(Fig. 6*e*), where copper atoms become brighter, while carbon and nitrogen atoms remain dark. It can be seen that the corresponding pairs show a close image contrast at the positions of atoms for crystals below the critical thickness (about 56 Å).

7. Validity and advantages of the PWPOA

Since the multislice method in image simulation is widely accepted and usually shows good agreement with the experimental results, it is reasonable to evaluate the limit of the validity of the PWPOA from the comparison of figures in Fig. 6. Obviously, PWPOA can be used to interpret the variation of the image contrast with the crystal thickness at the position of atoms for crystals below the critical thickness. Because in the PWPOA the Fresnel diffraction is taken into consideration while the multiple scattering is neglected, and because the PWPOA can be used for interpreting the image contrast at the positions of atoms but not on the background, we can say that below the critical crystal thickness the deviation of the image contrast from the pure kinematical treatment at the atom positions is mainly caused by the Fresnel diffraction from one slice to the next, while that of the background is by multiple scattering.

Besides, the PWPOA indicates a possibility of revealing preferentially light or heavy atoms in the images for crystals consisting of atoms of different atomic number in the image by choosing different crystal thicknesses. This seems to have more practical meaning for ultra-high-voltage high-resolution electron microscope observation, where the critical crystal thickness allows the crystal being examined to be thicker.

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The Symmetry Properties of Difference Patterson Functions

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Abstract

Difference Patterson functions can be constructed for difference structures arising from superlattice or incommensurate transformations. In each case the difference structure may belong to one of several symmetry types, namely the irreducible representations of the space group of the average structure, at the relevant symmetry **k** vector in reciprocal space. The relationship between the symmetry of the difference Patterson function and the irreducible representation is discussed. In particular it is shown that the difference Patterson function contains a 'character signature' of plus and minus signs, which, in the case of a one-dimensional irreducible representation, identifies that representation uniquely. Examples

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relating to superlattices and incommensurate structures are given, including the case of a higher-dimensional irreducible representation.

1. Introduction

It is often observed that diffracted intensity appears below the transformation temperature for a phase transition, at positions other than the Bragg reflections for the high-temperature phase. In the simplest case this intensity appears at superlattice positions related to a simple doubling of the unit-cell dimensions. Additional intensity may also appear, in the case of an incommensurate transition, at points distant $\pm\mathbf{q}_i$ from the Bragg positions, or the positions of absent superlattice reflections.

The present paper is concerned with the information on symmetry change in such transformations that can be obtained from the direct Fourier transform of the additional diffracted intensity, *i.e.* from Patterson data. We make use of the fact that, in the early stages of transformation, it is frequently possible to use Landau theory (Landau & Lifshitz, 1968), which requires that the loss of symmetry related to the appearance of an ordering or displacement scheme is associated with some irreducible representation of the high-temperature space group $\mathcal{G}$ other than the identity representation. To be precise, we write the structure as

$$\text{(average structure)} + \text{(difference structure)} \quad (1)$$

(Qurashi, 1963; Böhme, 1982), where the average structure is invariant under $\mathcal{G}$ and the difference structure has the symmetry of an irreducible representation Γ of $\mathcal{G}$. What we propose to demonstrate here is that there is a direct relationship between the relevant irreducible representation that appears at the transition temperature and the difference Patterson function that may be obtained by direct transformation of the additional intensity. It is *not* true that the difference Patterson has the symmetry of Γ, in fact it is usually invariant under the space group $\mathcal{G}$; but nevertheless it carries within its pattern of positive and negative weight a 'signature' of the irreducible representation Γ. In fact, the vectors of the difference Patterson carry the group characters of Γ suitably renormalized. We will show that when $\mathcal{G}$ is known the signature in the difference Patterson identifies the irreducible representation Γ.

