The author is very grateful to Dr B.T.M.Willis for constant encouragement. Thanks are also due to Dr A.C.Macdonald and Mr R.Jude for providing data on biphenyl and salicylic acid respectively, prior to publication.

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Acta Cryst. (1969). A**25**, 543

Phase Determination for Pseudo-Symmetric Centrosymmetric Crystals

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(*Received* 16 *November* 1968)

The Fourier transform of a symmetric atom group that is sampled asymmetrically by the reciprocal lattice may be deduced by inspection of the weighted reciprocal lattice. The symmetry of the atom group impresses a pseudo-symmetry on the weighted reciprocal lattice. Superposition of the pseudo-symmetric parts of the lattice gives an increased sampling of the whole Fourier transform, permits recognition of maxima and nodes, and hence provides phase information.

Introduction

The observed intensities of the X-ray diffraction maxima produced by a single crystal may be regarded as point samples of the continuous Fourier transform of the unit-cell contents (Taylor & Lipson, 1958). From some crystals, the sample interval provided by the reciprocal lattice is small enough to allow the whole transform to be deduced, as is essentially done in the 'heavy atom' method. Sample frequency may be increased by expansion of the unit cell, as in the case of horse haemoglobin (Boyes-Watson, Davidson & Perutz, 1947). In general, however, the sampling of the transform provided by the reciprocal lattice is too sparse to determine detail in the transform by examining the observed intensities.

Presence of pseudo-symmetry

A symmetric molecule or atom group has a symmetric Fourier transform. If the repeated atom groups comprising the crystal are not related by symmetry, the crystal itself will lack symmetry, and the reciprocal lattice will sample the transform asymmetrically.

Fig. 1(*a*) shows a hypothetical centro- and mirror-symmetric group of atoms, so arranged that the unit cell has only centrosymmetry. The weighted reciprocal lattice [Fig. 1(*c*)] has approximate mirror symmetry along the [45]* direction (shown in the Figure as a broken line). Such an approximate mirror will be called a pseudo-mirror. Comparison of Fig. 1(*b*) and (*c*) shows that on either side of the pseudo-mirror, reciprocal-lattice points give samples of different parts of a symmetric transform. The sample frequency provided by the reciprocal lattice can therefore be almost doubled by superimposing on the lattice its mirror image [Fig. 1(*d*)]. The same result is obtained if the pseudo-mirror along the $[\bar{5}4]^*$ direction is used. There is sufficient detail provided by Fig. 1(*d*) to derive the full Fourier transform, and in particular the sign of the transform at the reciprocal lattice points, if it is assumed that there is a sign change across nodes.

Examples

(1) $CrBr_2$

The structure of $CrBr_2$ has been described by Tracy, Gregory & Lingafelter (1962), who have listed structure factors for the *h*0*l* reciprocal lattice plane. The weighted *h*0*l* reciprocal lattice in Fig. 2(*a*) shows pseudo-mirror symmetry about the [103]* direction. Superposition of the reciprocal lattice on its mirror image [Fig. 2(*b*)] shows parallel ridges of high intensity separated by regions of low or zero intensity. Positive and negative regions of the transform can be assigned by inspection and the phases of the reflexions determined. Of 61 reflexions used, 51 are assigned the correct phase and 10 are near nodes and therefore uncertain. (The nodes of the transform can be assigned in three other ways, corresponding to the three other choices of origin that are symmetry centres in projection.)

(2) *Kyanite* (Al_2SiO_5)

The *hk*0 reciprocal lattice plane of kyanite (Burnham, 1963) shows marked pseudo-symmetry across a line normal to **a*** [Fig. 3(*a*)]. Superposition of the left and right hand sides [Fig. 3(*b*)] doubles the sample frequency for lattice rows with $k=2n+1$. Phase relations can be determined along each row for which *k* is odd by inspection of the intensity distribution. A similar but less certain determination can be made along rows with *k* even. The phase relations so deduced agree with the published phases (after an origin shift of $\frac{1}{2}a$) for all 25 reflexions with *k* odd and for 19 of 24 reflexions with *k* even. As there is no increase in sampling between the rows of lattice points, phase relations between rows cannot be determined. However, the number of unknown phases has been reduced from 50 to 6 (the number of reciprocal lattice rows considered).

