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The Application of the Isomorphous-Replacement Method in the Determination of Centrosymmetric Structures

By A. Hargreaves

Physics Department, College of Science and Technology, Manchester 1, *England*

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A description is given of a simple procedure for determining the signs and the absolute values of the structure factors of a pair of isomorphous crystals when only relative values of the structure amplitudes are known.

1. Introduction

Isomorphous-replacement methods (Lipson & Cochran, 1953; Robertson, 1953) have been successfully applied in the determination of many different kinds of crystal structures. They have the particular merit that they do not require the use of initial assumptions about the stereochemistry of the structure, and they are especially valuable, therefore, when the structure is very complex or of an unusual type.

Absolute values of the structure amplitudes are usually needed in isomorphous-replacement methods. For most structures it is unlikely that the statistical method of Wilson (1942) for placing relative intensities on an absolute scale will be sufficiently accurate; and facilities for measuring absolute intensities experimentally, such as those used by Robertson (1936), are not always readily available. This paper describes a method of applying the isomorphous-replacement technique which can be used when only relative values of the structure amplitudes are known. A brief account of the method has been given by Lipson & Cochran (1953). Besides enabling the phases of the structure factors to be determined it may also be used to place the structure amplitudes on an absolute scale and to derive a value for the constant B in the temperature factor $\exp(-B\sin^2\theta/\lambda^2)$. Isomorphous-replacement methods are less powerful and more complicated when the structures examined are non-centrosymmetric (Bokhoven, Schoone & Bijvoet, 1951; Harker, 1956), and the method discussed here can be applied to centrosymmetric structures only.

2. Theory and method

The structure factors of an isomorphous pair of centrosymmetric crystals A and B can be written as

$$F_A(hkl) = \sum_{n=1}^{N-M} f_n \cos 2\pi(hx_n+ky_n+lz_n) + \sum_{m=1}^{M} f_A \cos 2\pi(hx_m+ky_m+lz_m) \quad (1)$$

and

$$F_B(hkl) = \sum_{n=1}^{N-M} f_n \cos 2\pi(hx_n+ky_n+lz_n) + \sum_{m=1}^{M} f_B \cos 2\pi(hx_m+ky_m+lz_m) \quad (2)$$

in the usual notation, (x_m, y_m, z_m) being the parameters of the replaceable atoms and (x_n, y_n, z_n) those of the remaining atoms. It is assumed that corresponding atoms have identical parameters in the two crystals. Usually the M replaceable atoms occupy equivalent positions in the unit cell and the summation $\sum_{m=1}^{M} \cos 2\pi(hx_m+ky_m+lz_m)$ may be substituted by an expression giving the combined scattering from the set of replaceable atoms (*International Tables for X-ray Crystallography*, 1952).

Combining equations (1) and (2), we have

$$F_A(hkl)-F_B(hkl) = \sum_{m=1}^{M} (f_A-f_B) \cos 2\pi(hx_m+ky_m+lz_m)\,. \quad (3)$$

The scales of the experimentally observed structure amplitudes $F'_A(hkl)$ and $F'_B(hkl)$ are related to the absolute scale by constants C_A and C_B with magnitudes given by $F_A(hkl)=C_AF'_A(hkl)$ and $F_B(hkl)=C_BF'_B(hkl)$. Assuming that the temperature factors are the same for both crystals then $f_A = \{f_0\}_A \exp(-B\sin^2\theta/\lambda^2)$ and $f_B = \{f_0\}_B \exp(-B\sin^2\theta/\lambda^2)$, where $\{f_0\}_A$ and $\{f_0\}_B$ are the scattering factors at absolute zero. Equation (3) may now be re-written as

$$C_AF'_A(hkl)-C_BF'_B(hkl) = \sum_{m=1}^{M} (\{f_0\}_A-\{f_0\}_B) \times \cos 2\pi(hx_m+ky_m+lz_m) \exp(-B\sin^2\theta/\lambda^2)$$

