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The Determination of the Signs of Structure Factors by Optical Methods

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The signs of the structure factors for a trial arrangement of atoms may be determined quickly and without calculation by means of optical-transform methods. The determination involves a comparison of two transforms—one of the unit-cell contents of the proposed arrangement and the other of an identical arrangement with an extra atom at the centre of symmetry; positive regions of the transform are enhanced by the extra atom and negative regions are diminished. Practical details of the technique as applied to a specific crystal structure are given, and the reliability and certain advantages of the method are discussed.

Introduction

An important step in the process of crystal-structure determination by optical-transform methods (Hanson, Lipson & Taylor, 1953) is the derivation of the relative phases of the structure factors without calculation. The possibility of such a direct derivation has been mentioned several times (e.g. Lipson & Taylor, 1951; Hanson *et al.*, 1953), but so far no detailed account of the process has been given. The present paper describes in detail the techniques used and includes a discussion of their reliability and usefulness; for many purposes the method provides information that cannot readily be obtained by calculation. Centrosymmetrical projections only are treated in this paper and attention is confined to structures containing atoms of similar scattering factor. The general principles of optical-transform methods are assumed.

It has been pointed out (Taylor, 1952*a*) that the optical transform of a centrosymmetrical object consists of comparatively well-defined peaks separated by lines of zero intensity; the phase changes by π when one of these lines is crossed. The test of correctness of a trial structure is that each reciprocal-lattice point should lie at a point in the optical transform having an intensity corresponding to the observed intensity; each reciprocal-lattice point is thus assigned to a particular peak. If, therefore, the phase of each peak in the transform can be determined, the phase corresponding to each reflexion in the reciprocal-lattice section is known. Since only phase differences of 0 and π, relative to the central maximum, occur with centrosymmetrical projections, it is convenient to refer to the process as sign determination and to think of the peaks as regions of positive and negative amplitude.

Basic principle

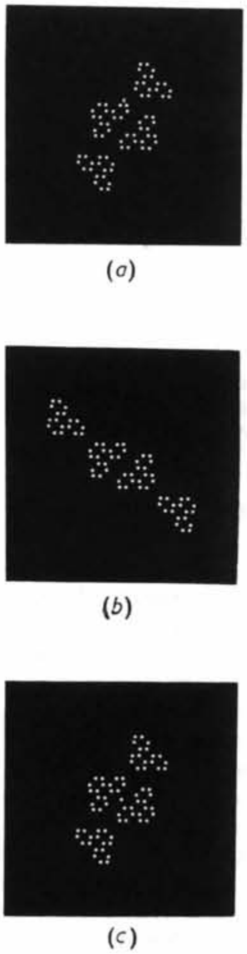
If a uniform positive amplitude could be added to the whole optical transform, it would increase the intensity of the existing positive regions and decrease that of the negative regions; the signs of these regions could thus be determined. In practice an extra hole is punched at the centre of symmetry of a mask representing the unit-cell contents of the proposed structure. This hole adds to the transform the required term of uniform positive amplitude. The technique is analogous to the changing of the scattering factor of the atom at the origin in the isomorphous-replacement method and also to the use of a coherent background in diffraction studies by Zernike (1946).

An important point is that it is necessary to choose a centrosymmetrical disposition of the unit-cell contents. Although the projection of the whole crystal lattice is centrosymmetrical it is possible to choose a single unit cell that does not have a centre of symmetry. In theory, of course, any arrangement of the asymmetric units according to the space-group rules will give the same result *at reciprocal-lattice points*, but the present technique is practicable only if the sharp distinction between the various regions of the transform, characteristic of centrosymmetrical structures, is achieved. It is also advisable to arrange the disposition of holes in the mask so that the distribution is as compact as possible, as shown in Fig. 1(*a*). The choice of an arrangement much longer in one direction than in the other (Fig. 1(*b*)) should be avoided if possible, as it leads to long narrow regions in the transform with steep gradients across the narrow direction, and the effect of errors in the relative positioning of the weighted reciprocal-lattice section and the transform is increased.

Experimental procedure

When the mask has been prepared, photographs are taken of its optical transform, with the extra hole covered and uncovered (Fig. 2(*b*) and (*c*)). Fig. 3(*a*) and (*b*) are enlargements of corresponding portions of two such transforms; the distinction between positive and negative regions can be clearly seen.