(3) *Naphthalene*

Fig. 4 shows the application of this method of sign determination to naphthalene (Knott, 1940). Fig. 4(*a*) shows the weighted reciprocal lattice, and the position of the pseudo-mirror. Fig. 4(*b*) shows, on the left, the

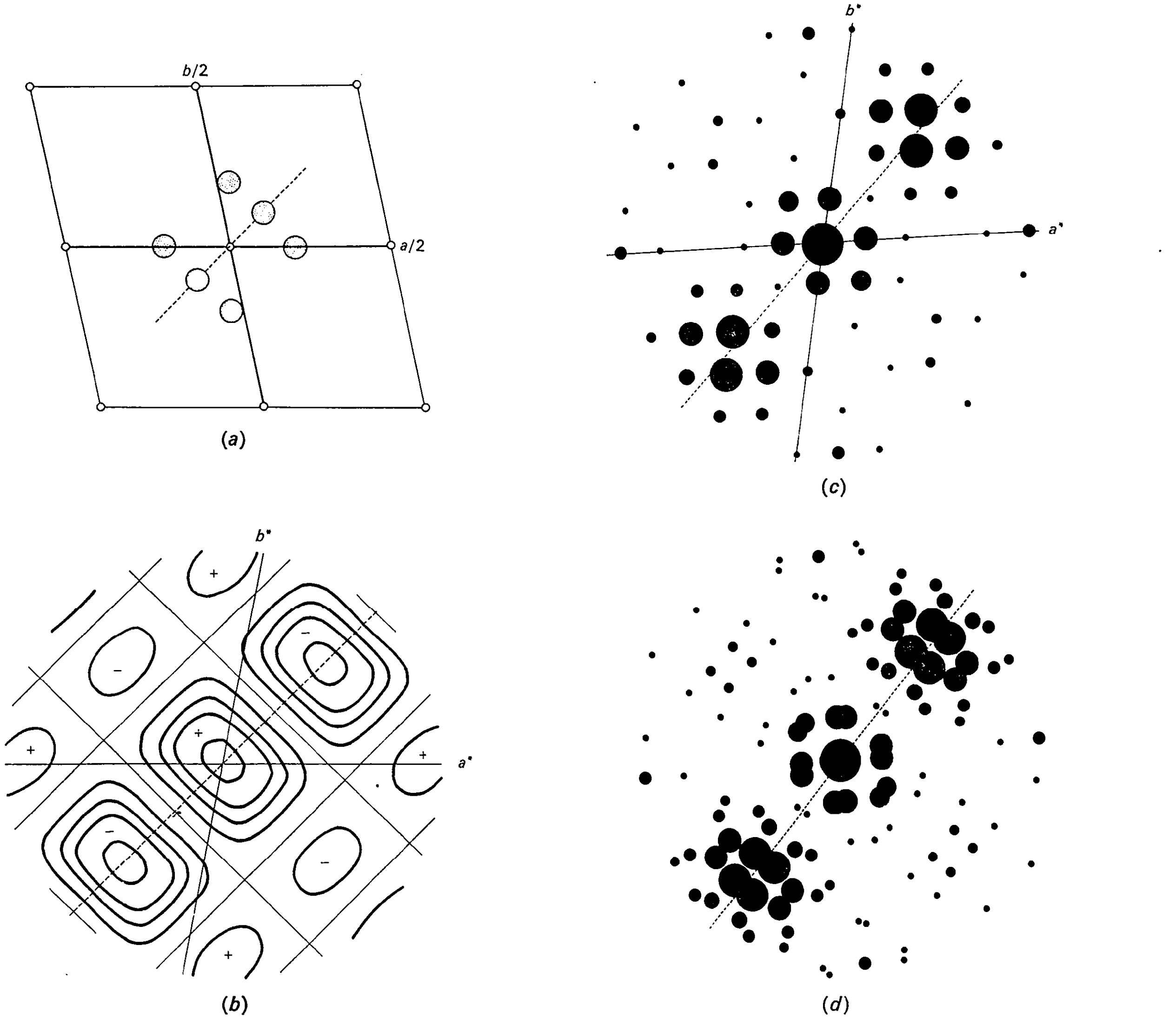


Fig. 1. (*a*) Hypothetical mirror symmetric group of 6 atoms. (*b*) Fourier transform of (*a*). (*c*) Weighted reciprocal lattice. (*d*) Superposition of (*c*) and its mirror image about the broken line.

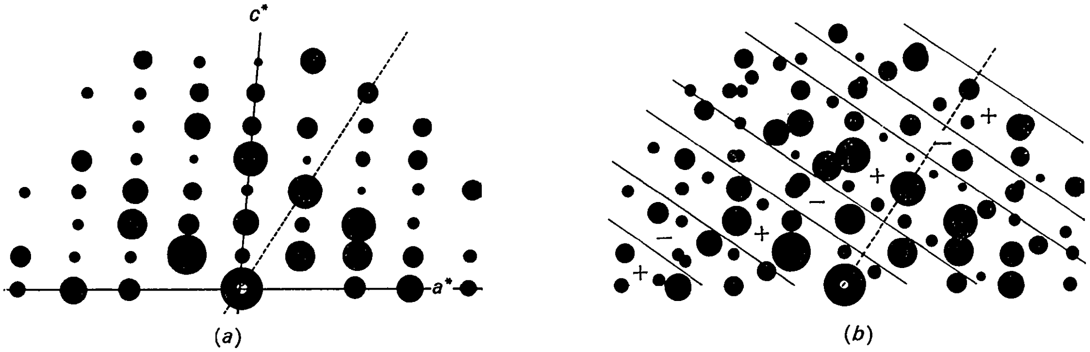
calculated transform, on the right the superimposed weighted reciprocal lattices. Deduced nodes are shaded, and can be compared with the calculated zero contour of the transform.

Transform origin

The Fourier transform deduced by this method must have its origin at one of the centres of symmetry of the unit cell in projection. The particular centre found will be that nearest the bulk of the scattering power of the molecule or atom group, for in examining the weighted reciprocal lattice one would search for as few nodes as possible, and thus select an origin close to the more powerful scatterers.