or

$$C_A\left\{\frac{F'_A(hkl)}{p(hkl)}\right\} = C_B\left\{\frac{F'_B(hkl)}{p(hkl)}\right\} + \exp(-B\sin^2\theta/\lambda^2)\,, \quad (4)$$

where

$$p(hkl) = \sum_{m=1}^{M} (\{f_0\}_A-\{f_0\}_B) \cos 2\pi(hx_m+ky_m+lz_m) \quad (5)$$

is a quantity which can be calculated for each reflexion *hkl* providing the parameters of the replaceable atoms are known. The determination of the positions of the replaceable atoms is an essential preliminary to all isomorphous-replacement methods but it is a relatively simple problem when the replaceable atoms are heavy in one of the isomorphous pair of crystals.

For reflexions within a small range of θ the exponential term in equation (4) will be almost constant and a plot of $F'_A(hkl)/p(hkl)$ against $F'_B(hkl)/p(hkl)$ will be linear. If $f_A > f_B$ then the plotted points will lie on a line such as *PS* in Fig. 1. In practice the points will have an appreciable scatter about *PS* because of errors in the experimental data.

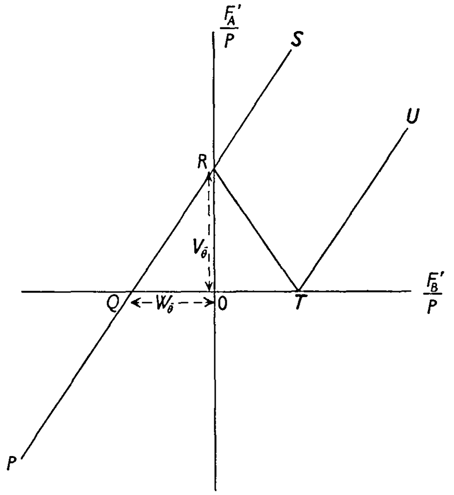

Fig. 1. The principle of the graphical method for determining the signs of F'_A and F'_B.

The first step is to plot $|F'_A/p|$ against $|F'_B/p|$ since the signs of F'_A and F'_B are unknown. Reflexions for which both F'_A/p and F'_B/p are positive will then lie on the portion *RS* of the straight line *PS*; those for which both F'_A/p and F'_B/p are negative will lie on *TU*, a straight line parallel to *PS*; those for which F'_A/p is positive and F'_B/p negative will lie on a straight line *RT* which has a slope numerically equal to that of *PS* but opposite in sign; there are no reflexions for which F'_A/p is negative and F'_B/p positive; this condition follows from the assumption $f_A > f_B$. The most satisfactory way of determining the correct signs for F'_A and F'_B is to change the signs of F'_A/p and F'_B/p until all the plotted points lie on *PS*. The signs of p are known and therefore the signs of F'_A and F'_B can be deduced immediately.

A separate graph is drawn for each of the ranges of θ into which the structure factors have been divided. The unknown structure can then be determined directly by computing a Fourier synthesis in which the coefficients F'_A or F'_B have the graphically determined signs.

A simple extension gives values for the temperature factor and the constants required to place the observed structure factors on the absolute scale. If the straight line *PS* cuts the axes of the graph (Fig. 1) with intercepts $RO = V_{\bar\theta}$ and $OQ = W_{\bar\theta}$, where $\bar\theta$ is the average value of θ over the range covered by the graph, then from equation (4)

$$C_A \,.\, V_{\bar\theta} = \exp\,(-B\sin^2\bar\theta/\lambda^2)$$

and

$$0 = C_B \,.\, W_{\bar\theta} + \exp\,(-B\sin^2\bar\theta/\lambda^2)\,.$$

The constants C_A, C_B and B are deduced from plots of $\log V_{\bar\theta}$ and $\log W_{\bar\theta}$ against $\sin^2\bar\theta$. It is sufficient to determine $V_{\bar\theta}$ and $W_{\bar\theta}$ for reflexions of small θ if only C_A and C_B are required; the exponential term can then be taken as unity or estimated more exactly (i) by assuming a value for B of the order of magnitude expected for the structure under examination or (ii) by Wilson's method.

