

No attempt was made to include contributions of non-random noise in the theoretical curve.

The agreement is satisfactory and indicates the robustness of the average structure concept. In fact, other examples, not given here, show that the agreement of first moments is as striking as was observed previously for the R_2 function (Petit, Lenstra & Van Loock, 1981).

Fig. 3 also shows that an even better prediction of the signal and the random noise can be made by using in (6) and (7) the actual sums $\sum_H E_o^p$ of the experimental data set.

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An Aid to the Structural Analysis of Incommensurate Phases

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Abstract

Group theory is used to establish three results likely to be useful in solving the crystal structures of complicated incommensurate phases. In the first of these it is demonstrated that an incommensurate structure with paired scattering vectors $\pm\mathbf{q}$ must contain two different component structures, one modulated with $\cos\mathbf{q}\cdot\mathbf{r}$ and the other with $\sin\mathbf{q}\cdot\mathbf{r}$. The second theorem states that the two components have different but related symmetries if the average structure has at least one element in its space group which turns \mathbf{q} into $-\mathbf{q}$. In that case, each aspect of the modulation is assigned uniquely by symmetry to either the cosine or sine factor. The third result concerns the Patterson function that may be constructed from the intensity scattered by the incommensurate modulation. This is also necessarily two-dimensional, the plus difference Patterson function being the sum of the Patterson functions obtained separately for the two component structures, while the minus difference Patterson function contains cross terms between the two components. Other symmetry arguments are mentioned, including symmetry signatures in Patterson functions, and systematic equalities in satellite intensities which

arise from systematic extinctions in the scattering from one component or the other.

1. Introduction: the use of two-component structures

This paper is concerned with the ramifications of one basic point, that the structure of a modulated incommensurate (IC) phase can always be expressed in the form of two components:

$$\begin{aligned} (\text{IC structure}) = & (\text{average structure}) \\ & + (\text{first component } C_1) \times \cos \mathbf{q} \cdot \mathbf{r} \\ & + (\text{second component } C_2) \times \sin \mathbf{q} \cdot \mathbf{r}. \end{aligned} \quad (1.1)$$

This has a number of advantages which we shall develop, especially for solving complicated IC structures such as some minerals. We emphasize that on general group-theoretical grounds there can be, and so presumably usually are, *two* independent modulation component structures ('components' for short) C_1 and C_2 oscillating 90° out of phase with one another in (1.1) (McConnell, 1978, 1981a). Fig. 1 illustrates the situation. Much of the utility of this

approach rests on the fact that C_1 and C_2 have different symmetry, given minimal symmetry in the average structure, as we shall prove. Note that the components C_1 , C_2 are crystal structures (or rather difference structures in the usual sense: Buerger, 1959) with the periodicity of the lattice, the modulating factor having been separated out in (1.1). Here, 'structure' includes magnetic orientation where relevant. Of course, the underlying periodicity is the superlattice defined by the $\frac{1}{2}\mathbf{g}$ in the case of a phase giving satellite reflections at $\frac{1}{2}\mathbf{g} \pm \mathbf{q}$ where the \mathbf{g} are reciprocal-lattice vectors. [We define our reciprocal space such that the phase of a wave is $\mathbf{q} \cdot \mathbf{r}$ as in (1.1), with reciprocal-lattice vectors \mathbf{g} giving $\mathbf{g} \cdot \mathbf{l}$ equal to 2π times an integer where \mathbf{l} is a lattice vector.] Materials with more than one modulation wave can have (1.1) applied to each. In only a few cases are both components C_1 and C_2 known: in ThBr_4 an optic and acoustic mode (Bernard, Currat, Delamoye, Zeyen, Hubert & de Kouchovsky 1983), in NaNO_2 the NO_2 ordering and an xy shear (Kucharczyk, Pietrasko & Lukaszewicz 1978*a, b*), in the mineral mullite and the intermediate plagioclase feldspars two different ordering patterns (McConnell, 1978, 1981*a*, 1984*a*). Other cases include $\text{K}_2\text{PbCu}(\text{NO}_2)_6$ (Noda, Mori & Yamada, 1978; McConnell & Heine, 1982), thio-urea (Parlinski & Michel, 1984) and nepheline (McConnell, 1981*b*, 1984*b*). These examples show that the two components can be but need not be very different in nature, and that sometimes one of them has a dominant amplitude.

