

Identification of Enantiomorphically-Related Space Groups by Electron Diffraction – a Second Method

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A method is described for enantiomorphic space-group determination which depends upon a simple analysis of a single convergent-beam diffraction pattern. The method, which in principle may be applied to any enantiomorph, is here used to identify the space group of dextrorotatory α -quartz. In this, a four-beam pattern is analysed by visual matching to an analogue computer display.

Introduction

In a recent publication (Goodman & Secomb, 1977) a method was described for distinguishing between two enantiomorphous space-groups, and this was illustrated by a space-group determination for dextrorotatory α -quartz. This method was essentially a classical one of combining data from several settings reached by crystal goniometer rotations of known sense about a particular axis. An essential step in this procedure was the determination of direction in one, or more, non-centrosymmetric projections and this determination involved numerical N -beam calculation.

Following this, an effort was made to find an alternative method for enantiomorphic determination which was firstly non-numerical and secondly which could be applied to a single diffraction pattern involving if possible a simple interaction (*i.e.* a three or four-beam interaction). In the first aim we have been unsuccessful and some reasons for this are given in our discussion. We present here a single-pattern four-beam analysis which, although still dependent upon numerical evaluation, has the advantage over the classical method of depending only upon information contained in one convergent-beam pattern. Furthermore, in point of convenience, the calculation required involves only four-beam coupling and hence can be performed with an analogue-computer video-display system (Johnson, 1968).

Enantiomorphic determination from a four-beam pattern

Fig. 1 shows a convergent-beam pattern from dextrorotatory α -quartz in which the main dynamic effect is a four-beam interaction involving the $\bar{2}240$, $\bar{3}301$ and $\bar{5}141$ reflexions. The same pattern was used in the earlier work (Goodman & Secomb, 1977, Fig. 8) simply to obtain an estimate for $V_{\bar{3}301}$. However, additional information relating to structure-factor phases is contained in the main diffracted-beam intensities. The most obvious features of these three intensity

distributions are (i) a marked asymmetry within the $\bar{2}240$ pattern about the four-beam interaction intersection point; (ii) a break in the patterns of all three diffracted beams at this point with an additional peak in the case of the $\bar{5}141$ beam. It was found from the computation that the central peak of the $\bar{5}141$ beam is the intensity feature most sensitive to enantiomorphic change. Other features were either only weakly or inappreciably dependent on enantiomorph. Reasons for this, and criteria for selecting suitable patterns for enantiomorphic determination are given in the next section.

Table 1 shows the scattering amplitudes and phases for the zero and first upper layer of $D_3^+(P3_121)$ α -quartz, *i.e.* the space-group allocated by de Vries (1958) to laevorotatory α -quartz.

The structure factor of a crystal and its enantiomorph are related by complex conjugation. A convincing 'experimental' demonstration of this is obtained by the following considerations. The transformation of one space group into its enantiomorph is achieved by a single reflexion in any mirror-plane. This transformation applies to both real and reciprocal space. The criterion for the choice of the mirror plane is that it should contain the c axis and one other specific symmetry axis: in this case the anti-symmetry axis parallel to $[\bar{1}\bar{1}20]$. With any other choice of mirror plane the resulting enantiomorph would require a rotation in order to bring its kinematic diffraction pattern into directional coincidence with that of the first crystal. The symmetry-imposed condition means that the scattering vectors in a particular diffraction pattern have scattering factors which are either unchanged and real, or complex-conjugated with enantiomorphic transformation. The scattering vectors involved in the present problem are given in Fig. 2, which is a diagrammatic representation of the four-beam interaction of Fig. 1. The line of intersection of the transforming mirror plane with the plane of the zero and first upper layers is indicated by the lines $r-r$ in Table 1. The relevant scattering factors for the two enantiomorphs are given in Table 2.

Table 1. Structure factors for α -quartz in hexagonal display

(a) and (b) give the amplitudes and phases for the zero layer; (c) and (d) the amplitudes and phases for the first upper layer. The tabulation is for the space group D_3^4 . Values for D_3^6 are obtained by reflexion in the vertical mirror plane whose intersection with the layers is indicated 'r-----r'. Debye-Waller factors of $B_{Si} = 0.39$, $B_O = 0.8$ were used in the structure-factor calculation. The 2240, 3301 and 5141 reflexions used in the experiment are encircled.