3. Application of the method

The method described in § 2 has been used in the determination of the structure of zinc *p*-toluene sulphonate hexahydrate, $(CH_3.C_6H_4.SO_3)_2.Zn.6H_2O$, (Hargreaves, 1957), which is isomorphous with magnesium *p*-toluene sulphonate hexahydrate. For these materials the space group is $P2_1/n$ and there are two formula units in the unit cell; the replaceable atoms (zinc and magnesium) therefore lie in special positions at the symmetry centres (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the trigonometrical factor in equation (5) becomes unity for all *h0l* reflexions. There are two replaceable atoms in each unit cell and equation (5) may now be written as

$$p(h0l) = 2(\{f_0\}_{Zn} - \{f_0\}_{Mg})\,.$$

Fig. 2(*a*) gives a plot of F'_{Zn}/p against F'_{Mg}/p for all observed *h0l* reflexions over the range $\sin\theta = 0{\cdot}0$–$0{\cdot}4$; points for which either F'_{Zn}/p or F'_{Mg}/p is negative were initially plotted in the positive quadrant of Fig. 2(*a*) at positions indicated by crosses. It can be seen that there is no difficulty in deducing the correct signs for each pair of structure factors; for 20 pairs both signs are positive and for 9 pairs both are negative whilst for the 10,0,0 reflexions F_{Zn} is positive and F_{Mg} negative.

In Fig. 2(*b*) F'_{Zn} is plotted against F'_{Mg} for the reflexions shown in Fig. 2(*a*). The scatter of the points about *P'S'* in Fig. 2(*b*) is not much greater than that about *PS* in Fig. 2(*a*) in spite of the variation in p from 36 to 25 over the range $\sin\theta = 0{\cdot}0$–$0{\cdot}4$. It is clear that the signs of F_{Zn} and F_{Mg} can be determined just as easily from Fig. 2(*b*). The signs of the other structure factors $F(h0l)$ were therefore determined simply by plotting F'_{Zn} against F'_{Mg} for five more ranges of $\sin\theta$. Sign determinations from $F'_{Zn}-F'_{Mg}$ plots are only possible, of course, because the replaceable atoms occupy special positions for which the trigonometrical part of p is constant.

The structure of the zinc salt was determined from a Fourier synthesis which included all of the 165 observable reflexions. On calculating $F(h0l)$, using the atomic positions deduced from the electron-density map (Hargreaves, 1957), it was found that with the exception of $F(\overline{18},0,2)$ their signs agreed with those determined by the graphical method. The one error in sign arose because none of the photographs of the magnesium salt was as dense as the most dense photograph of the zinc salt. The $\overline{18},0,2$ reflexion is so weak that it was only just observable in the densest film of the zinc salt; $F(\overline{18},0,2)$ should be more strongly negative for the magnesium salt than for the zinc salt, which has a negative calculated value, but in fact the $\overline{18},0,2$ reflexion was not observed at all in the less dense magnesium photographs.

The experimental values of $F(h0l)$ were deduced by visual estimation of the intensities of reflexions recorded on multiple-film Weissenberg photographs. The usual precautions were taken to obtain reliable intensities for the zinc salt since its structure was required; about half a dozen reflexions were scarcely visible in the photographs, however, and their estimated intensities are subject to large error. For the magnesium salt the intensity of each reflexion was estimated once only, and the size and shape of the crystal specimen were such that up to 25% *variation* can be expected in the absorption factor for different reflexions at a given Bragg angle. Errors in the intensities are partly responsible for the scatter of the plotted points about *PS* in Fig. 2(*a*). The correct determination of the signs of the structure factors for the zinc and magnesium salts shows that the isomorphous-replacement method can be successfully applied with relatively crude measurements of intensity.

In the example discussed here the replaceable atoms are in special positions and make the maximum possible contribution to all reflexions. When the replaceable atoms are in general positions it will not usually be possible to determine the correct signs graphically for all the structure factors; the errors in plotting will become too large when the replaceable atoms make very small contributions to the scattering, i.e. for reflexions with small values of $p(hkl)$; also the errors introduced by assuming that the atomic co-ordinates are exactly the same in the two structures become more important and may considerably reduce the proportion of high-angle reflexions which can be given the correct signs.

