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Optical Methods in X-ray Analysis. III. Fourier Synthesis by Optical Interference

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A method of Fourier synthesis by optical interference is described, which involves the representation of a reciprocal-lattice section by an array of holes in an opaque plate. Intensities can be controlled by varying the orientation of mica plates between crossed nicols, while phase changes sufficient for the synthesis of centro-symmetrical projections are effected by interference between the fast and slow components into which the mica resolves the incident light. Experiments are described which illustrate the application of the method to those problems involving conventional Fourier synthesis, to the determination of structures by trial of sign combinations, and to the testing of proposed structures by means of error syntheses.

Introduction

It is well known that the ultimate problem in crystal-structure determination is the production of the image of a structure from the X-radiation diffracted by it, in the absence of any means of causing the diffracted beams to interfere to form the image directly. The image is usually produced mathematically by Fourier synthesis, but this process is laborious, and it would be more satisfactory if some substitute could be devised, so that the image of a structure could be produced automatically.

Bragg (1939) was the first to propose such a substitute. He suggested simulating the X-ray diffraction pattern by an array of beams of light, which by the use of an ordinary lens system could be made to interfere. Three conditions must be satisfied: first, each beam of light must correspond in position to a point of a principal section of the reciprocal lattice; second, the intensity of each beam must be proportional to the intensity of the corresponding X-ray reflexion; third, the relative phase of each beam must be the same as that of the corresponding X-ray reflexion.

These conditions were satisfied in the experiment described by Bragg by the use of a plate containing an array of holes representing the $h0l$ reciprocal-lattice section of diopside, [$CaMg(SiO_3)_2$], each hole having an area proportional to the structure amplitude of the corresponding X-ray reflexion. (It might appear that the diameter should be proportional to the structure amplitude; however, the nature of the diffraction pattern of a hole is such that the intensity at the centre of the pattern is proportional, not to the area of the hole, but to the square of the area.) The correct phase relations are achieved automatically because the b-axis projection of the structure contains superimposed calcium and magnesium atoms, and if these are assumed to lie at the origin, all the diffracted beams (with an unimportant exception) are in phase with each other. The diffraction pattern of the array of holes was an acceptable representation of the projection of the structure.

In order to apply the method to structures for which equality of phases does not occur, it is necessary to introduce phase differences in the various beams. For complete generality, a method must permit the introduction of any phase difference, from 0 to 2π; this paper is concerned only with phase differences of 0 and π, which are sufficient to deal with centro-symmetrical projections. In addition to being simpler, this case is more important, since the infinity of possible phase angles for each reflexion given by a non-centro-symmetrical projection allows too much freedom for such methods to be of much use in structure determination.

Several methods of introducing the required phase differences are possible; Buerger (1950), for example, has used tilted mica plates, which give the required phase differences by increasing the optical paths. This method, like Bragg's, achieves intensity control by variation of hole size, and must inevitably involve errors except at the centre of the diffraction pattern. Our method (Hanson, Taylor & Lipson, 1951), by making full use of the properties of mica, achieves intensity control without variation of hole size, as well as the introduction of phase changes of 0 or π. The method, and the use we have made of it, will be described in the sections which follow.

Theory of the method

Our method of phase and intensity control exploits the biaxial nature of mica in a manner suggested by Dr C. A. Taylor of this department. A beam of polarized light incident normally on a sheet of mica will in general be resolved into two perpendicularly polarized components, one of which travels through the mica slightly faster than the other. If these components are themselves resolved by being passed through an analyser which is crossed with respect to the initial plane of polarization, the two final components will be equal in magnitude, this magnitude depending on the orientation of the mica with respect to the initial plane of polarization. The relative phase of the two components will depend on their optical path difference; if this difference is nil, or some integral multiple of the wavelength, the components will be in antiphase, and will cancel each other completely. Otherwise there will be a resultant component, which will be greatest when the optical path difference is some odd integral multiple of half the wavelength. The phase of the resultant component, relative to some independent standard, remains constant if the orientation of the mica is changed, until the magnitude of the resultant component passes through zero. When this happens, the relative phase of the component is altered by π, so that a method is at hand for controlling the intensity of a beam of light, and at the same time introducing the necessary phase changes. This point may be made clearer by reference to Fig. 1.