The purpose of the present work is first to show conclusively that there must be in general the *two* independent components C_1 and C_2 , and then to develop the *utility* of this representation for structural analysis, to discuss the necessary *symmetry relation*

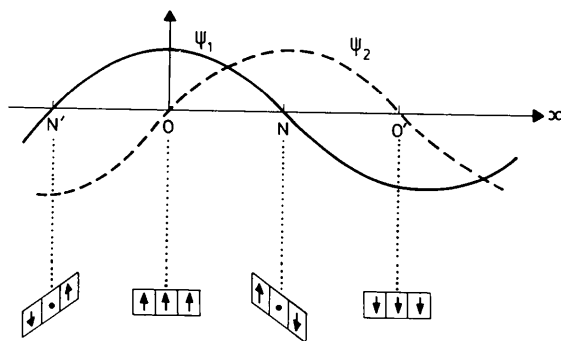


Fig. 1. Schematic representation of NaNO_2 to show the general structure of an incommensurate modulation, showing the order parameters ψ_1 (full line) and ψ_2 (dashed) of the two components C_1 and C_2 , respectively. Lower level: the appearance of unit cells near N' , O , N and O' in the modulation, showing the polarization component C_1 as arrows and the shear C_2 of the cells. Note the overall *odd* symmetry of the whole pattern under 180° rotation in the plane of the paper about O , but the different *local* symmetry of the shear, namely *even* under 180° rotation about N .

ship between C_1 and C_2 , and to show how *Patterson functions* and some further symmetry arguments can be used to help identify them. In some materials the existence of two components appears to be the mechanism responsible for the presence of the incommensurate modulation (Heine & McConnell, 1981, 1984), in which case it certainly is important to find what both of them are: but we emphasize that the results in the present work derive purely from the group-theoretical principles associated with the IC phase so that they are generally valid and we shall hardly mention the matter of mechanism further.

Must there always be two components C_1 and C_2 ? We believe so in principle, except in the simplest materials where no displacement or ordering mode with the required symmetry of the second component can be formed. In the Landau theory of second-order or nearly second-order phase transitions (Landau & Lifshitz, 1968), the order parameters $\psi_{\mathbf{q}}$, $\psi_{-\mathbf{q}}$ associated with an IC phase are complex Bloch functions in whose real and imaginary parts the two components may be found as we shall show in § 2. We can find no symmetry argument that would require one of the components to be identically zero, and indeed wide experience of computing electron wave functions to which the same group theory applies exhibits both the real and imaginary components. Unfortunately, many studies, including some of those on the more complex materials, have worked only with the cosine term in (1.1), the possibility of a second component apparently having been overlooked, an approach we believe to be in principle incomplete. The object of structural analysis should be to determine both components. The utility of grouping all aspects of the modulation into two-component structures in (1.1) is that each can be handled as a whole. For example, each has to make sense physically, chemically and mineralogically in terms of atom packing and arrangement since each in a loose sense occupies half the crystal in (1.1). This can be especially suggestive in the early stages of analysing a complicated IC mineral structure (McConnell, 1978, 1981*a, b*, 1983). Of course, if the second component turns out to be zero within experimental error, then that is positive information about the material. We note that C_2 seems to be often (but not always) an acoustic displacive mode, diffracting strongly only into regions of reciprocal space far from the origin.

The most important part of our analysis applies when the system has at least what we shall call 'minimal symmetry', namely that the space group \mathcal{G} of the *average* structure in (1.1) has at least one symmetry element S that turns \mathbf{q} into $-\mathbf{q}$:

$$S\mathbf{q} = -\mathbf{q}. \quad (1.2)$$

For a material with satellites near superlattice points $\frac{1}{2}\mathbf{g}$, the \mathbf{q} to which (1.2) applies may be measured