Thus the group-theoretical character labelling within the Patterson function we will refer to in future as the *character signature.*

In the treatment that follows we deal first (§ 2) with the symmetry properties of the difference Patterson function for a very simple example. Here the difference Patterson is not directly obtainable from experiment but can be constructed by inspection and will serve to illustrate what we mean by the signature. We will also provide arguments for its uniqueness. In § 3 we consider a difference Patterson function obtained from intensity at superlattice points only. In this case data on the relevant irreducible representations of all space groups are contained in convenient form in Bradley & Cracknell (1972). The characteristics of the character signatures for two-dimensional irreducible representations are discussed next in § 4. Finally, in § 5 we address the important problem of the symmetry data available in the Patterson functions for an incommensurate phase. At this point we utilize the concept of component structures in the incommensurate phase, and the use of plus and minus difference Patterson functions (McConnell & Heine, 1984) in the way already applied to the structure of nepheline (McConnell, 1985).

2. The symmetry properties and character signature in the difference Patterson function

We will illustrate in the simplest possible way the relationship between the irreducible representation Γ associated with the difference structure in (1), and the symmetry of the difference Patterson corresponding to it. Consider the symmorphic space group *Pmm*2 with a set of four general equivalent positions as shown in Fig. 1(*a*). We will assume the difference structure to consist of some ordering process on these sites, with positive and negative weight signifying a probability greater or less than average of having some atomic species at the site concerned. Let us ignore what may go on in other cells so that our set of four sites has point-group symmetry *mm*2 and generates the Patterson function with the set of nine vectors shown in Fig. 1(*b*).

The possible ordering patterns of the group *mm*2 are four, with characters listed in Table 1. The corresponding ordering difference structures are shown in Figs. 1(*c*) to (*f*) and their difference Patterson functions in Figs. 1(*g*) to (*j*). We note that *each* difference Patterson has overall the full point-group symmetry *mm*2. However, they are all four different, and since we are dealing with general equivalent positions *the set of nine vectors with the signs of their weights identifies the irreducible representation uniquely.* It is in fact the pattern of signs (and weights) that constitutes what we define as the character signature of the irreducible representation.

We can see how the uniqueness relation between signature and irreducible representation arises. In the difference Patterson each vector arises from one or more pairs of sites connected by a single symmetry element of the group *mm*2 as shown in Fig. 1(*k*). Thus the sign of the weight at a Patterson vector is the same as the sign of the corresponding symmetry element in the irreducible representation, and the characters of the representation can be written down by comparing the weights in the difference Patterson

in Figs. 1(*g*) to (*j*) with the elements shown in Fig. 1(*k*). These in turn specify the irreducible representation uniquely. We believe this proof of the uniqueness between signature and irreducible representation can be applied to any case of one-dimensional representations where only characters ±1 appear. A second argument of the uniqueness can be obtained as follows. In any one-dimensional representation with characters ±1, the elements with character +1 form a subgroup in one to one correspondence with the irreducible representation. The subgroup in general is a space group and it is known that the Patterson function may be used to identify the space group uniquely apart from a certain limited number of cases listed by Buerger (1959, Table 2, p. 213). We have no general proof of the uniqueness relation. However, we have found that the two arguments we have given, particularly the first, suffice to establish the uniqueness in all the cases we have considered. The situation with two- and three-dimensional irreducible representations is more complicated, as we shall discuss in § 4.