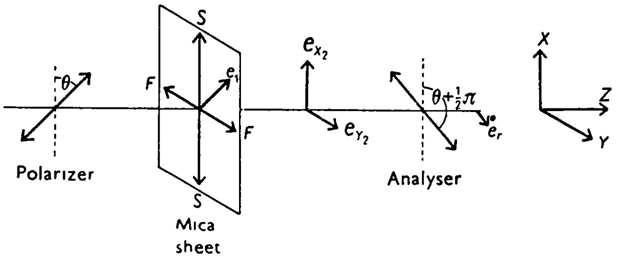


Fig. 1. *S–S*, slow direction; *F–F*, fast direction.

In the diagram, the polarizer is so placed that the incident electric vector makes an angle θ with the X axis. If the amplitude is assumed to be unity, the relative states of the X and Y components of the vector can be given by the equations

$$e_{X_1} = \cos\theta \cos 2\pi\left(\frac{t}{T}-\frac{z}{\lambda}\right),$$

$$e_{Y_1} = \sin\theta \cos 2\pi\left(\frac{t}{T}-\frac{z}{\lambda}\right).$$

The mica is placed with its slow and fast directions parallel to the X and Y axes respectively, so that the relative states of the X and Y components of the vector, after transmission by the mica, can be given by

$$e_{X_2} = \cos\theta \cos 2\pi\left(\frac{t}{T}-\frac{z+d}{\lambda}\right),$$

$$e_{Y_2} = \sin\theta \cos 2\pi\left(\frac{t}{T}-\frac{z}{\lambda}\right),$$

where d is the optical path difference for the two components, i.e. the product of the thickness of mica and the difference between refractive indices for slow and fast directions.

The components are now resolved by the analyser in a direction making an angle $\theta+\frac{1}{2}\pi$ with the X axis. The state of the resultant electric vector in this direction is given by

$$\begin{aligned} e_r &= e_{X_2}\cos(\theta+\tfrac{1}{2}\pi)+e_{Y_2}\sin(\theta+\tfrac{1}{2}\pi) \\ &= -e_{X_2}\sin\theta+e_{Y_2}\cos\theta \\ &= -\sin\theta\cos\theta\cos 2\pi\left(\frac{t}{T}-\frac{z+d}{\lambda}\right) \\ &\qquad\qquad +\sin\theta\cos\theta\cos 2\pi\left(\frac{t}{T}-\frac{z}{\lambda}\right) \\ &= \tfrac{1}{2}\sin 2\theta\left[-\cos 2\pi\left(\frac{t}{T}-\frac{z+d}{\lambda}\right)+\cos 2\pi\left(\frac{t}{T}-\frac{z}{\lambda}\right)\right] \\ &= -\sin 2\theta \sin\frac{\pi d}{\lambda}\sin 2\pi\left(\frac{t}{T}-\frac{z+\frac{1}{2}d}{\lambda}\right). \end{aligned}$$

This equation indicates that, at a given time and position, the length of the electric vector is proportional to $\sin 2\theta$, and is thus continuously variable through a range of positive and negative values by the operation of the parameter θ. A change of sign is interpreted simply as a phase change of π, so that the desired phase and intensity control is available.

It is also seen that, for a given value of θ, the amplitude of the electric vector is proportional to $\sin \pi d/\lambda$, so that for systems where the transmitted intensity is to be kept high, the thickness of the mica should be as near as possible to that for which $d=\frac{1}{2}\lambda$, although this condition is not critical.

Experimental procedure

A suitable sheet of mica was selected from a number of old condenser plates which were available, the criteria of suitability being clarity, optical uniformity, and correct thickness. Clarity was established by inspection, while optical uniformity was distinguished by an appearance of uniform colour when the mica was examined in an ordinary polarizing strain tester. The thickness was deemed to be suitable when the maximum transmission of the system consisting of the mica between crossed nicols was at least 90% of the maximum transmission of the same system with the nicols parallel. It is easily shown that then the actual thickness of the mica is within 10% of the optimum figure of about 0·0025 cm. From the selected sheet were punched several hundred discs of about 3 mm. diameter.