either from the origin or from $\frac{1}{2}g$. Of course, for C_1 and C_2 to be present in the same modulation they must have the same symmetry under elements of \mathcal{G} which leave \mathbf{q} invariant, *i.e.* they must transform according to the same irreducible representation of 'the group of \mathbf{q} ' (Bradley & Cracknell, 1972). But group elements of type (1.2) give an extra *symmetry relationship theorem* between the symmetries of C_1 and C_2 which can be expressed most simply as (§ 3):

$$\text{symmetry of } C_1 = \text{symmetry of } [(\mathbf{q} \text{ or } \xi \text{ or } \partial/\partial\xi) \times C_2] \quad (1.3)$$

and *vice versa*, where ξ is a coordinate on the direction of \mathbf{q} . This result covers all elements of type (1.2). In practice it means either C_1 or C_2 is even and the other one odd under any particular S , but which C_j is even or odd depends on S in accordance with their irreducible representations under the group $\mathcal{G}_{\pm\mathbf{q}}$ of elements which turn \mathbf{q} into either \mathbf{q} or $-\mathbf{q}$. Fig. 2 illustrates the full symmetry relation of C_1 and C_2 for the modulation of Fig. 1. We have used such a symmetry relation (1.3) in our work on mechanisms leading to IC phases [equation (3.2) of Heine & McConnell, 1984], but our derivation in § 3 is based purely on symmetry arguments. The result is clearly an aid to structural analysis in that it limits what C_2 can be once the symmetry of one component (C_1 say) is known or postulated, often from a commensurate phase at lower temperature (McConnell, 1981*a*, 1984*a*). For example, it allows us to fix immediately the phase of the shear wave in NaNO_2 which was found by Kucharczyk *et al.* (1978) but whose phase was left undetermined by these authors: it should be displaced by a quarter wavelength from the suggested position shown in their sketch. While such symmetry requirements have been used directly or indirectly in a few specific cases

like ThBr_4 (Bernard *et al.*, 1983) we wish to develop them here in their generality.

The symmetry connection (1.3) is almost obvious from Fig. 1 where we can regard one component, say C_1 , setting the overall symmetry which is odd with respect to a 180° rotation through the origin O in the figure. This symmetry of C_1 automatically produces *locally* an even symmetry about the nodes N, N' where the amplitude of C_1 passes through zero (Fig. 1). More generally, the symmetry around the nodes is that of $\text{grad } \psi_1$ because a gradient of the order parameter ψ_1 is what one has there. A material cannot have two different symmetries at the same place and hence the symmetry around the nodes N, N' set by $\text{grad } \psi_1$ (in a sense $\text{grad } C_1$) must be followed by C_2 , giving (1.3). This argument shows incidentally that in general there actually will be a second component C_2 . All displacements and orderings that have the same symmetry in a material can and will interact. Hence, locally in the regions around N, N' , if we picture a long modulation wavelength, the presence of $\text{grad } \psi_1$ will stimulate other displacements or/and orderings in response to itself. Thus one is led to the 'exaggerated gradient ploy' (Heine & McConnell, 1984) as an aid to discovering the nature of the second component whether or not it is responsible for the incommensurateness. Another result follows from this picture: the magnitude of $\text{grad } \psi_1$ is proportional to \mathbf{q} and hence so will be the amplitude of the C_2 which it induces, which means that we may expect it to be small in many cases. However, other factors would make C_2 significant when it is part of the mechanism producing the IC phase in the manner of Heine & McConnell (1984), and there are cases like spiral structures where C_1 and C_2 have inherently equal amplitudes. Sometimes C_2 does not only have the symmetry of $\text{grad } C_1$, it actually *is* $\text{grad } C_1$, *e.g.* in ThBr_4 (Bernard *et al.*, 1983).