It is desirable to have clear separations within the

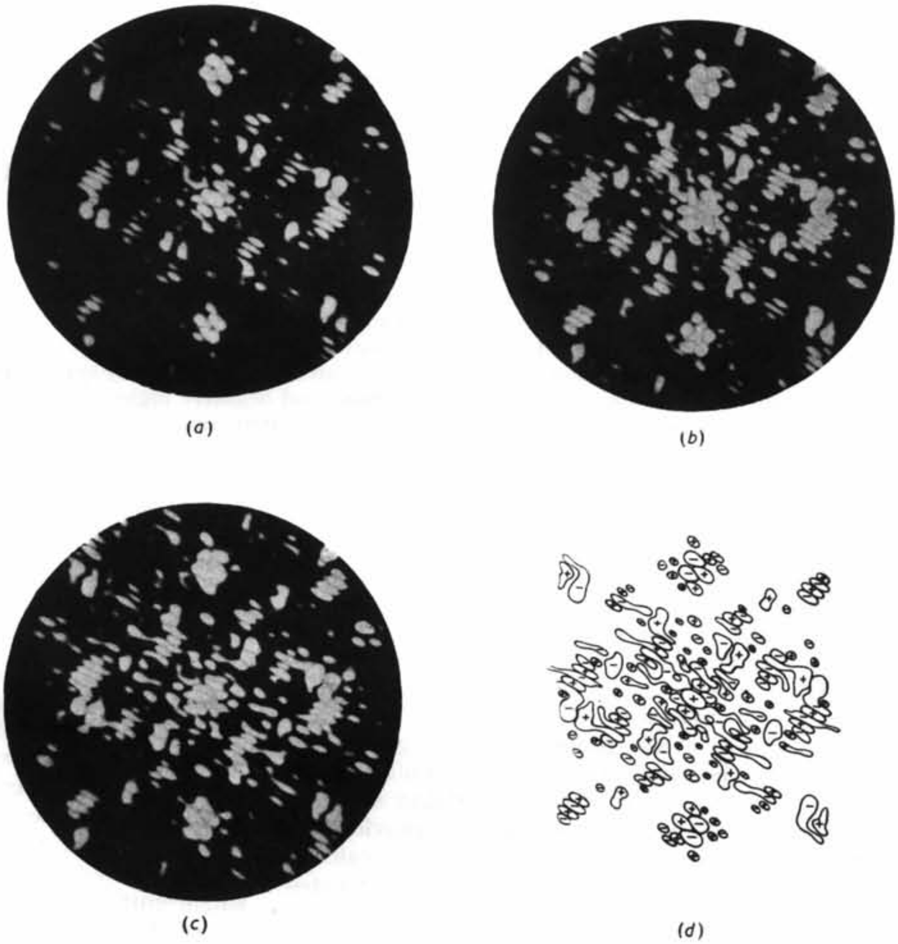


(a)

(b)

(c)

Fig. 1.



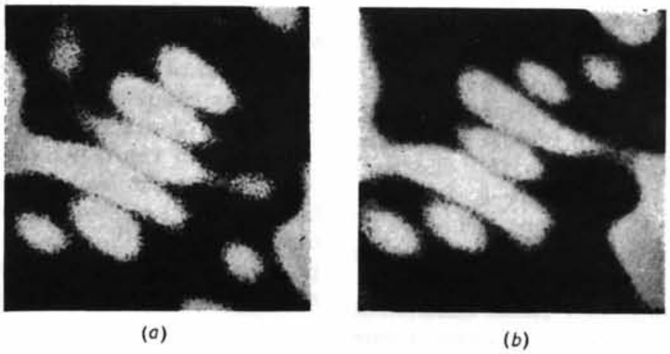
(a)

(b)

(c)

(d)

Fig. 2.



(a)

(b)

Fig. 3.

Fig. 1. (*a*) Mask representing the unit-cell contents of a proposed structure. (*b*) Mask representing the same structure as (*a*) but with a badly selected disposition of the contents. (*c*) Mask with the extra hole at the centre of symmetry; all the holes are covered by gauze except the centre one.