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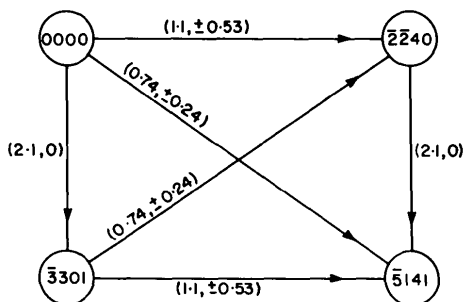


Fig. 2. A diagrammatic representation of the four-beam interaction evident in Fig. 1. Real and imaginary components of the scattering factors are given in brackets beside the appropriate scattering vector, showing alternative signs corresponding to the two enantiomorphs.

Table 2. Values of the real and complex amplitudes of the scattering vectors shown in Fig. 2 for the two space groups of α -quartz

Space group	$\bar{2}240$	$\bar{3}301$	$\bar{5}141$
D_3^4	$1.1 + i(0.53)$	2.1	$0.74 + i(0.24)$
D_3^6	$1.1 - i(0.53)$	2.1	$0.74 - i(0.24)$

The four-beam problem was set up on an analogue computer, an earlier version of which was described by Johnson (1968), and calculations carried out for both the space groups with the two sets of structure factors given in Table 2. The results appear in Fig. 3.

Initially, a crystal thickness was assumed which was determined kinematically from the weak $\bar{1}\bar{1}20$ re-

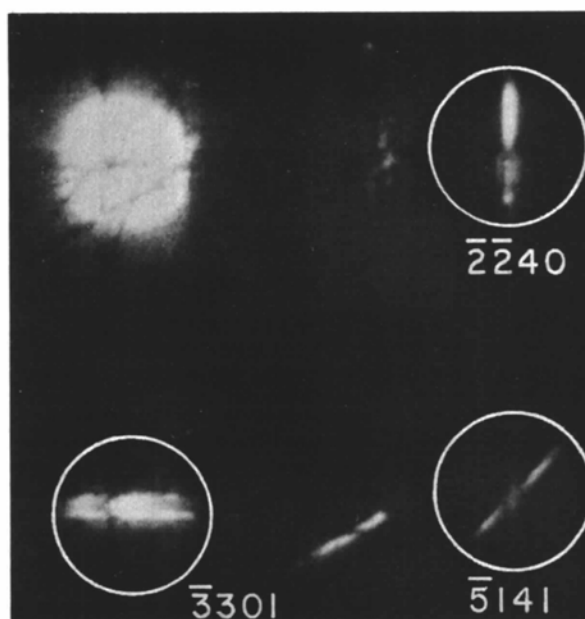
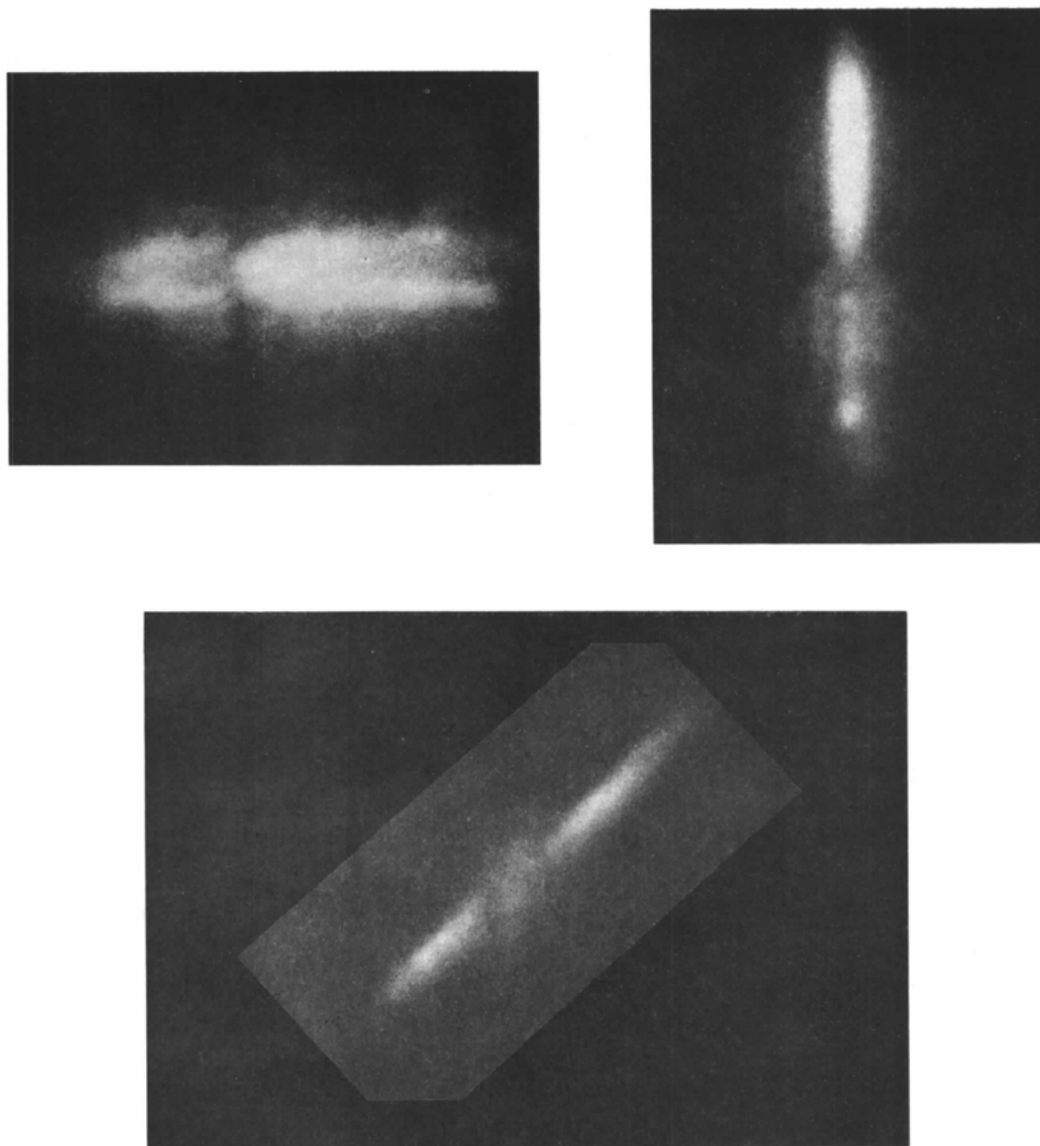