Our symmetry relationship theorem (1.3) can be expressed in another way useful for structural analysis of IC phases when one or both modulated components is quite complicated. For example, in $\text{K}_2\text{PbCu}(\text{NO}_2)_6$ the main C_1 component involves ordering of the Cu^{2+} magnetic moments, shear of the $(\text{NO}_2)_6$ octahedra, rotation of the octahedra and displacement of the Pb atoms, without even considering the K atoms or rotations or internal distortions of the NO_2 groups (Noda *et al.*, 1978). We shall call each of these an *aspect* of the component structure (corresponding to the parts of the eigenvector in a normal mode analysis). From some average structure one can consider all possible aspects in the sense of all possible orderings and displacements of all the atoms, modulated with wave vector \mathbf{q} . The symmetry relation (1.3) then implies an alternative form of the symmetry-relationship theorem which must certainly have been recognized in lattice-dynamical calculations on specific materials though we know of no general

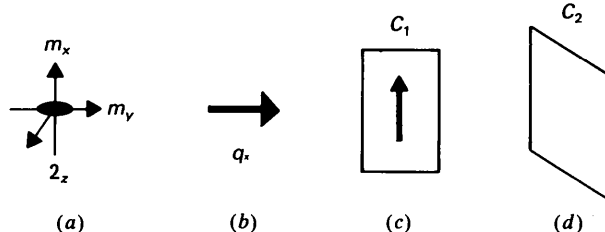


Fig. 2. Symmetry relation of the two pure components of the simplified IC structure of Fig. 1. (a) The point-group symmetry of the average structure with space group $Pm_x m_y 2_z$. (b) The direction of the \mathbf{q} vector of the modulation, here the x direction. (c) and (d) Unit cells of the pure C_1 and C_2 components of the modulation. Note that C_1 and C_2 have the same symmetry (odd) under m_y , the generator of the group of \mathbf{q} , and hence can co-exist in the modulation. Under the element 2_z , which turns \mathbf{q} into $-\mathbf{q}$, C_1 and C_2 have opposite symmetries, namely odd and even, respectively. They also have opposite symmetries (C_1 even, C_2 odd) under m_x which also turns \mathbf{q} into $-\mathbf{q}$, in accordance with equation (1.3).

treatment:

with minimal symmetry S (1.2) all aspects inherently even in the unit cell under S are in phase with one another, and all aspects odd under S are 90° out of phase with the former. (1.4)

Arbitrary phase relationships need never be considered as done by some authors (see, for example, comments by Yamamoto & Nakazawa, 1982, and Nakazawa, Yamamoto & Morimoto 1979): and all aspects with zero phase can be lumped together into C_1 and all those with 90° into C_2 . The result does not depend on approximating \mathbf{q} to be small. A bit of care is needed with acoustic displacement waves: since a uniform displacement is meaningless in a pure component structure, the modulation has to be included as a uniform shear or compression in the other component. In all cases the even/odd symmetry under the elements (1.2) uniquely assigns each aspect to its correct C_1 or C_2 . In the absence of minimal symmetry the relative phases may be arbitrary. However, the concept of components C_1 and C_2 (1.1) can be retained, though less usefully, because an arbitrary wave $\cos(\mathbf{q} \cdot \mathbf{r} - \varphi)$ can be split into waves $\cos \mathbf{q} \cdot \mathbf{r}$ and $\sin \mathbf{q} \cdot \mathbf{r}$ with amplitudes $\cos \varphi$, $\sin \varphi$, respectively: it simply means that there is no symmetry reason to prevent any given aspect from appearing in both C_1 and C_2 .

In § 4 we turn to the plus and minus difference Patterson functions (plus and minus DPFs) that can be formed from the satellite intensities (Cochran, 1968; Parker, 1971; Wilkinson, Knapp & Forsyth, 1976) to show how information about the components C_1 , C_2 is contained in them. In practice this involves the approximation that \mathbf{q} is small, notionally merging the satellite reflections onto the reciprocal-lattice points (or onto $\frac{1}{2}\mathbf{g}$ as appropriate), so that the resulting DPFs have the periodicity of the lattice (or superlattice). The IC modulation reflects only into the satellites and we shall show that the plus DPF formed from the added intensities $I(\mathbf{g} + \mathbf{q}) + I(\mathbf{g} - \mathbf{q})$ is the sum of the Patterson functions for C_1 and C_2 separately. It has been used for nepheline $\text{Na}_3\text{K}_{1-2x}\text{Al}_{4-2x}\text{Si}_{4+x}\text{O}_{32}$ where earlier work (Hahn & Buerger, 1955; McConnell, 1981b) had shown that the IC phase involved both K^+ ion/vacancy ordering and displacements of the oxygens. One might naively guess that these belong to C_1 and C_2 , respectively, but a strong showing of the K^+ to oxygen vectors in the plus DPF proves they are present in the same component and establishes their phase relationship (McConnell, 1984b; Parker, 1971). One might also hope to derive symmetry information about C_1 and C_2 from the plus DPF, a possibility which involves a point about Patterson functions generally. It is well known that although the Patterson function of C_1 , say, would have the overall symmetry of $\mathcal{G}_{\pm\mathbf{q}}$ (often of \mathcal{G}), nevertheless it retains