About eighty brass cylinders were prepared, each about 1 cm. long, with outer diameter 4 mm. and inner diameter 2 mm. One end was counterbored to a diameter of 3 mm., and a depth of about 2 mm. A mica disc was placed in the end of each cylinder, and held firmly in place with a piece of wire spring.

Reciprocal-lattice sections were represented by drilling holes of 2 mm. diameter at appropriate points in an opaque plate about 1 cm. thick, counterboring these holes to a depth of about 7 mm., and a diameter of 4 mm., and placing a brass cylinder in each hole. The required intensities and phase relations could then be introduced by appropriate rotations of the cylinders.

First, however, it was necessary to distinguish between the fast and slow directions of the mica in each cylinder, in order that any angle θ could be distinguished from the angle $\theta+\frac{1}{2}\pi$, and phase differences could be introduced without ambiguity. This was done as follows. One cylinder was selected as a standard, and placed in one of two adjacent holes in an opaque plate. The plate was placed in the object plane, O, of the Diffraction Spectrometer (Fig. 2) (Taylor, Hinde & Lipson, 1951) and the cylinder was rotated until the transmitted light was a minimum. The position was arbitrarily selected as the 'correct' zero position, and a saw-cut was made in the upper end of the cylinder at an agreed orientation relative to the spectrometer. The cylinder was then rotated clockwise through 45°, and a second cylinder was placed in the remaining hole. This cylinder was rotated until the resulting diffraction pattern was the ordinary pattern for two holes scattering in phase, namely, a circular area crossed with bright and dark fringes, with a bright fringe coinciding with a diameter. This was easily distinguished from the pattern for two holes scattering with a phase difference of π, for which a dark fringe coincided with a diameter. The second cylinder was then rotated counterclockwise until its contribution to the pattern was nil, and a saw-cut was made in the upper end, at the agreed orientation. This procedure was repeated for all the remaining cylinders, when it was possible to define the 'correct' zero positions as the ones for which the saw-cuts pointed in the agreed direction, and arbitrarily to designate clockwise rotations up to 90° as introducing a relative phase of 0, and anti-clockwise rotations up to 90° as introducing a relative phase of π.

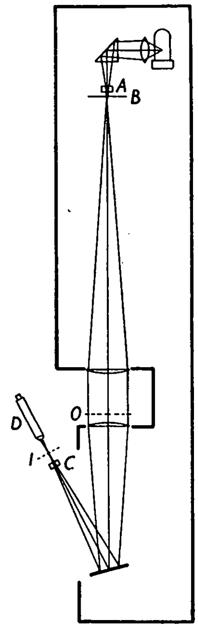


Fig. 2. The Diffraction Spectrometer. A, polarizer; B, pin hole; C, analyser; D, microscope; O, object plane; I, image plane.

It was then possible to complete the representation of a reciprocal-lattice section by turning each cylinder in its hole in the appropriate opaque plate through the required angle in the required direction. The starting point for each rotation was of course the position for which the saw-cut pointed in the agreed direction. The angles were determined by making the experimentally determined structure factors proportional to sin 2θ, the factor of proportionality being established by making $\sin 2\theta = 1$, or $\theta = 45°$, for $F(000)$. In general, $F(000)$ is much larger than any of the other structure factors, and it was found convenient to reduce the amount of light actually reaching the cylinders other than the one representing $F(000)$ in order that their angles should be of manageable size. This was done by placing a sheet of fine wire gauze, with a hole in the centre, over the array of cylinders, so that the amplitude of the light reaching all the cylinders except the one representing $F(000)$ was reduced by a factor of about 0·3.

An unexpected difficulty was encountered at this point, when it was found that the parallel light passing the plane (Fig. 2) was not uniformly polarized. Fig. 3, which is a photograph of the object plane as seen from the image plane, illustrates this point; in the dark area the plane of polarization is perpendicular to the polarizing direction of the analyser, as specified by the method; in the bright areas it is not. The effect is a consequence of the fact that the polarizer is placed in a convergent beam of light (Fig. 2); the state of polarization of those rays for which the plane of the electric vector, or of the magnetic vector, contains a diameter of the lens aperture is unchanged by passage through the lens, while all other rays suffer some rotation. The rotation is clockwise for two opposite quadrants, and anti-clockwise for the remaining two. The error introduced by this effect can, to a very good degree of approximation, be eliminated by applying a small correction to the zero position of any affected cylinder.