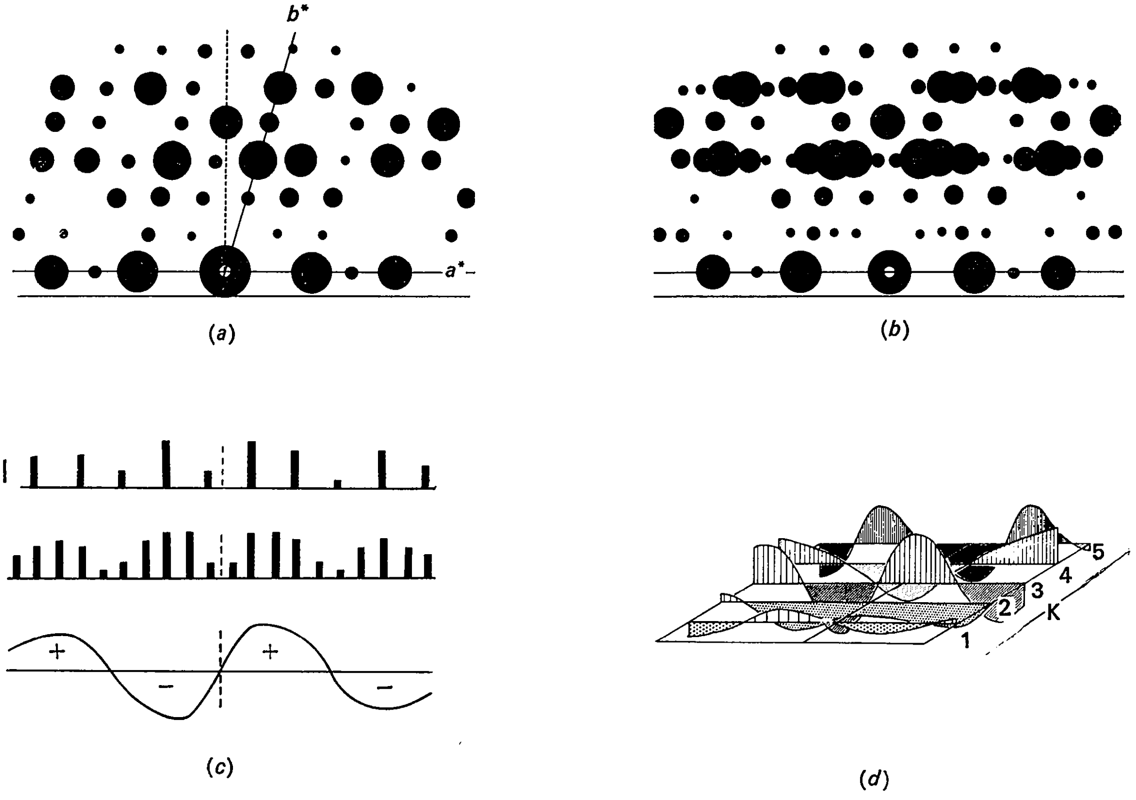
Phase change at nodes

A node in the transform need not delineate a phase change, it may be an intensity low flanked by intensity highs of the same sign. Some degree of distinction be-



(a) (b)

Fig. 2. $CrBr_2$. (*a*) Weighted *h*0*l* reciprocal lattice (*l* positive). (*b*) Superposition of Fig. 2(*a*) and its mirror image about the pseudo-mirror (broken line). Nodes in the transform are shown as continuous lines.



(a) (b)

(c) (d)

Fig. 3. Kyanite. (*a*) Weighted *hk*0 ($k \geq 0$) reciprocal lattice, the pseudo-mirror is shown as a broken line. (*b*) Superposition of Fig. 3(*a*) and its mirror image about the pseudo-mirror. (*c*) (Top) the reciprocal lattice row *h*30. (Centre) superposition of *h*30 about the pseudo mirror. (Bottom) interpretation of sign regions. (*d*) Sign interpretation for each row having *k* constant in the *hk*0 reciprocal lattice (stripes positive, dots negative).

tween these two kinds of node may be made from the rate of intensity change across the node. For a simple sinusoidal transform, a node with sign change would be narrow, the intensity variation across it rapid [Fig. 3(*c*)]; a node without sign change would be broad, the intensity variation more uniform (Fig. 5). This distinction may be impracticable in a more complicated transform, but at least the nodes outline regions of like phase, and so reduce the number of unknown phases.

Translation symmetry

If the pseudo-symmetry in the reciprocal lattice is introduced by translation symmetry in the asymmetric unit, the magnitude of mirror-related parts of the transform will be equal along rows of lattice points, but their signs will differ if the relevant index is odd. Where this index is not integral, the magnitudes of pseudo-symmetric parts of the transform are not equal, and no information is provided. These effects are shown by kyanite: lattice rows with k odd change sign across the pseudo-mirror, those with k even are unchanged, and no information is provided between lattice rows (k not integral) [Fig. 3(*c*) and (*d*)].

If the crystal has true translation symmetry, systematic zeros are introduced into the reciprocal lattice. These are not necessarily zeros in the transform of the asymmetric unit, and should not be regarded as nodes in the composite (Taylor & Lipson, 1958).