within it information about the symmetry of C_1 (Buerger, 1959). The information is contained in what we have called elsewhere the 'signature' of the irreducible representation describing the symmetry of C_1 (McConnell & Heine, 1984). This signature consists of a particular pattern of positive and negative weights in the Patterson, as illustrated in Fig. 3, which identifies the irreducible representation uniquely. Thus, one might hope to find two signatures in the plus DPF from C_1 and C_2 , respectively. The minus DPF obtained from $I(\mathbf{g} + \mathbf{q}) - I(\mathbf{g} - \mathbf{q})$ is a cross-correlation between C_1 and C_2 . Thus, if it is found to be zero, apart from noise, that would indicate that C_2 was zero within some limit of error. On the other hand, we would expect the minus DPF to show some strong features when C_1 and C_2 involve different ordering patterns on the same set of sites (see Fig. 4 of Heine & McConnell, 1984) due to the same set of vectors occurring in both C_1 and C_2 .

The diffraction amplitudes $A(\mathbf{g} \pm \mathbf{q})$ in the satellites can be expressed in terms of the amplitudes A_1 , A_2 from the pure components C_1 , C_2 taken as whole structures. The satellite amplitudes take the form

$$A(\mathbf{g} + \mathbf{q}) = \frac{1}{2}A_1(\mathbf{g} \pm \mathbf{q}) \pm i\frac{1}{2}A_2(\mathbf{g} \pm \mathbf{q}), \quad (1.5)$$

where the extra factor of $\pm i$ comes from the displacement of C_2 by an extra quarter wavelength from C_1 along the IC modulation. Now A_1 or A_2 may show systematic extinctions due to their space-group symmetries, and from (1.5) these will show up as *systematic equalities* between the satellite intensities for the IC structure (§ 5). Incidentally, in general the A_j in (1.5) are complex, but a particular simplification occurs when \mathcal{G} contains an inversion centre. Then

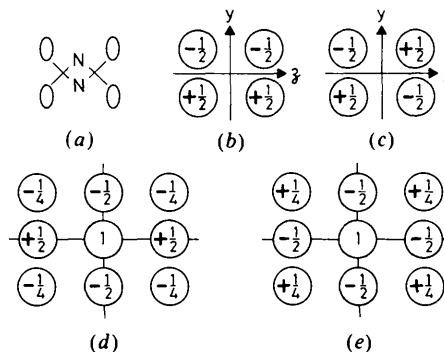


Fig. 3. (a) Average structure of the NO_2 group in NaNO_2 showing its two positions occupied with equal probability of $\frac{1}{2}$ in the disordered phase. (b) The corresponding difference function, i.e. the site occupation probabilities for an upward pointing NO_2 group minus the average structure, showing the oxygen atoms only by way of further simplification. (c) A hypothetical difference function on the same set of sites as (b) but with a different symmetry. (d) and (e) Patterson functions corresponding to (b) and (c). Note that each Patterson has the same overall point-group symmetry 2_2m_2 , of Fig. 2(a) but each has a different pattern of weights which constitute the symmetry signatures of (b) and (c).

one of the components, say C_1 , is even under inversion giving A_j real and the other, C_2 , is odd under inversion giving A_2 as pure imaginary, equal to iA_2' say. The amplitudes (1.5) then both become real:

$$A(\mathbf{g} \pm \mathbf{q}) = \frac{1}{2}A_1(\mathbf{g} \pm \mathbf{q}) \pm \frac{1}{2}A_2'(\mathbf{g} + \mathbf{q}). \quad (1.6)$$

In § 5 we will discuss our ideas in relation to the full space-group symmetry of the crystal. As long as one works with first-order satellites only, the modulation is purely sinusoidal at least in a probabilistic (ensemble average) sense and the symmetries of C_1 and C_2 are describable vigorously as irreducible representations of $\mathcal{G}_{+\mathbf{q}}$. We shall show how these relate to the usual space-group labels for the symmetries of C_1 and C_2 , and how the complete character table establishes which related pairs can belong to C_1 , C_2 . However, irreducible representations have a richer symmetry than space groups: for example, they can give rise to a greater variety of extinctions than space groups (and hence systematic equalities for the IC satellites) due to some group elements having characters -1 .