The need for the correction, however, is almost entirely eliminated by the following method of setting the cylinders. The reciprocal-lattice plate was mounted in a graduated cylinder, capable of azimuthal rotation in the object plane of the Diffraction Spectrometer, as shown in Fig. 4. The microscope was removed, and, by placing the eye at the image plane, the reciprocal-lattice section could be viewed directly, as an array of bright spots on a black background. In order to set a given cylinder at, say, 20°, and introducing a phase change of π, the circle was turned clockwise from a given datum through 20°. The cylinder was then rotated independently of the plate until it transmitted no light, that is, until the spot disappeared.

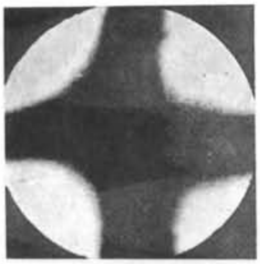


Fig. 3. Object plane of the Diffraction Spectrometer, as seen from the image plane.

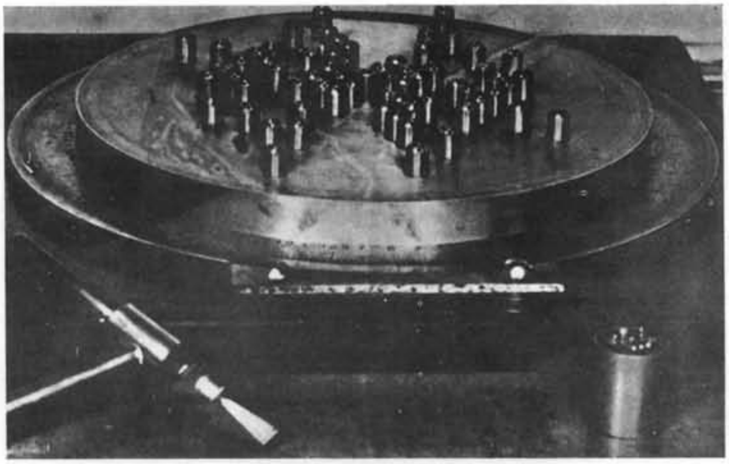


Fig. 4. A reciprocal-lattice plate, showing the cylinders and the arrangements for azimuthal rotation.

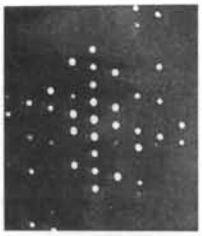


Fig. 5. The reciprocal-lattice section for hexamethylbenzene.

Fig. 6. Synthesis of durene.

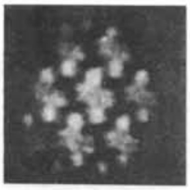
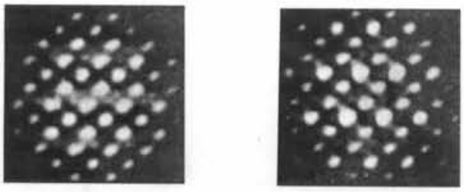
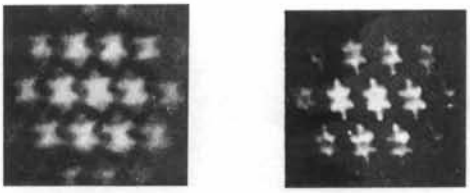


Fig. 7. Synthesis of diphenylene-naphthacene.



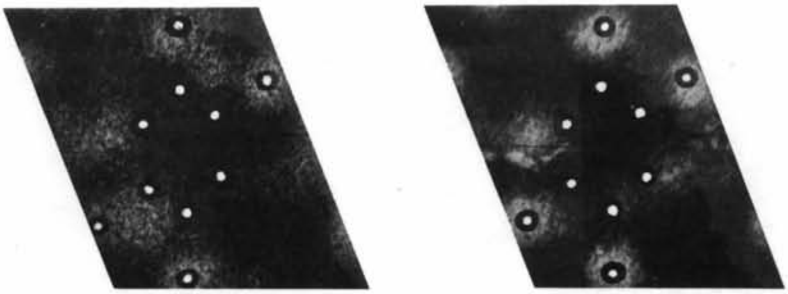
(*a*) (*b*)

Fig. 8. (*a*) Hexamethylbenzene synthesis with 10 terms, one of which is wrong. (*b*) Same as (*a*), but with $F(000)$ reduced.