Fig. 2. (*a*), (*b*) Optical transforms of the mask shown in Fig. 1(*a*), showing two levels of intensity. (*c*) Optical transform of the mask shown in Fig. 1(*c*). (*d*) Tracing of Fig. 2(*b*), showing the signs of the peaks.

Fig. 3. (*a*), (*b*) Enlargements of corresponding parts of Fig. 2(*b*) and Fig. 2(*c*) respectively.

transform and to this end fairly high-contrast photographic techniques are used. The film is Kodak Panmicrofile and it is developed in a two-bath developer described in Appendix I. Microfile has the advantage of only recording regions that are above a certain level of illumination (the critical level depends, of course, on the exposure), and anything below this level will not be recorded. Thus there is no general gradation towards the edge of a peak but a sharp boundary between the peaks and the background. For the same mask a series of exposures may be made which will give a corresponding series of photographs showing the relative levels of intensity within the transform (Fig. 2(*a*) and (*b*)). Microfile, used in this way, has the additional advantage of having a very fine grain and gives suitable negatives for the considerable enlargement (100×) required in this work.

It has been found advantageous to draw the outline of the peaks of the original transform (Fig. 2(*d*)) on tracing paper and to record the signs on the tracing rather than on the photograph itself. A reciprocal-lattice net is then laid over the tracing and the signs of the reflexions are recorded.

In the weighted reciprocal lattice, equivalent reflexions occur twice for oblique plane groups and four times for rectangular ones. This repetition may be used as a means of checking, as the signs may be read off independently for equivalent reflexions and subsequently compared. For example, in the plane group *pgg* the reflexions appear four times in the reciprocal-lattice section with relationships

$$F(hk0) = F(h\bar{k}0) = F(\bar{h}k0) = F(\bar{h}\bar{k}0) \text{ if } h+k \text{ is even,}$$
$$F(hk0) = -F(h\bar{k}0) = -F(\bar{h}k0) = F(\bar{h}\bar{k}0) \text{ if } h+k \text{ is odd,}$$

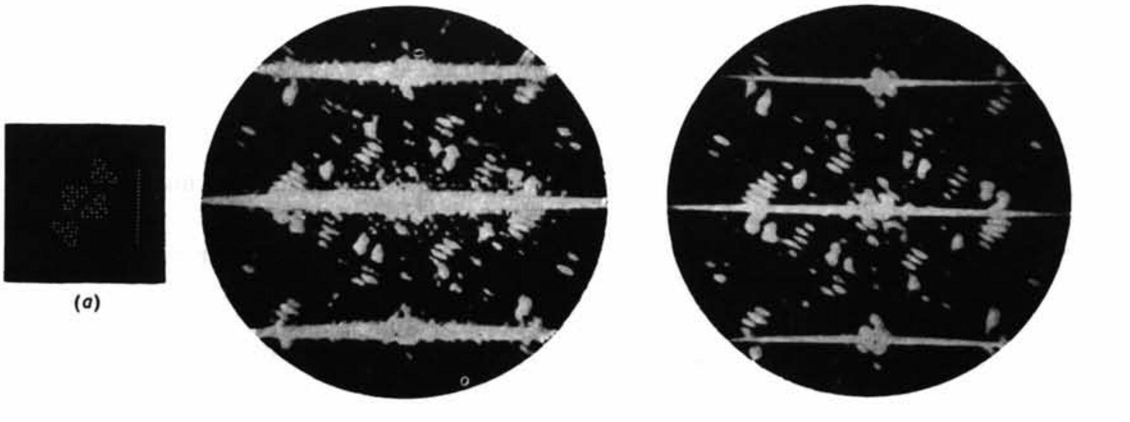
leading to a set of signs as shown in Table 1; a mistake would be immediately obvious. It should be noted that for plane groups containing glide planes the optical transform does not have the full symmetry of the X-ray diffraction pattern.