It remains to discuss the degree of generality of our ideas and their relation to the symmetry description of IC phases by Janner & Janssen (1977, 1979). We have pictured the pure component structures C_1 and C_2 as what one sees (Fig. 1) in cells where the phase is 0 or 90° , respectively, when one mentally takes the repeat distance $2\pi/q$ to infinity. How does one define the components C_1 , C_2 rigorously for the real structure with non-zero \mathbf{q} ? We do this algebraically in § 2, but Janner & Janssen have an equivalent and useful geometrical construction. An IC structure is basically unchanged if the wave is moved along by an arbitrary phase φ , which can be used to define a four-dimensional (4D) space (x, y, z, φ) of which the real 3D IC structure is a diagonal cut with slope given by q (Fig. 4). Such a 4D structure *rigorously* has the symmetry of a 4D space group and our 3D components C_1 , C_2 are the non-sloping cuts $\varphi = 0$ and $\varphi = 90^\circ$ which have perfect 3D space-group symmetry. That defines them rigorously with the periodicity of the underlying (3D) lattice, and incidentally puts their

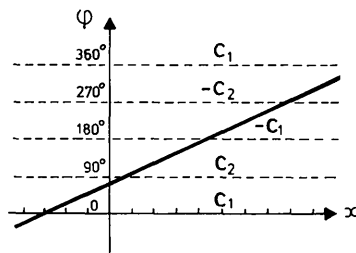


Fig. 4. The four-dimensional space of Janner & Janssen (1977, 1979) showing the phase coordinate φ and one spatial dimension x . The three-dimensional cut represented by the sloping line gives the observed incommensurate structure, while the horizontal lines represent the three-dimensional pure component difference structures C_1 and C_2 with positive or negative sign.

other symmetries in an interesting light. Just as normal 3D space groups have points, lines and planes of special symmetry, so $\varphi = 0$ and $\varphi = 90^\circ$ define 3D cuts of special symmetry for the 4D space group. Thus our whole analysis is implicit in the 4D formalism. However, Janner & Janssen (1980) appear to have ignored the C_2 component in their scheme, for example in their discussion of NaNO_2 although they refer to the Polish work where the second component was identified. The 4D construction remains rigorously applicable even if the modulation wave 'squares up' into a 'soliton lattice' as the temperature is lowered. The 4D space group cannot change discontinuously and thus the definition of the C_1 , C_2 components and their symmetries remain valid. From the form of the wave the regions of predominantly C_2 structure may get progressively smaller but the amplitude will tend to be stronger because $\text{grad } \psi_1$ is increased (Fig. 5). Similarly, a \mathbf{q} cut, where \mathbf{q} is some rational fraction $m\mathbf{g}/n$ with large n , will slice through both C_1 and C_2 regions of 4D space in much the same way as an incommensurate \mathbf{q} : such a high-order commensurate phase may therefore be included within the present analysis. Finally, in materials having several pairs $\pm \mathbf{q}_i$ of modulation wave vectors our ideas can be applied to each pair.

2. Demonstration of the two components

Following the Landau treatment of phase transitions (Landau & Lifshitz, 1968) we describe an IC phase in terms of Bloch functions $\psi_{\mathbf{q}}(\mathbf{r})$, $\psi_{-\mathbf{q}}(\mathbf{r})$ (Bradley & Cracknell, 1972) where we use the continuous position variable \mathbf{r} simply to denote that ψ contains a specification of all that goes on in every unit cell. Certainly the spin density and ensemble probability density of every nuclear species as a continuous function of \mathbf{r} would give a complete specification of the system, but in practice one tends to use a finite set of displacement vectors and site occupation probabilities. A phase factor $\exp(i\mathbf{q} \cdot \mathbf{r})$ is to be interpreted similarly as applied to anything at point \mathbf{r} .