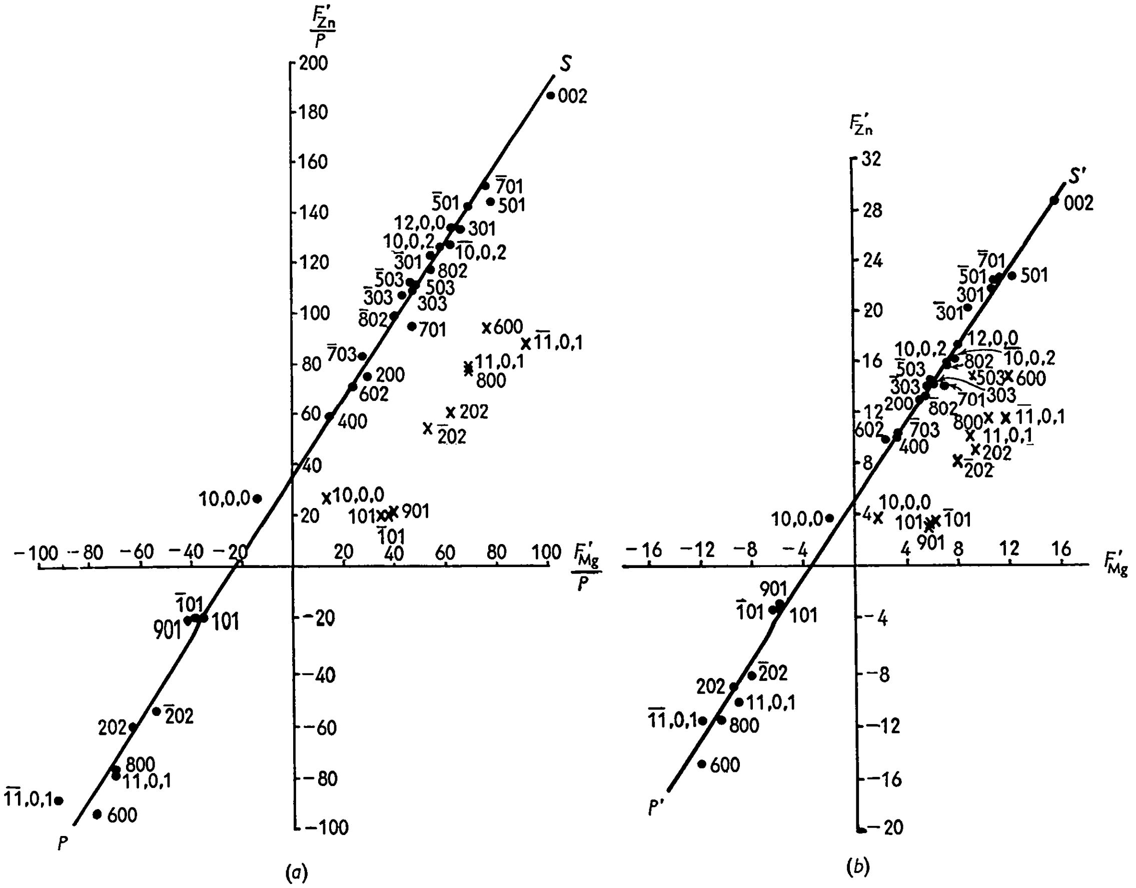

Fig. 2. (*a*) Determination of the signs of the structure factors of zinc *p*-toluene sulphonate hexahydrate for *h0l* reflexions with values of sin θ ranging from 0·0 to 0·4. (*b*) Simplified method of determining the signs of the structure factors shown in (*a*)

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The Structure of $BaBOF_3$

By D. M. CHACKRABURTTY

Department of General Physics and X-rays, Indian Association for the Cultivation of Science, Calcutta 32, India

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With the help of Lipson's method, $BaBOF_3$ was shown to be orthorhombic with $a = 8{\cdot}78 \pm 0{\cdot}03$, $b = 5{\cdot}41 \pm 0{\cdot}02$, $c = 7{\cdot}16 \pm 0{\cdot}02$ Å. On the basis of the space group *Pnma*, the structure was worked out and is discussed in detail.