Fig. 1. Convergent-beam pattern, taken at 80 kV, from a sample of dextrorotatory α -quartz. Diffracted beams involved in an approximate four-beam interaction are encircled and indexed.



(a)

Fig. 3. (a) Enlargements of the diffracted beams $\bar{2}\bar{2}40$, $\bar{3}301$, $\bar{5}141$ from Fig. 1.

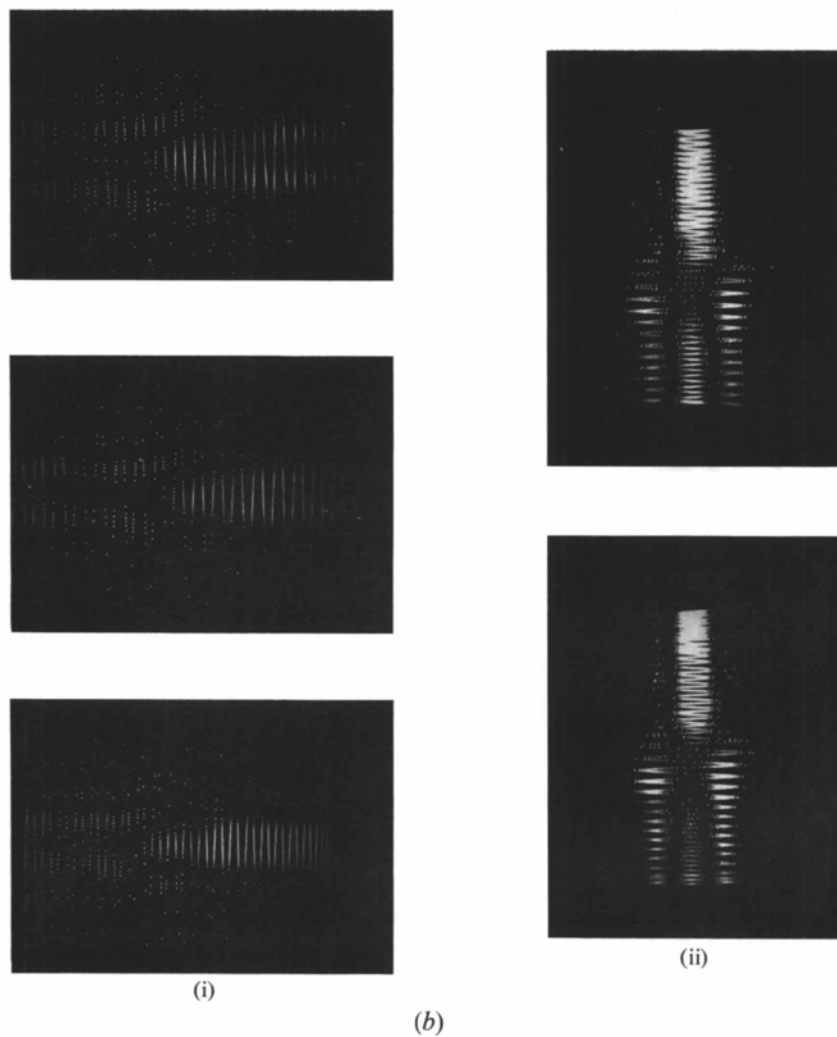


Fig. 3. (*cont.*) (*b*) Results of a four-beam dynamic calculation from the video-display of an analogue computer for the following beams and thicknesses: (i) 2240 beam with the thicknesses 1600 \AA (top pattern) and 1760 \AA , and (ii) 3301 beam with the thicknesses (proceeding from the top): 1600 , 1760 and 1930 \AA respectively.