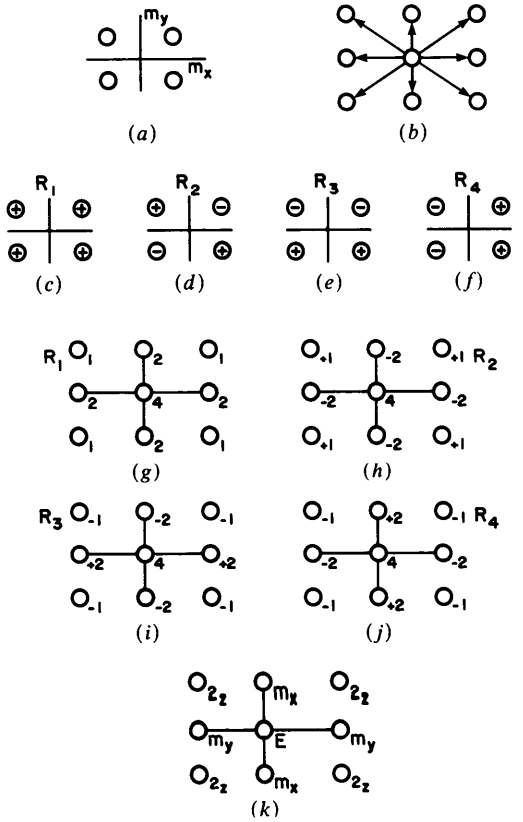

Fig. 1. Difference structures associated with possible ordering schemes in the point group *mm*2 of Table 1. The general equivalent positions and their vectors are shown in (*a*) and (*b*). (*c*), (*d*), (*e*) and (*f*) label the general equivalent positions in accordance with the representations R_1, R_2, R_3 and R_4, respectively. The corresponding difference Patterson functions are shown in (*g*), (*h*), (*i*) and (*j*) with correct weightings. Finally, in (*k*) the vectors associated with the symmetry elements are labelled.

Table 1. *Character table of the point group mm*2

	E	m_x	2_z	m_y
R_1	1	1	1	1
R_2	1	−1	1	−1
R_3	1	−1	−1	1
R_4	1	1	−1	−1

So far we have considered difference structures for ordering transformations but the same general considerations can also be applied to displacive transformations.

3. Character signature in the difference Patterson function for a simple superlattice

We turn now to consider a realistic simple example, namely a transformation and difference structure with a twofold superlattice (Fig. 2). We again use the space group *Pmm*2, and doubling along the *b* axis. The difference structure must transform according to an irreducible representation of the 'group of **q**' where **q** is the Bloch wave vector $\frac{1}{2}\mathbf{b}^*$. This group and its irreducible representations may be looked up in Bradley & Cracknell (1972). They (the irreducible representations) are a bit more complicated than in § 1 because we are dealing with a space group and the translation **b** has to be represented by taking the negative since $\mathbf{q} = \frac{1}{2}\mathbf{b}^*$. However, there are again four one-dimensional irreducible representations R_1 to R_4, which relate to those in Table 1 as regards the characters of the four elements listed. Fig. 2(*b*) shows a particular difference structure with symmetry R_2. The full difference Patterson function is shown in Fig. 2

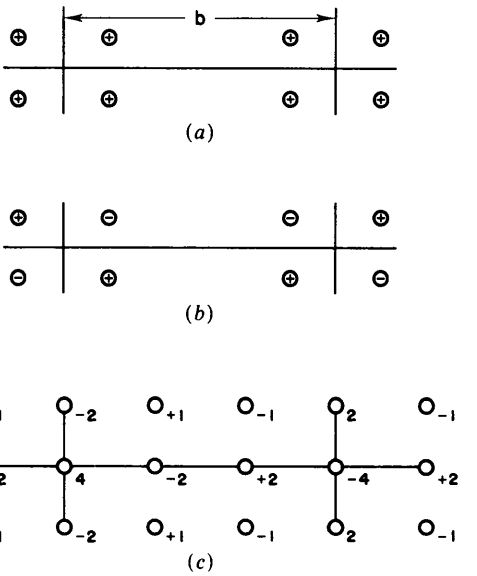

Fig. 2. The effect of doubling the *b* axis of the unit cell and selecting the representation R_2 for the point group *mm*2 from Table 1. (*a*) corresponds to the average structure, (*b*) to the difference structure and (*c*) to the complete difference Patterson function. The origin is the point with weight +4.

and we can pick out the part formed from vectors connecting the four atomic sites near the origin in one cell. Comparison with Fig. 1 therefore immediately establishes the correct irreducible representation from the difference Patterson.

4. Character signatures in the Patterson functions for a two-dimensional irreducible representation

Two-dimensional irreducible representations occur in at least three cases of importance for phase transitions. The first of these relates to the presence of a screw axis or glide plane, which requires that certain irreducible representations at the Brillouin zone boundary are at least doubly degenerate. The second case arises when threefold, fourfold or sixfold axes give higher two- and three-dimensional irreducible representations. The third case, which will be discussed separately in § 5, refers to simple incommensurate structures based on the pair of vectors $\pm\mathbf{Q}_i$ that necessarily define an irreducible representation that is at least two-dimensional (McConnell & Heine, 1984).