Introduction

The spacings and $\sin^2\theta$ values of $BaBOF_3$, obtained in powder form by Roy (1955), were calculated from the powder patterns taken with Cu $K\alpha$ radiation. As the substance was found, by the application of the method of Hesse (1948), not to belong to the cubic, tetragonal or hexagonal systems, Lipson's method (1949) for orthorhombic systems was tried and used successfully.

For orthorhombic crystals $\sin^2\theta = Ah^2+Bk^2+Cl^2$. It was shown by Lipson that if $\sin^2\theta_{100}=A$, $\sin^2\theta_{010}=B$ and $\sin^2\theta_{001} = C$ then in general,

$$\sin^2\theta_{1kl}-\sin^2\theta_{0kl} = \sin^2\theta_{100};$$

and similarly for the constants B and C. Here A occurs as differences between the $\sin^2\theta$ values provided the h values differ by unity and the kl values for the two lines are the same.

To find such differences in $BaBOF_3$, the diagrammatic method described by Lipson (1949) was used. From the plot the possible values deduced were $A = 0{\cdot}0077$, $B=0{\cdot}02031$ and $C=0{\cdot}0116$. Since $A=\lambda^2/4a^2$, $a = 8{\cdot}78 \pm 0{\cdot}03$ Å (λ(Cu $K\alpha$) $= 1{\cdot}5418$ Å); similarly, $b = 5{\cdot}41 \pm 0{\cdot}02$ Å and $c = 7{\cdot}16 \pm 0{\cdot}02$ Å. The possible space group, after indexing of all lines, is *Pnma*. The calculated density, D_x, is 4·27 g.cm.$^{-3}$ and the observed density, D_m, is 4·25 g.cm.$^{-3}$. The number of molecules per unit cell is 4.

Atomic coordinates

On the basis of the space group *Pnma*, and taking into consideration similar structures like $BaSO_4$ (James, 1925) and $KMnO_4$ (Mooney, 1931), and placing 8 F atoms in general positions, and 4 Ba, 4 B, 4 F, and 4 O atoms in special positions, the following atomic coordinates were derived after matching fairly the observed and calculated intensity of each line:

4Ba	in 4(*c*)	with $x = 0{\cdot}182$,	$y = 0{\cdot}25$,	$z = 0{\cdot}162$.
4B	in 4(*c*)	with $x = 0{\cdot}069$,	$y = 0{\cdot}25$,	$z = 0{\cdot}695$.
$4F_I$	in 4(*c*)	with $x = -0{\cdot}072$,	$y = 0{\cdot}25$,	$z = 0{\cdot}595$.
4O	in 4(*c*)	with $x = 0{\cdot}191$,	$y = 0{\cdot}25$,	$z = 0{\cdot}562$.
$8F_{II}$	in 8(*d*)	with $x = 0{\cdot}080$,	$y = 0{\cdot}042$,	$z = 0{\cdot}816$.

If the positions of F_I and O were interchanged, a fair discrepancy in the observed and calculated intensities of some important lines was observed. On the basis of the above coordinates the intensity of each line was calculated. For each calculated intensity, the polarization factor, multiplicity factor and absorption factor were taken into account. The absorption factor was calculated in the manner given in the *Internationale Tabellen* (1935). No correction was made, however, for the temperature factor. The values of $\sin^2\theta_o$, $\sin^2\theta_c$, I_o, I_c and the spacings are given in Table 1, in which some of the unobserved lines (such as 101, 121, 013, 200) are included to justify the correctness of the coordinates derived. Owing to heavy background scattering at low angles, the 101 and 200 reflexions, being very weak, were masked and could not be measured. The calculated d values of all the above unobserved lines are included in the table.

Discussion of the structure

The unit cell of the orthorhombic structure found for $BaBOF_3$, projected on its b face, is shown in Fig. 1.