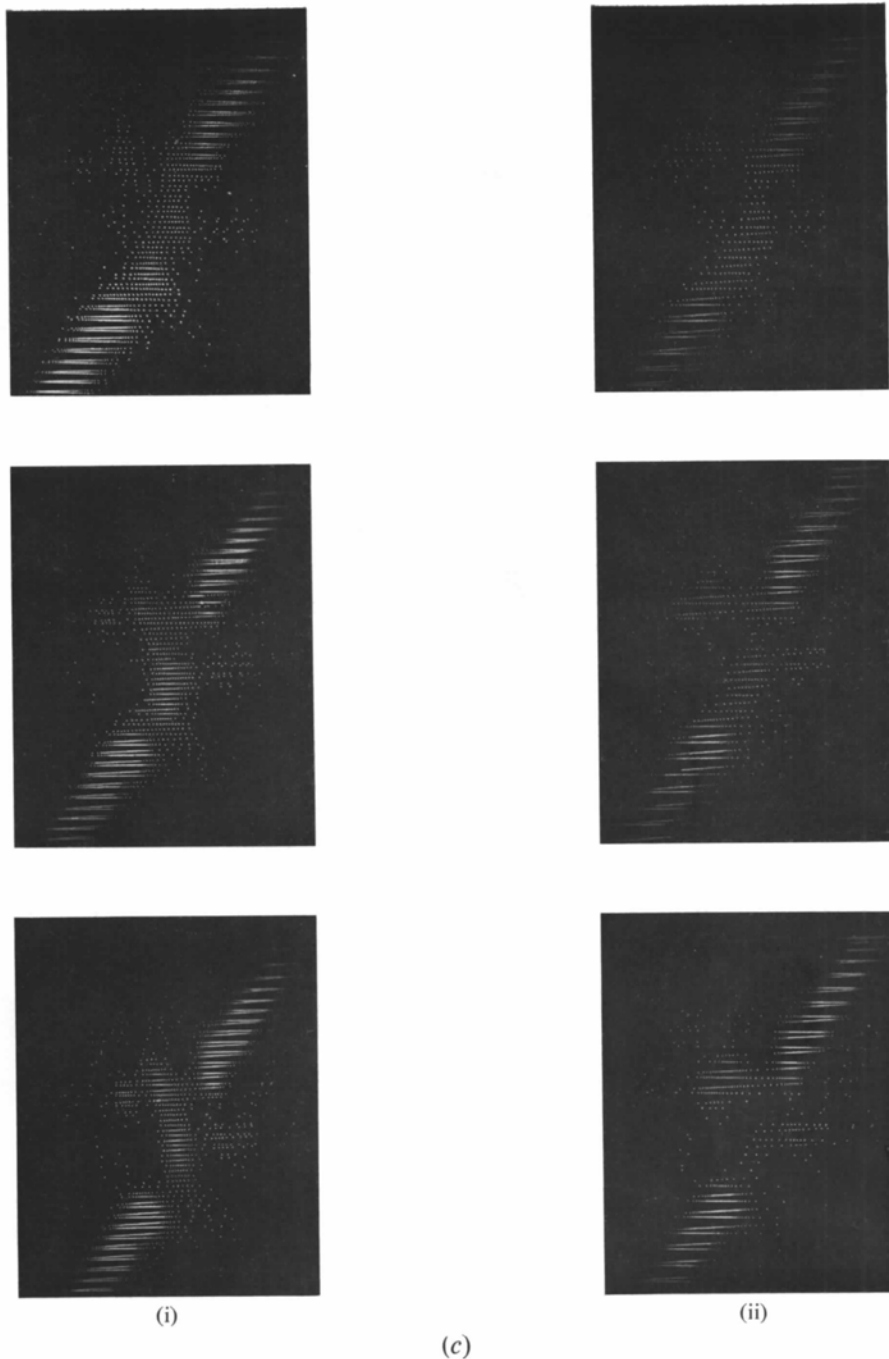


Fig. 3. (*cont.*) (c) Results from the same calculation for the $\bar{3}141$ beam, showing the contrasting result from the two enantiomorphically related space-groups, (i) D_3^2 , and (ii) D_3^4 . The thickness sequence in both these figures is 1600, 1760 and 1930 Å running from top to bottom.

flexion. This value, which may be fairly near the actual crystal thickness, is 2200 Å (Goodman & Secomb, 1976). However, an effective thickness now had to be determined from internal evidence within the four-beam pattern. This was done by matching the four-beam-calculated results for the 2240 and 3301 (relatively space-group insensitive) intensity distributions, and finally those for the $\bar{5}141$ distribution, to the observed distributions. A different, and in this case a lower, 'thickness' value is obtained in this way as a result of the neglect of weak-beam interactions. Results for the $\bar{2}240$ reflexion show that the effective thickness lies between 1600 Å and 1760 Å. Results for the $\bar{3}301$ reflexion, which has more thickness-sensitive detail, give a best-fit thickness value of 1760 ± 150 Å. An examination of the results for the $\bar{5}141$ beam shows that a clear space-group identification is possible for thickness values between 1600 Å and 2200 Å. Within this range the space group D_3^4 ($P3_121$) yielded a central minimum, in contrast with the central maximum given by the space group D_3^6 ($P3_221$) and observed experimentally. The best fit with experiment was at the thickness 1760 Å and for the space-group D_3^6 ; D_3^4 gave no agreement at any thickness within the range of the calculations. It was therefore concluded that our space group was in fact D_3^6 in agreement with our previous determination for this specimen.

Criteria for selecting four-beam patterns

The possible use of three-beam interactions for identification of enantiomorphs was earlier mentioned by Kambe & Molière (1970) in a review article, although they gave no practical details. Kambe's (1957) earlier example was confined to centrosymmetric phase determination. Mathematically the separation of enantiomorphs presents the same problem as the identification of polar direction in a non-centrosymmetric structure, namely that of distinguishing between a given set of structure factors, and the set related by complex conjugation. This involves the phenomenon now known as the 'break-down of Friedel's law' in dynamic diffraction.

Although it is certainly possible to obtain a Friedel's law break-down in a three-beam interaction, a four-beam interaction is greatly to be preferred in practice. There are two main reasons for this. (1) In general, the four-beam interaction has a greater dynamic content, *i.e.* there are a greater number of scattering paths for each order process, and a greater N -beam to two-beam contribution to particular diffracted beams (see later note). (2) In all but triclinic structures (and these do not contribute to the enantiomorphic-pair space groups), a four-beam pattern is more readily obtained in the useful region of reciprocal space neighbouring a zone axis.

To determine whether a particular four-beam pattern is a good choice for enantiomorphic analysis, one first has to examine the principles involved.