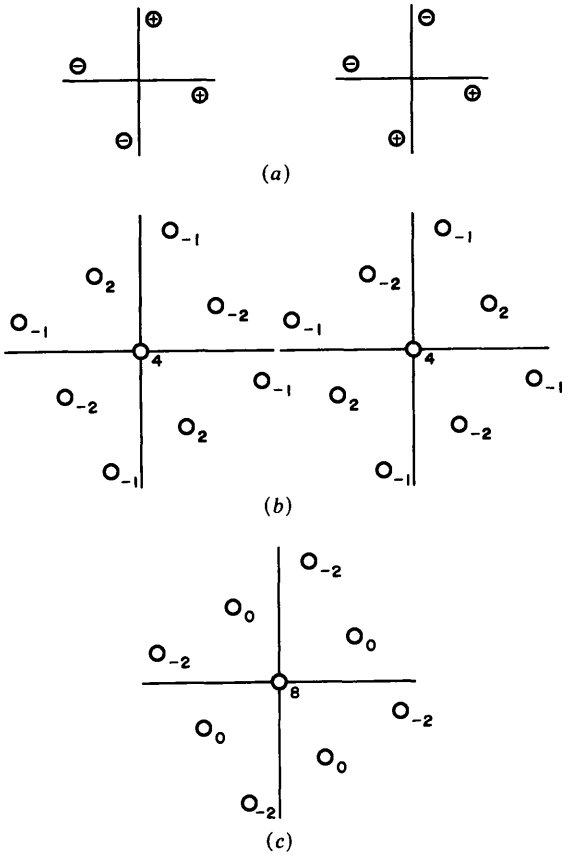

Fig. 3. Patterson functions associated with two chosen basis functions for R_3 of point group 4 (Table 2). The two chosen basis functions are illustrated in (*a*). Their Pattersons are shown in (*b*). Note that they lack fourfold symmetry. Finally, the sum of the Pattersons in (*b*) is shown in (*c*). Here the Patterson possesses full fourfold symmetry.

Table 2. *Character table of the point group* 4

	E	C_4^+	C_2	C_4^-
R_1	1	1	1	1
R_2	1	−1	1	−1
R_3	2	0	−2	0

In order to illustrate the Patterson properties of a very simple two-dimensional irreducible representation, we choose the point group 4 and consider the two-dimensional representation R_3 of Table 2. In Fig. 3(*a*) we choose two suitable basis functions while hastening to add that the pair may be chosen in many different ways. (We also assume that the four sites in Fig. 3 are involved in an ordering transformation.)

In practice both basis functions (or any linear combination) are equally likely, and in Fig. 3(*b*) we show the corresponding Patterson functions exhibiting appropriate character signatures. We note that, unlike the Patterson functions for one-dimensional irreducible representations, they do not individually have overall fourfold symmetry. Nor are they orthogonal as were the original basis functions.

In practice the transformation proceeds *via* a particular basis function determined by higher-order terms in the Landau expansion of the free energy, *i.e.* by some particular linear combination of the two functions of Fig. 3(*a*). Another example would be displacement in the $\mathbf{a}+\mathbf{b}$ direction rather than the $\mathbf{a}$ or $\mathbf{b}$ direction in a displacive transformation. Even then there remains a twofold degeneracy analogous to displacements in the $\mathbf{a}+\mathbf{b}$ and $\mathbf{a}-\mathbf{b}$ directions. If the transformed crystal is a single domain, one would observe some difference Patterson such as one of those in Fig. 3(*b*), which identifies uniquely not only the R_3 representation but also the particular basis function. However, in other cases the material may consist of random domains of the two structures, say those of Fig. 3(*a*), and the scattering intensity is then the average of the two intensities for the two structures. The observed difference Patterson would then be the average of those for the two structures as shown in Fig. 3(*c*), We note this now has overall fourfold symmetry. Moreover, it is easy to show by an orthogonal transformation that such a sum of two difference Pattersons is invariant under the choice of basis functions. Thus, in a multi-domain situation the observed difference Patterson function still identifies uniquely the R_3 irreducible representation, but no longer gives any information about the individual basis functions, *i.e.* particular difference structures in the domains.