(*a*) (*b*)

Fig. 9. (*a*) Hexamethylbenzene synthesis, with 10 terms, all correct. (*b*) Hexamethylbenzene synthesis, with about 30 terms, all correct.



(*a*) (*b*)

Fig. 10. (*a*) Error synthesis for durene, with proposed molecule superimposed. (*b*) Same as (*a*), but with term added at the origin of the reciprocal-lattice section.

There are of course two mutually perpendicular orientations of the cylinder for which this will occur; the correct one is that for which the saw-cut points in the agreed direction. The circle was then returned to its initial position, so that the total effect of the operation was to turn the cylinder 20° anti-clockwise from the agreed direction. This was done successively for all the terms of the reciprocal-lattice section. The appearance, from the image plane, of the reciprocal-lattice section of hexamethylbenzene is shown in Fig. 5.

It may be objected that the setting to zero is done when the cylinder is not in its normal position in the field, so that the effective rotation is in error. This error tends to be small, however, because terms represented by large angles (say, greater than 10°) are almost always found near the origin, where the rotation of the plane of polarization is slight. On the other hand, terms which lie in the seriously affected parts of the field are usually represented by small angles, and so change their positions only slightly during the setting process. A map was made of the error in the zero position of a cylinder in any part of the field, so that corrections to any term could be estimated by taking the difference between the errors for the setting, and for the final, positions. It was found that only in quite exceptional cases did the correction exceed 1°, and this is considered to be the limit of accuracy of the setting process.

Applications

The uses of this method of Fourier synthesis fall into three main groups, which will be considered in turn:

(1) *Normal Fourier synthesis*

At some stage in a structure determination, the signs of a number of structure factors will have been inferred with reasonable certainty. At this stage a Fourier synthesis can be produced by the method described, and this in entirely equivalent to producing a rough Fourier synthesis by the conventional methods. A synthesis of durene based on the experimental structure factors of Robertson (1933) is shown in Fig. 6. This was the first synthesis attempted by this method. Fig. 7 shows a synthesis based on a proposed structure of diphenylene-naphthacene (Bennett & Taylor, 1952); this synthesis provided a useful verification of the correctness of the proposed structure. This application of the method may save much tedious calculation, but this is probably its only real value in the determination of structures.

(2) *Structure determinations by trial of sign combinations*

In the initial stages of a structure determination, only the magnitudes of the structure factors are known; the signs must be inferred. The methods described provide a line of attack by making possible, in a relatively short time, the critical examination of the syntheses of a large number of sign combinations. The speed of the method is due partly to the ease with which the phase of a given term can be altered; since the structure factor is proportional to sin 2θ, rotating a cylinder through a right angle leaves the transmitted amplitude unchanged, but alters the phase by π. Phases are thus easily changed with the help of a 'right-angle screw-driver', a simple device which engages with the saw-cut of a cylinder, and allows a right angle rotation between click stops.

The general procedure to be followed is best described in terms of an experiment in which the authors 'determined' the structure of hexamethylbenzene (Lonsdale, 1929; Brockway & Robertson, 1939). The experimentally determined magnitudes of the structure factors of the ($hk0$) reciprocal-lattice section were provided, along with the chemical structure formula. The ten strongest terms, including $F(000)$, were selected for experiment, and cylinders were set in the appropriate holes of the reciprocal lattice plate. The terms were all given positive signs, and three terms, $F(100)$, $F(010)$ and $F(110)$, were arbitrarily fixed as positive. This can always be done, as the first two merely fix the origin of the synthesis with respect to the molecule, while the third determines whether peaks of the synthesis shall be represented by positive vectors, or negative—a purely formal consideration. This left seven variables, or 2^7 possible sign combinations, and to perform even rough Fourier syntheses for all of these, by conventional methods, would be prohibitively laborious. Using the optical method, the syntheses of all the combinations were examined in about two hours. Most of the syntheses were rejected regardless of appearance because, while the correct pattern must be composed almost entirely of peaks (or what amounts to the same thing, almost entirely of troughs), most wrong patterns are composed of both peak and trough. The method of detecting trough is illustrated in Fig. 8. Fig. 8(a) shows the synthesis for a given sign combination, while Fig. 8(b) shows the synthesis of the same combination, but with $F(000)$ reduced. Reducing $F(000)$ has the effect of raising the zero level of the synthesis, so that peaks are reduced and troughs are increased; comparison of the two syntheses reveals that the first is composed of trough and peak, and this sign combination must therefore be rejected. It should be observed that $F(000)$ was left as a variable, so that two combinations can be examined for trough with manipulation of only the cylinder representing $F(000)$. All but one of the remaining syntheses were rejected because of their unlikely appearances; some of these bore too little resemblance to the expected structure, while others, like the example of Fig. 8, bore no resemblance to any conceivable structure.