Conclusion

Recognition of pseudo-symmetry in a reciprocal-lattice plane may lead to a great reduction in the number of signs of structure factors to be determined. In some crystals all phases may be determined. In others sufficient may be found to make trial and error practicable for the remainder. So little time is needed to apply the method that nothing is lost if it fails, while a great deal may be gained if it succeeds. The method has been

Fig. 5. Xanthophyllite. Superposition of the pseudo-mirror related 02l and 11l reciprocal lattice rows. All phases positive.

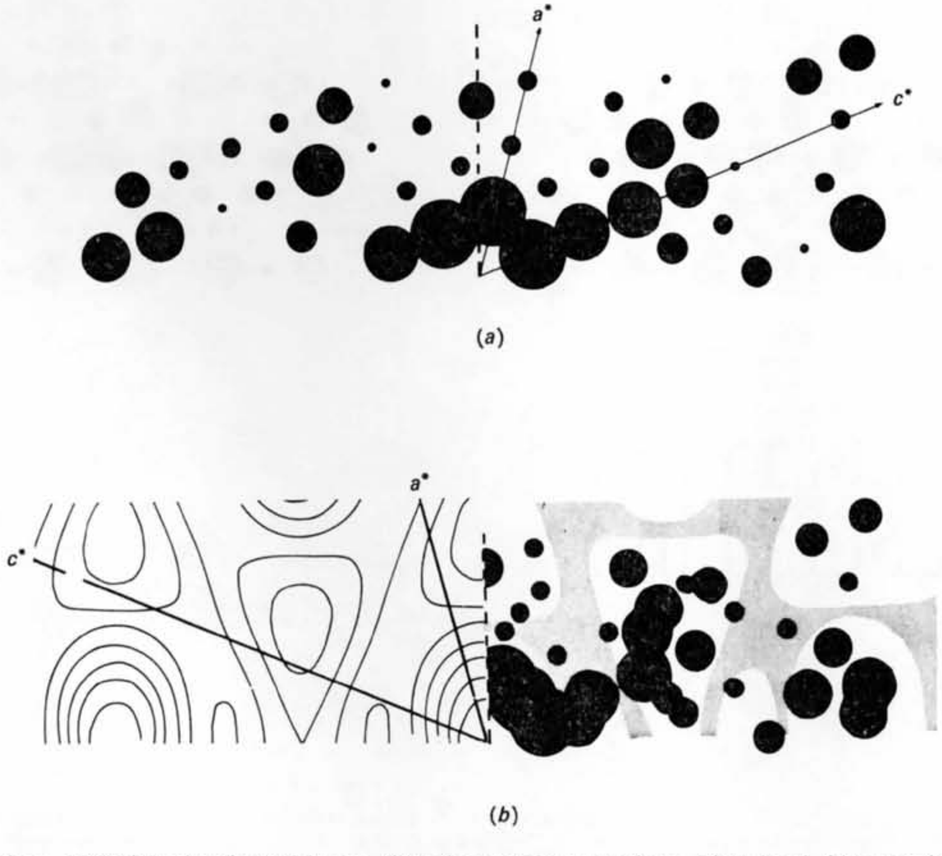


Fig. 4. Naphthalene. (*a*) Weighted reciprocal lattice. (*b*) Left hand side: transform. Right hand side: superimposed weighted reciprocal lattice.

successfully applied to the determination of the crystal structure of brazilianite [$NaAl_3(PO_4)_2(OH)_4$] (Eggleton & Finney, in preparation).

The author is most grateful to Dr I. M. Threadgold and Dr S. W. Bailey for their helpful criticism and suggestions for improvements to the manuscript. Dr C. W. Burnham & Dr J. W. Tracy kindly permitted the use of their experimental data.