The two interference phenomena observable in Fig. 1 and directly attributable to the four-beam interaction are the line asymmetries and the central breaks in the intensities of the diffracted beams at the point corresponding to simultaneous exact excitation of the three reflexions. The line asymmetries, as in the three-beam case, can be demonstrated to be sensitive to structure-factor phases (and hence useful in a general structure analysis), but insensitive to enantiomorphic transformation.* We therefore concentrate on the central, or 'thin-phase-grating' point, so called here because we need only the thin-phase-grating terms from the general solution (Cowley & Moodie, 1962) to evaluate the four-beam interaction result for this point. (This is of value in analysis rather than calculation since the Born series is tedious to evaluate numerically.)

Using the Born series expansion for the thin-phase-grating (Cowley & Moodie, 1962), one can show that this break-down of Friedel's law occurs as a result of adding the n -even terms (where ' n ' is the order of a scattering path) to the n -odd terms (see for example Goodman & McLean, 1976). Following equation (4) from Goodman & McLean (1976), a break-down of Friedel's law will occur, provided either one of the contributing structure-factor products $En(\mathbf{hk})$, for n -odd or n -even respectively, is complex. This condition in turn is met when any one of the contributing structure factors is complex in a non-trivial way, *i.e.* being a Fourier component of an asymmetric potential distribution in 'real' space. To obtain a substantial or readily observable break-down requires that the complex structure factor or structure factors concerned have substantial moduli, $|V_{\mathbf{h}}|$, and phase angles $\alpha_{\mathbf{h}}$ differing appreciably from 0 or π .

It can be shown by a more detailed examination of the relevant products $En(\mathbf{hk})$ for the four-beam configuration depicted in Fig. 2 that these requirements are met for the $\bar{2}240$ and $\bar{5}140$ beams but not for the $\bar{3}301$ beam (the scattering factor V_{3301} being real). The fact that the corner $\bar{5}140$ beam has the greater sensitivity to enantiomorphic change, as found for example by calculation, is due to the relatively low value of $|V_{\bar{5}140}|$ resulting in a lesser domination of the intensity distribution by the two-beam contribution (which, on its own, contains no phase information). This can be seen experimentally by inspection of Fig. 1.

From these considerations, we may examine the structure-factor phases for hexagonal or β -quartz. The phases for the first upper layer of D_6^5 ($P6_422$) β -quartz are shown in Table 3(a). The phases for the zero layer are all 0 or π , since the hexagonal structure has a centrosymmetric projection. We can see from the encircled phases that the same orientation used in

* In four-beam cases such as shown in Fig. 1 it is often possible to understand the line asymmetry in the two strongest reflexions from a three-beam interaction ignoring the diagonal beam, and that in the diagonal beam from the four-beam interaction. With these simplifications, a ready interpretation of the line asymmetries can be made, for example, by the procedure outlined by Goodman (1973).

Table 3. (a) Hexagonal display of structure-factor phases for the first upper layer of β -quartz [space group $D_6^2(P6_422)$];
 (b) Equivalent structure-factor phases obtained by calculating for the Si atoms only in β -quartz

