see fairly easily how to alter the disposition of the contents of the unit cell so that a neighbouring strong peak comes nearer to the reciprocal-lattice point. The central maximum of the diffraction pattern can be very useful in this way, often severely limiting the possible orientation of a molecule in the structure; to obtain the equivalent information mathematically would take considerable time.

There are no limitations to this method, except those of molecular size discussed in § 3; it applies to all space groups and all types of crystal, molecular or ionic. But in certain circumstances, it can be more powerful still. If the unit cell of a crystal contains only one molecule, then knowledge of the transform of this molecule allows all possible orientations to be tested, merely by rotating the transform about the origin of the reciprocal lattice until a fit is found. Crystals with one molecule in the unit cell are rare, but the principle can be applied to projections of which the effective unit cell contains only one molecule. For example, if a crystal belonging to space group $P2_1/a$ has two molecules in the unit cell, the projections of those molecules on the plane (010) are parallel and separated by $\frac{1}{2}a$; thus the effective unit cell of this projection has dimensions $\frac{1}{2}a$ and c , and contains only one molecule. The method of procedure when these conditions hold is described in the next section.

In certain space groups to which these considerations do not apply, it is sometimes possible to investigate the X-ray diffraction effects from molecules in all orientations by making use of a principle pointed out by Knott (1940): if there are two projections which are symmetrically inclined to the cell edges, then the values of the transform *along the cell edges* is twice that of either individual transform. To deal with such a

structure, therefore, it is necessary to rotate the single transform until a fit is found for the reflexions along the axes of the reciprocal lattice; when this is found, the more complete check with the complete unit-cell contents can be carried out. This is the basis of the method used by Klug (1950*b*) in the determination of the structure of triphenylene.

The methods so far described are all simple and can be rapidly carried out. The accuracy of assessment of any particular intensity is low, but this fact is outweighed by the considerable advantage of being able to survey the whole of the Fourier transform, and so to bring into consideration all the reflexions in the reciprocal-lattice section.

5. Some practical examples

The use of the optical method for testing a proposed structure is illustrated in Fig. 4. The diffraction pattern is that of a mask representing the projection of the naphthalene structure (Robertson, 1933*b*) on the (100) plane, and the superimposed reciprocal-lattice section shows that, in the main, reasonable agreement can be expected. There are some slight disagreements, possibly due to inaccuracy of punching the masks, but the correspondence is reasonably clear.

The use of the method for determining the orientation of the molecule in a crystal of space group $P2_1/a$ is neatly illustrated by the compound durenene, $C_{10}H_{14}$ (Robertson, 1933*a*), which has the required two molecules in the unit cell. The diffraction pattern of the idealized molecule is shown in Fig. 5(*a*), and the observed $h0l$ reciprocal-lattice section in Fig. 5(*b*). It will be noted that the reciprocal lattice is much finer than the texture of the diffraction pattern; this is so because the molecular dimensions are much smaller than the cell dimensions, as explained in § 1; the extreme distances between atomic centres are 3 Å. in the breadth and 5 Å. in the length, whereas the values of $\frac{1}{2}a$ and c are 6 and 7 Å. respectively. The grouping of reflexions into peaks of the transform should therefore occur, and this leads immediately to the structure, since the correspondence between Figs. 5(*a*) and 5(*b*) is easily seen.

Admittedly there is no direct evidence of three groups of reflexions along the c^* axis, but knowledge of the approximate scale of the diffraction pattern makes it unlikely that the reflexions from $l = -3$ to $l = +3$ are included within the same group. Acceptance of the existence of three groups gives the general correspondence sought, but there is still some misfit; the reflexions $00l$ agree well, but the other groups of strong reflexions are too far out. This indicates that the molecule is tilted; tilting of the molecule about any line shortens its projection and thus broadens the diffraction pattern in a direction perpendicular to that line. To make Figs. 5(*a*) and 5(*b*) fit, the former must be broadened by a factor of 1.3, corresponding to a tilt of $\sec^{-1} 1.3 = 40^\circ$ with respect to the (010) plane. Some

slight changes of orientation are also suggested, and the final form of the diffraction pattern of the tilted molecule, with the weighted reciprocal-lattice section superimposed, is shown in Fig. 5 (c).

Perfect agreement must not, of course, be expected. Exact planarity and equality of interatomic distances have been assumed, and, from the stage reached by optical methods, orthodox methods of refinement must be used.

It is interesting to note that the diffraction patterns of all planar molecules that consist essentially of hexagons have important features in common; they have six strong peaks distributed symmetrically at distances of 0.83 \AA^{-1} from the origin. They differ, of course, in the detail between these peaks, but these strong peaks are often sufficient by themselves to fix the orientation of the hexagons and perhaps of the whole molecule. In effect this is the method used by Robertson & White (1945) to find the structure of coronene; they made use of certain strong high-order reflexions, which represent these strong peaks of the diffraction patterns of the individual hexagons.

Methods similar to those used for durene can be used for the (010) projections of naphthalene (Robertson, 1933*b*) and phthalocyanine (Robertson, 1936). The former problem is similar to that of durene, but the latter is complicated by the largeness of the molecule, which causes the 'texture' of the diffraction pattern to be about the same as the reciprocal-lattice dimensions. Nevertheless, there was no difficulty in determining the orientation of the molecule (Taylor & Lipson, 1951); the regions of small intensity proved particularly useful, and it is likely that such regions will assume greater importance in dealing with large molecules such as phthalocyanine.

6. Determinations of relative phases in Fourier transforms

It must be remembered that the diffraction pattern of an object is not its Fourier transform but the 'square' of the transform, in the sense that we are observing intensities, not amplitudes, of the constituent waves. In the uses described in § 5, this is an advantage, since the data obtained are X-ray intensities, not structure amplitudes. But, for some purposes, it would be advantageous to be able to derive relative phase angles in the transform.