Table 1

	Signs derived from each quadrant				Confirmed sign,	Calculated structure factor for comparison,
hkl	hkl	$h\bar{k}l$	$\bar{h}\bar{k}l$	$\bar{h}kl$	hkl	hkl
410	−	?	+	?	?	$\bar{2}$
430	−	?	−	?	− ?	$\bar{1}$
450	+	−	+	−	+	27
470	+	−	+	−	+	7
490	−	+	−	+	−	$\overline{18}$
420	−	−	−	−	−	$\overline{26}$
440	+	+	+	+	+	21
460	+	+	+	+	+	19
480	−	−	?	−	− ?	$\bar{1}$
4,10,0	+	+	+	+	+	18

It will be seen that the only doubtful signs are those for reflexions of which the calculated amplitude is very small. The corresponding parts in the transform lie on a steep gradient and are therefore very sensitive to small changes in the proposed structure. Such reflexions should obviously be omitted from a Fourier synthesis, particularly if the corresponding observed intensity is large.

The reciprocal-lattice net may be matched accurately with the drawing, both in scale and orientation, by making use of calibration fringes; an extra row of holes is punched in the mask which has already been prepared (Fig. 4(*a*)). The direction of the row is made parallel to one of the cell edges and the holes within the row are at known regular intervals (usually equivalent to 1 Å). The effect of these extra holes is to produce a set of parallel fringes superimposed upon the original optical transform (Fig. 4(*b*)). In practice the row is punched at some distance from the other holes so that it may be covered and exposed separately.


(*a*)

(*b*)

(*c*)

Fig. 4. (*a*) Mask with a row of calibration holes. (*b*) Optical transform of the mask shown in (*a*) with the atomic arrangement and calibration holes exposed simultaneously. (*c*) Optical transform of the mask shown in (*a*) with the atomic arrangement and calibration holes exposed in succession.

Since the distance apart of the holes and the direction of the row in the mask are known, the dimensions and direction of the fringes superimposed on the optical transform are known. If the spacing in the row were equivalent to 1 Å, the spacing of the fringes would be equivalent to 1 $Å^{-1}$ and the fringes are perpendicular to the row.

In preparing the photographic enlargement of the optical transform the fringes can be used to adjust the scale to match that of the reciprocal-lattice net. (The scale usually used is 5 cm. to represent 1 $Å^{-1}$.)

The fine detail produced by interference between the fringes and the original transform sometimes makes the identification of particular peaks difficult. To eliminate this effect the holes representing the atomic arrangement and the calibration row are punched on separate masks and exposed in succession instead of simultaneously. These effects are illustrated by Fig. 4(*b*) and (*c*).

Limitations

The extra hole only has an appreciable effect with a mask containing less than 30 holes. One method of overcoming this limitation is to cover all the holes except the centre one with a fine copper wire gauze (e.g. 200 mesh) which transmits only 10% of the incident intensity. The hole at the centre thus has an enhanced effect. The method can then be used with masks containing up to about 100 holes.

Before the gauze technique had been developed another method was devised for dealing with a large number of atoms and was used successfully on purpurogallin (Taylor, 1952*b*). While this method is not as satisfactory as that just described, a combination of the two may be used to deal with structures containing more than 100 atoms, and therefore a brief description of the way it was applied to purpurogallin is included here.

Signs are determined first as though the cell contained only one pair of centrosymmetrically related molecules instead of two. The transform of the unit cell is the resultant of the transforms of the two pairs, the rules for the combination at the reciprocal-lattice points being that the transforms add at those points for which $h+k$ is even and subtract at those for which $h+k$ is odd. Thus, if the transform of one pair shows positive signs at the point hk and $h\bar{k}$ (which is the point hk for the transform of the related pair), then the sign of the structure factor is positive if $h+k$ is even, but is indecisive if $h+k$ is odd; in the latter case the sign depends upon which intensity is greater, a decision which can easily be made in general, and if there is any difficulty the structure factor must be near zero and the sign doubtful by any method.

Some advantages of the method

Apart from the obvious saving of time (the signs for a zone of 120 reflexions can be determined in about 2 hr.) a number of other features give the method a considerable advantage over more conventional methods. These features all arise from the fact that the transform represents the value of the structure factors everywhere in the reciprocal-lattice section, not only at the reciprocal-lattice points.

Consider a reflexion that is observed as medium but for the trial structure in question has a calculated value that is much too small. A study of the position of the corresponding reciprocal-lattice point relative to the nearby peaks of the transform might reveal that the 'calculated' value is small either because the general intensity of the transform is low at that point or because it lies close to the edge of a strong peak. In the first case the sign would not be regarded as reliable, as obviously some fairly drastic change in the transform would be needed; but in the second case the reflection would be given the sign of the strong peak because a small change might put the magnitude right.