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Acta Cryst. (1969). A**25**, 547

Resolution of a Triple Axis Spectrometer

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(*Received* 30 *December* 1968)

A new method for obtaining the resolution function for a triple-axis neutron spectrometer is described, involving a combination of direct measurement and analytical calculation. All factors which contribute to the finite resolution of the instrument may be taken into account, and Gaussian or experimentally determined probability distributions may be used. The application to the study of the dispersion relation for excitations in a crystal is outlined.

1. Introduction

An important property of a triple-axis spectrometer is its resolution function, defined as the probability distribution for momentum and energy which a neutron, registered in the counter, has transferred to the sample under investigation. Several papers have treated the resolution of triple-axis spectrometers by various methods; analytically (Collins, 1963; Stedman & Nilsson, 1966; Cooper & Nathans, 1967); graphically (Peckham, Sanderson & Sharp, 1967; Bergsma & van Dijk, 1965) or by direct measurements (Møller, Houmann & Mackintosh, 1968; Møller, 1968). The present paper describes the determination of the resolution by a combination of measurement and calculation, in which no prior knowledge of collimations and mosaic spreads is necessary. Non-Gaussian probability distributions and curvature of the dispersion relation may be taken into account with this method.

Because of finite collimations in the triple-axis spectrometer and the mosaic spreads of the monochromator and analyser crystals, there is, for a fixed position of the spectrometer, a spread of the incoming and scattered neutron wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ around their average values $\mathbf{k}_{10}$ and $\mathbf{k}_{20}$. As a result, there will be a finite probability that the neutron scattering vector $\boldsymbol{\kappa}=\mathbf{k}_1-\mathbf{k}_2$ differs from its average value $\boldsymbol{\kappa}_0=\mathbf{k}_{10}-\mathbf{k}_{20}$, and that the energy transfer $E=E_1-E_2=\hbar^2/2m(k_1^2-k_2^2)$ will differ from the average energy transfer $E_0=\hbar^2/2m(k_{10}^2-k_{20}^2)$. This probability function is called the resolution function $R(\boldsymbol{\kappa}-\boldsymbol{\kappa}_0, E-E_0)$; it is a four-dimensional function. Since the component of $\boldsymbol{\kappa}-\boldsymbol{\kappa}_0$ normal to the scattering plane is not correlated with the other two components of $\boldsymbol{\kappa}-\boldsymbol{\kappa}_0$ or with E, we need only consider the resolution function in the remaining three dimensions, that is, energy transfer, E, and momentum transfer in the scattering plane.

This resolution results from four independent contributions, each of which gives a finite resolution along a line in the three-dimensional $\boldsymbol{\kappa}E$-space. We will denote the vectors along these lines, with length equal to the half-width of the distributions, by $\mathbf{X}_1$, $\mathbf{X}_2$, $\mathbf{X}_3$, and $\mathbf{X}_4$ [see Fig. 1(*b*)].

$\mathbf{X}_1$ results from the finite collimation of the monochromator system. With zero mosaic spread of the monochromator crystal the probability distribution of the monochromator system is $P_1(\chi_1/X_1)$ along the $\mathbf{X}_1$ direction. Mosaic spread of the monochromator system introduces an independent probability distribution $P_2(\chi_2/X_2)$ along the $\mathbf{X}_2$ direction, so that the total resolution function of the monochromator system is $P_M(\chi_1, \chi_2)=P_1(\chi_1/X_1)P_2(\chi_2/X_2)$. $\mathbf{X}_3$ and $\mathbf{X}_4$ are the corresponding vectors for the analyser system.

2. Calculation of resolution

(1) *Gaussian case*

By the use of the Bragg law $\mathbf{X}_1$, $\mathbf{X}_2$, $\mathbf{X}_3$ and $\mathbf{X}_4$ are easily calculated (Nielsen & Møller, 1968). Below are given the projections of $\mathbf{X}_i$ on the E axis, X_{iE}, and on the $\boldsymbol{\kappa}$ plane, $X_{i\kappa}$, and the orientation of $X_{i\kappa}$ in the $\boldsymbol{\kappa}$ plane.