5. Character signatures in the difference Patterson functions for incommensurate phases

In a recent paper we pointed out that the full space-group irreducible representation for an incommensurate structure with scattering at $\pm\mathbf{Q}_i$ was of

necessity at least two-dimensional (McConnell & Heine, 1984). Two-dimensionality results in two pure component structures C_1, C_2 such that

$$\begin{aligned}&\text{(Incommensurate structure)}\\&\quad=\text{(average structure)}\\&\qquad+C_1\cos\mathbf{Q}_i.\mathbf{r}+C_2\sin\mathbf{Q}_i.\mathbf{r},\end{aligned}\qquad(2)$$

where $\mathbf{Q}_i$ is measured from the nearest symmetry position in reciprocal space (reciprocal-lattice point or half reciprocal-lattice point). The components C_1, C_2 are periodic in the lattice (or twofold superlattice), and transform according to a matched pair of irreducible representations (in the sense defined by McConnell & Heine, 1984) at the relevant symmetry point in reciprocal space. An alternative superspace group description, and its relationship to the normal space-group approach, is given by Janssen & Janner (1984).

We now ask whether or not it is possible from Patterson criteria to establish the individual symmetries of the components C_1 and C_2. The two-dimensionality inherent in a pair C_1, C_2 is reflected in independent scattering intensities at the satellites with $+\mathbf{Q}_i$ and $-\mathbf{Q}_i$, from which one can construct the plus difference Patterson function using the sum of the two intensities and the minus difference Patterson function using their difference. As discussed by McConnell & Heine (1984), the plus difference Patterson function is simply the sum of the Pattersons of C_1 and C_2, so that one expects to see in it the two separate signatures relating to the irreducible representations applying to C_1 and C_2. This is shown in Fig. 4 for a modulation in the b direction based on component structures C_1, C_2 with symmetries R_2 and R_3 of the space group $Pmm2$. Fig. 4(a) illustrates component structures C_1, C_2 with orderings of symmetry R_2, R_3 on different equivalent positions in the unit cell of the high-temperature structure. Comparison of the plus difference Patterson function in Fig. 4(b) with Figs. 1(h) and (i) shows the two expected separate signatures. In some cases the components C_1, C_2 relate to different orderings on the *same* suite of sites: it is left as an exercise for the reader to verify that certain vectors have zero weight in the plus difference Patterson function as in Fig. 3(c), but that one can still distinguish between the two possible matched symmetry pairs R_2, R_3 and R_1, R_4, which are the only combinations allowed by the symmetry relation of McConnell & Heine (1984).

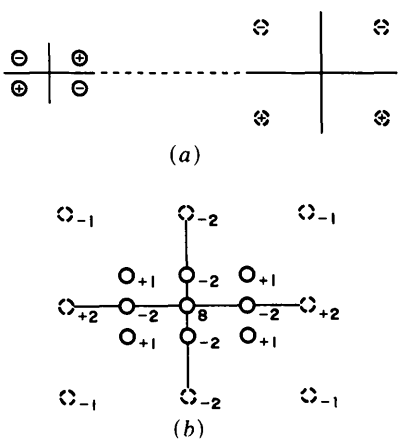

Fig. 4. The character signatures in the plus difference Patterson function for an incommensurate phase based on the high-temperature space group $Pmm2$, and modulated with wave vector $\mathbf{Q}_i$ in the $\mathbf{b}^*$ direction. Component structures C_1 and C_2 in the modulation have symmetry defined by representations R_2 and R_3 of the point group $mm2$. (a) Component structures C_1 and C_2 in the modulation parallel to $\mathbf{b}$, and separated by $\lambda/4$ (phase $\pi/2$). (b) The plus difference Patterson function for the modulation. This is simply the sum of the Patterson functions for C_1 and C_2. Note that the full symmetry of C_1 or C_2 can be determined from the Patterson function since the symmetry acts on a different suite of general equivalent positions in C_1 and C_2.

The plus difference Patterson function has been applied to elucidate the structure of nepheline, in particular the ordering symmetry of the K^+ ions with respect to that of the O^{2-} ions (McConnell, 1985).

Finally it is possible to construct the minus difference Patterson function (not shown) for the modulation of Fig. 4, which contains only cross vectors between the structures C_1 and C_2. It is more complicated and less useful from a symmetry point of view.

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