A closely related point is that it is possible to begin the process of refinement during the sign-determination stage. Thus, in the example just given, if the reciprocal-lattice point lay in a zero region of the transform but close to one fairly large peak, it would be given the sign corresponding to that peak because, if the trial is somewhere near the correct structure, the only way to make the magnitude right by a small change in the transform would be to move the peak on to the reciprocal-lattice point under consideration. Structure determination can, in fact, be regarded as proceeding in two stages—first the assignment of each reflexion to a particular transform peak (phases correct) and then the location of the exact point within each peak (magnitude correct). In purpurogallin (Taylor, 1952*b*) the residual for the first trial structure obtained optically was about 0·50 but one Fourier synthesis, using signs derived optically, reduced the residual to about 0·25.

It is also useful to study the shapes of the individual peaks in a transform. There is often a very marked characteristic shape, and the signs of the weak reflexions, if required, can often be deduced—even though they lie on regions too weak to be recorded photographically—by studying the shapes of the neighbouring peaks and remembering that the sign changes every time a zero line is crossed.

Reliability

The two most probable sources of error are first in the superposition of the reciprocal net upon the original transform and secondly in enlargement. The accuracy of both these operations depends very strongly on the quality of the calibration fringes.

Errors of a more fundamental kind may occur because of the inaccurate representation of variation in scattering factor. In addition to the obvious differences in the form and magnitude of the scattering factor for different atoms, there may also be differences for atoms of the same type in different chemical configuration; no account is taken, for example, of the difference between a single carbon atom and carbon in a methyl group. In sign determination, these errors are important only for reflexions at small angles, and of small amplitude.

Experimental determinations have been checked against normal computational methods and in a typical example out of 126 reflexions only 17 were found to have doubtful signs. These reflexions had an amplitude less than 5% of the maximum observed and, as pointed out earlier, would not be included in a Fourier synthesis.

The method has now been used in this department on a number of unknown structures, e.g. purpurogallin (Taylor, 1952*b*), triphenylene (Pinnock, Taylor & Lipson, 1955), bishydroxydurylmethane (Chaudhuri & Hargreaves, 1955), and is at present being used on a number of other structures as yet incompletely determined.

APPENDIX I

Formula for the Leitz two-bath developer as quoted in *Wall's Dictionary of Photography* under 'Fine-grain development':

Bath 1

Metol	5 g.
Sodium sulphite (anhydrous)	100 g.
(or Sodium sulphite (7 H_2O)	200 g.)
Water	to 1000 cm.^{3}

Bath 2

Borax	10 g.
Water	to 1000 cm.^{3}

Develop 3–6 min. in Bath 1 and 2–4 min. in Bath 2.

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The Structure of $MoBe_{12}$*

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The structure of $MoBe_{12}$ has been determined. Formal valences of 3·36 for molybdenum and 1·85, 2·27 and 2·59 for beryllium have been calculated using Pauling's single-bonded metallic radii, and are interpreted in terms of electron shift.

Introduction

In recent years considerable attention has been given to intermetallic compounds of the type MX_{12} and MX_{13}. Most structures investigated have been complex (such as $ZrBe_{13}$ (Baenziger & Rundle, 1949), and $TiBe_{12}$ (Raeuchle & Rundle, 1952)). The structure of the latter, in fact, is not yet completely known. When, therefore, the opportunity arose to study the molybdenum analog, which promised to be simpler, a structural study was undertaken in the hope of finding an underlying structural principle for this group of compounds.

The Mo–Be compound was first reported by Gordon. McGurty, Klein & Koshuba (1951). Although our samples were obtained from ingots prepared by Gordon and Koshuba, there is some doubt as to the actual identity of the two compounds. Chemical analysis showed the composition of the crystals used in the present investigation to be $MoBe_{12}$, while Gordon *et al.* reported $MoBe_{13}$. The structural analysis subsequently confirmed our composition for the samples studied. Their lattice constants indicated a unit cell which, if it had the structure found by us, would be face centered. (We have chosen a smaller cell which is body centered.) There is, however, good agreement between our lattice constants and theirs, when transformed to identical axes. We find the space group to

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