<p>(a)</p> <table style="width: 100%; text-align: center; border-collapse: collapse;"> <tr> <td>-0.8</td><td>$\frac{2\pi}{3}$</td><td>0.6</td><td>$-\pi$</td><td>-0.6</td><td>$-\frac{2\pi}{3}$</td><td>0.8</td> </tr> <tr> <td>-2.7</td><td>$\frac{2\pi}{3}$</td><td>-1.8</td><td>1.8</td><td>$-\frac{2\pi}{3}$</td><td>2.7</td><td></td> </tr> <tr> <td>$\frac{\pi}{3}$</td><td>-0.3</td><td>$-\frac{\pi}{3}$</td><td>π</td><td>$\frac{\pi}{3}$</td><td>0.3</td><td>$-\frac{\pi}{3}$</td> </tr> <tr> <td>2.4</td><td>$\frac{\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$-\frac{\pi}{3}$</td><td>-2.4</td><td></td> </tr> <tr> <td>r -----</td><td>0</td><td>π</td><td>0</td><td>-</td><td>0</td><td>π</td><td>0</td><td>-----</td><td>r</td> </tr> <tr> <td>-2.4</td><td>$-\frac{\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$\frac{\pi}{3}$</td><td>2.4</td><td></td> </tr> <tr> <td>$-\frac{\pi}{3}$</td><td>0.3</td><td>$\frac{\pi}{3}$</td><td>π</td><td>$-\frac{\pi}{3}$</td><td>-0.3</td><td>$\frac{\pi}{3}$</td> </tr> <tr> <td>2.7</td><td>$-\frac{2\pi}{3}$</td><td>1.8</td><td>-1.8</td><td>$\frac{2\pi}{3}$</td><td>-2.7</td><td></td> </tr> <tr> <td>0.8</td><td>$-\frac{2\pi}{3}$</td><td>-0.6</td><td>π</td><td>0.6</td><td>$\frac{2\pi}{3}$</td><td>-0.8</td> </tr> </table>	-0.8	$\frac{2\pi}{3}$	0.6	$-\pi$	-0.6	$-\frac{2\pi}{3}$	0.8	-2.7	$\frac{2\pi}{3}$	-1.8	1.8	$-\frac{2\pi}{3}$	2.7		$\frac{\pi}{3}$	-0.3	$-\frac{\pi}{3}$	π	$\frac{\pi}{3}$	0.3	$-\frac{\pi}{3}$	2.4	$\frac{\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$-\frac{\pi}{3}$	-2.4		r -----	0	π	0	-	0	π	0	-----	r	-2.4	$-\frac{\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$\frac{\pi}{3}$	2.4		$-\frac{\pi}{3}$	0.3	$\frac{\pi}{3}$	π	$-\frac{\pi}{3}$	-0.3	$\frac{\pi}{3}$	2.7	$-\frac{2\pi}{3}$	1.8	-1.8	$\frac{2\pi}{3}$	-2.7		0.8	$-\frac{2\pi}{3}$	-0.6	π	0.6	$\frac{2\pi}{3}$	-0.8	<p>(b)</p> <table style="width: 100%; text-align: center; border-collapse: collapse;"> <tr> <td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td> </tr> <tr> <td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td> </tr> <tr> <td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td> </tr> <tr> <td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td> </tr> <tr> <td>r -----</td><td>0</td><td>0</td><td>-</td><td>0</td><td>0</td><td>0</td><td>0</td><td>-----</td><td>r</td> </tr> <tr> <td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td> </tr> <tr> <td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td> </tr> <tr> <td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td><td>$\frac{2\pi}{3}$</td><td>$-\frac{2\pi}{3}$</td> </tr> <tr> <td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td> </tr> </table>	0	0	0	0	0	0	0	0	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	0	0	0	0	0	0	0	0	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	r -----	0	0	-	0	0	0	0	-----	r	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	0	0	0	0	0	0	0	0	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	$\frac{2\pi}{3}$	$-\frac{2\pi}{3}$	0	0	0	0	0	0	0	0
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Fig. 1 would give an enantiomorphic determination, since the diagonal terms for $\bar{5}141$ are complex with $\alpha_{\bar{5}141} = 0.8$. Because of the relatively small value of $V_{\bar{5}141}$, however, it would be advantageous to change the orientation slightly so as to excite the $\bar{2}241$ and $\bar{3}300$ reflexions together with the $\bar{5}141$ reflexion, and hence obtain two complex terms from the first upper layer (since both the $\bar{2}240$ and $\bar{3}300$ structure factors are now real).

It is informative to compare the phases of Table 3(a) with those of Table 3(b) calculated for the same β -quartz structure with only the Si atoms. With this table we can see that neither of these beam combinations would be sensitive to enantiomorphic change. For this simplified structure, working only from the information provided by this table, one would be forced to use a three-beam pattern for this purpose.

This comparison points out the numerical nature of the present determination, and its dependence upon oxygen coordinates to show up a space-group property.*

A more detailed discussion of the problem of phase

* The inability to find a non-numerical, thickness-independent solution to this particular space-group problem, as mentioned in our introduction, can be appreciated in a more general way as follows. If we consider only elastic scattering (without absorption) and therefore have an Hermitian scattering matrix, the scattering matrix for the crystal and its enantiomorph are related by the complex conjugation of the non-diagonal terms. In other words, the matrix for the enantiomorph is the transpose of that for the crystal:

$$M_{\text{enant.}} = M^T.$$

This means that the eigenvalues obtained for equivalent settings for the two cases are identical, and the eigenvectors are related by complex conjugation. This close relation (which follows from the known properties of M^T) virtually rules out the possibility of a simple, non-oscillating solution to this problem, and points out the difference between this and all other space-group-identification problems.

determination from three and four-beam patterns will be given elsewhere (Goodman, 1977).