For non-centrosymmetrical molecules this would not appear to be possible by any simple means; but for centrosymmetrical molecules, where the relative phase angles are limited to 0 or π , two possibilities present themselves. First, the change from 0 (positive amplitude) to π (negative amplitude) can take place only by passing through a region of zero amplitude. Thus if the lines of zero amplitude (nodal lines) can be clearly recognized, the signs of all the other peaks should be deducible from the fact that the central peak is always positive. This operation is easily carried out for the

durene transform, but obviously it would be far less easy to carry out for phthalocyanine.

The difficulty lies in the possibility that the transform may have zero, or vanishingly small, intensity without changing sign, and one false step of this sort will lead to further incorrect deductions. A more dependable method can, however, be used; this is based on the addition to the transform of a term of uniform positive amplitude, which increases the positive regions of the transform and decreases the negative regions. For durene, this wave may be most easily produced by adding another hole at the centre of symmetry of the mask representing the molecule, and the diffraction pattern is then modified to that shown in Fig. 5 (d). Comparison with Fig. 5 (a) shows clearly which parts of the latter are positive, and therefore enhanced, and which are negative, and therefore depressed in intensity. This simple method may not give such clear information for molecules of greater complexity, since the one extra hole at the centre will have proportionately less effect, but some modifications are being considered that would allow more general application of the principle.

7. Further possibilities

It is evident that the use of the method for determining molecular orientations, as distinct from the testing of proposed structures, is severely limited by the existence of several molecules in the unit cell. There would, however, appear to be no fundamental difficulty in making use of superposed transforms, but, since the superposition is governed by a 'fringe function' which determines whether two transforms reinforce each other or not at any particular point, it will be realized that considerable practical difficulties have to be overcome. With non-centro-symmetrical molecules, the difficulties are even greater.

A further difficulty lies in the application of the method to non-planar molecules. Theoretically, it would be possible to work with small three dimensional models instead of masks, but the difficulty then is that the central maximum would be so bright that it would tend to obscure the finer detail. It would probably be best to continue with two-dimensional methods, punching a set of masks to correspond with the various possible orientations of the molecules.

Since the method is as yet in its infancy, it seems reasonable to expect developments that will ultimately make it of use in all types of structural work. Certainly there seems to be every hope that it will speed considerably the earlier stages of most structural investigations.

We wish to express our thanks to Mr W. Hughes, whose painstaking care in the construction of the various devices used has been an important factor in their success. Our thanks are also due to the Department of Scientific and Industrial Research for a grant towards the cost of construction of the diffraction spectrometer.

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The Structure of NiSi

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The structure of NiSi has been determined from Weissenberg and rotating-crystal photographs using Cu $K\alpha$ radiation. Dimensions of the unit cell, determined by the powder method, are: $a=5.62$, $b=5.18$, $c=3.34$ Å. The space group is $Pbnm$, and there are four molecules in the unit cell. The structure is a deformed NiAs arrangement.

Introduction

The structure of nickel silicide was first studied by the powder method by Borén (1933) who described this compound as cubic ($a=4.437$ Å.) of the FeSi type. Later work, also by the powder method, was undertaken by Osawa & Okamoto (1939). These authors, on the basis of thermic, dilatometric and metallographic investigations, revised the Ni-Si system and tried to measure the dimensions of the unit cells of individual phases. NiSi was found to be tetragonal ($a=7.655$, $c=8.45$ Å.) with twenty molecules in the unit cell. The latest work dealing with the structure of NiSi is by Pauling & Soldate (1948), who determined once again the structure of FeSi, on the basis of work on single crystals, and discussed the interatomic distances for FeSi, CrSi, MnSi, CoSi and NiSi. The discussion of these silicides, other than that of FeSi, is based on the data of Borén (1933).

Preparation of the crystals

A small block of alloy was prepared by melting very pure nickel and silicon in stoichiometric ratio in a vacuum induction furnace. After cooling in the furnace the block was broken, and inside there was found a cavity with imperfectly developed prismatic crystals whose constitution corresponded to the phase of NiSi. A powder photograph, prepared from the powdered crystal, was identical with that published by Osawa & Okamoto (1939).

Unit-cell dimensions and the space group

On the basis of rotation and Weissenberg photographs (Cu $K\alpha$ radiation), orthorhombic symmetry was established. The dimensions of the unit cell, determined from rotation photographs and from powder photographs in a 19 cm. camera (Co $K\alpha$ radiation), after correction by the method of Heavens & Cheesman (1950), were found to be

$$a=5.62, \quad b=5.18, \quad c=3.34 \text{ Å.}$$

The absent reflexions, $(0kl)$ where $k=2n+1$, $(h0l)$ where $h+l=2n+1$, $(00l)$ where $l=2n+1$, indicate the probable space group Pbn or $Pbnm$.

The density is 5.86 g.cm.^{-3} and the unit cell therefore contains four NiSi. In the case of the group $Pbnm$ a special fourfold position with atoms in the plane of symmetry (001) satisfies, while in the case of the group Pbn the general fourfold position satisfies. The final decision is possible on the basis of the determination of $z_{\text{Ni}}-z_{\text{Si}}$, which for Pbn may have all the values from 0 to $\frac{1}{2}$, for $Pbnm$ only 0 or $\frac{1}{2}$.

Intensity measurements

For intensity measurements oscillation photographs were taken about the c axis, with Cu $K\alpha$ radiation. Measurements were made in the planes $(hk0)$ using visual comparison with an intensity scale having exposures in the ratios 10:6.6:5.0:3.3:1.8:1.0. Measured intensities were corrected in the usual way using polarization and Lorentz factors. The measured