At this point, reference to the literature revealed that the sign combination associated with the chosen synthesis (Fig. 9(a)) was indeed correct. This synthesis indicated the orientation of the molecule with sufficient accuracy for the application of existing optical methods (Taylor & Lipson, 1951; Hanson & Lipson, 1952), which provided the signs of about thirty of the more important terms. Fig. 9(*b*) shows the synthesis resulting from the inclusion of all these terms. The whole experiment was performed largely without resort to photographic processes, and was completed in two half-days. This simple case does not of course constitute a severe test of the method; it may be that complicated structures will not yield to it. It is felt, however, that the trial of many sign combinations, perhaps assisted by an appeal to the Kasper & Harker (1948) inequalities, constitutes the most promising application of optical methods of Fourier synthesis.

(3) *Error synthesis*

At some later stage of a structure determination a comparison between the magnitudes of the experimental structure factors and those based on a proposed structure may reveal serious discrepancies. It is sometimes possible to decide what changes are necessary by means of an error synthesis, which is simply a Fourier synthesis for which the terms are the differences between the experimental and calculated structure factors (Crowfoot, Bunn, Rogers-Low & Turner-Jones, 1949). The only differences which can be used are those involving fairly large calculated structure factors, and fairly small experimental ones, since the signs of the experimental structure factors are not known. Strong peaks in the synthesis generally coincide with incorrectly placed atoms; the presence of troughs may yield some information regarding the proper positions, though this information is seldom without ambiguity. The rough nature of the technique makes it most suitable for optical methods; moreover, the inconveniently large $F(000)$ of the ordinary Fourier synthesis does not occur, and if the method of the previous section has been used in the determination of the structure, the reciprocal-lattice plate will be available.

Fig. 10(*a*) is an error synthesis based on an incorrect structure of durene, while Fig. 10(*b*) is the same synthesis, the zero level of which has been raised by the addition of a term at the origin of the reciprocal-lattice section, in order to distinguish peak from trough. In each photograph the incorrect structure has been superimposed, and it is clear that the CH_3 radicals are not correctly placed.

Limitations of the method, with suggestions for improvement

The most drastic limiting factor of the method is the low resolving power, which is probably due to a variety of causes. The mica plates are relatively thick; and small, random amounts of tilt among the various cylinders may introduce random phase shifts due to actual lengthening of the optical paths. It is proposed to construct a new set of cylinders, and to improve the fit between the cylinders and the reciprocal-lattice plate, in order to reduce the possibility of any tilting. The lenses used are spherical, and suffer from a significant degree of spherical aberration; it is also proposed to construct a new spectrometer embodying corrected lenses. These improvements should materially increase the resolving power. A further improvement could almost certainly be effected by representing the reciprocal-lattice section on a smaller scale; however, the practical difficulties of this course are considerable, and we do not propose to follow it at present.

It has been customary to drill a new reciprocal-lattice plate for each new compound investigated. This procedure is somewhat tedious, and it is proposed to use a standard plate, with a square lattice, for at least the preliminary stages of any investigation. Some distortion of the molecule would be involved, but this would probably not be objectionable.

It is felt that the methods described in this paper, while subject to some limitations, have a definite place in the armoury available to the crystallographer. It should be remembered that the techniques described are only exploratory; it may well be that new developments may vastly increase the scope and usefulness of this aesthetically appealing subject.

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