Summary

The method for enantiomorphic identification outlined here has the advantage over the first method, referenced above, of requiring much less experimental and computational effort. It also offers a more reliable identification by eliminating the need to correlate experimental rotations of the specimen with those of a model structure.

It should always be possible in practice to find suitable three and four-beam patterns sensitive to enantiomorph, and with a real structure four-beam patterns should be available. Since four-beam patterns contain, in principle, a great deal more phase information than do three-beam patterns, they are to be preferred for this identification.

The use of three or four-beam patterns for enantiomorph analysis depends upon our ability to distinguish between upper and lower-layer reflexions. If we were unable to distinguish between the pattern involving $\bar{3}301$ and that involving $\bar{3}30\bar{1}$, the space-group could not be identified. We are able to make this distinction without recourse to manipulation history of the crystal by examining the weak reflexions accompanying the four involved in the strong interaction, a fact which can be understood by examining the appropriate Ewald constructions. In other words, we are dependent upon the finite curvature of the Ewald sphere to give us the sign of the third dimension, revealed by the sign of Ewald sphere curvature in the three-dimensional lattice. Thus, we solve a three-dimensional symmetry problem from a planar interaction, the out-of-plane information being supplied by other reflexions in the same pattern.

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The Systematization of Molecular Crystal Structures

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A scheme of classification of molecular crystal structures is proposed. The structures are divided into homo-, hetero and quasiheteromolecular. The next step of the classification is the division into chiral types which define the character of the systems of equivalent positions occupied by the molecules. Finally, the subdivision into chiral classes reflects the equality or inequality of symmetrically unrelated molecules. Statistical data are given about the distribution of quasiheteromolecular structures into chiral classes. The concept of an expanded (non-Fedorov) space group is proposed to describe such structures.

The rapid development of X-ray structural investigations has led to a large expansion in information about the structure of crystals. However most crystal chemists concentrate on the details of the molecular structure; the problem of the relative disposition of molecules in the crystal is often ignored or treated only superficially. Details of the architecture of molecular crystals are of interest because the solid-state reactivity and many physical and physico-chemical properties of crystalline substances depend on the molecular packing.

In this paper we propose a scheme of classification of molecular crystal structures. The Fedorov space groups are basic to this systematization but in certain cases this apparatus turns out to be insufficient. The geometrical features of some crystal structures can be described only with the aid of expanded non-Fedorov space groups.

First, we divide molecular crystals into *homomolecular* and *heteromolecular*. The former are built up of molecules having the same chemical composition and identical structural formula. The latter are composed of chemically different molecules. There is a smooth transition between these two types.

Naphthalene is a typical homomolecular crystal (Abrahams, Robertson & White, 1949; Cruickshank, 1957) where the molecules occupy the single system of

equivalent positions [$P2_1/c$, $Z=2$ ($\bar{1}$)*]. Here all the molecules are symmetrically related and therefore have the same structure and environment. In crystals of tolane (Robertson & Woodward, 1938; Samarskaya, Myasnikova & Kitaigorodsky, 1968) molecules occupy two systems of positions [$P2_1/c$, $Z=4$ ($\bar{1}$, $\bar{1}$)] and, though the symmetrically unrelated molecules are practically identical in geometry, their environments differ. In such cases, molecules of different structure can coexist in the same crystal. Thus, in crystalline isoleucine (Torii & Iitaka, 1971) half the molecules are *gauche*, the other half *trans* [$P2_1$, $Z=4$ (1, 1)]. We call crystals in which chemically identical molecules occupy more than one system of equivalent positions *quasiheteromolecular*.

Crystals of tolane-diphenylmercury are heteromolecular [$P2_1/c$, $Z=2$ ($\bar{1}$, $\bar{1}$)] (Kitaigorodsky, Myasnikova & Samarskaya, 1963). However, they do resemble tolane itself. The similarity between the molecules of diphenylmercury and diphenylacetylene (tolane) permits them to replace each other without significantly affecting the packing. A typical heteromolecular crystal with quite different molecules is the molecular complex α -D-glucose-urea (Snyder & Rosenstein,

* The symbol of the structural class to which naphthalene crystals belong is given; this concept is discussed below.