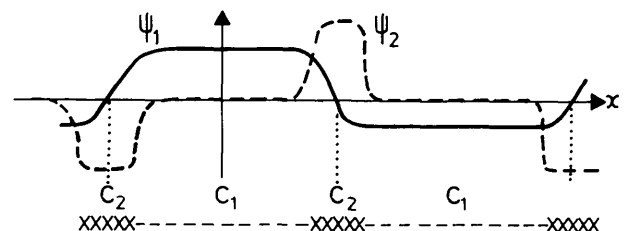


Fig. 5. Order parameters ψ_1 and ψ_2 (above) with regions of predominantly C_1 and C_2 structure (below) in the incommensurate phase when the modulation wave 'squares up'. Note the enhancement of $\text{grad } \psi_1$ and hence of the amplitude of ψ_2 as the width of the C_2 region narrows.

The phase of $\psi_{-\mathbf{q}}$ is conveniently specified by

$$\psi_{-\mathbf{q}} = T\psi_{\mathbf{q}}, \quad (2.1)$$

where the time-reversal operator T means taking the complex conjugate. A real IC phase is described by the real function

$$\psi_{1C}(\mathbf{r}) = \exp(i\varphi)\psi_{\mathbf{q}}(\mathbf{r}) + \exp(-i\varphi)\psi_{-\mathbf{q}}(\mathbf{r}), \quad (2.2)$$

where varying φ translates the whole modulation by a phase φ . We now define the real function

$$\Psi_1(\mathbf{r}) = \exp(-i\mathbf{q} \cdot \mathbf{r})\psi_{\mathbf{q}} + \exp(i\mathbf{q} \cdot \mathbf{r})\psi_{-\mathbf{q}}, \quad (2.3)$$

which is easily shown to be *periodic* with the periodicity of the lattice (or superlattice in the sense of § 1). To prove this we use the Bloch property

$$\psi_{\mathbf{q}}(\mathbf{r} + \mathbf{l}) = \exp(i\mathbf{q} \cdot \mathbf{l})\psi_{\mathbf{q}}(\mathbf{r}) \quad (2.4)$$

where \mathbf{l} is any lattice vector and find

$$\Psi_1(\mathbf{r} + \mathbf{l}) = \Psi_1(\mathbf{r}). \quad (2.5)$$

This Ψ_1 defines our pure component C_1 and similarly

$$\Psi_2(\mathbf{r}) = i[\exp(-i\mathbf{q} \cdot \mathbf{r})\psi_{\mathbf{q}} - \exp(i\mathbf{q} \cdot \mathbf{r})\psi_{-\mathbf{q}}] \quad (2.6)$$

defines C_2 , also periodic in the lattice. This construction for C_1 , C_2 is completely equivalent to the geometrical representation of § 1 in the 4D space of Janner & Janssen (1977, 1979): Fig. 1 shows that C_1 along the x axis may be mapped out by moving the sloping line up and down, *i.e.* by phase shifting the real IC modulation around, which is exactly what (2.3) does as comparison with (2.2) shows. We can solve (2.3), (2.6) for $\psi_{\mathbf{q}}$, $\psi_{-\mathbf{q}}$ to express them in terms of Ψ_1 , Ψ_2 :

$$\begin{aligned} \psi_{\mathbf{q}}(\mathbf{r}) &= \frac{1}{2} \exp(i\mathbf{q} \cdot \mathbf{r})[\Psi_1(\mathbf{r}) - i\Psi_2(\mathbf{r})] \\ \psi_{-\mathbf{q}}(\mathbf{r}) &= \frac{1}{2} \exp(-i\mathbf{q} \cdot \mathbf{r})[\Psi_1(\mathbf{r}) + i\Psi_2(\mathbf{r})]. \end{aligned} \quad (2.7)$$

Thus Ψ_1 and Ψ_2 are approximately the real and imaginary parts of $\psi_{\mathbf{q}}$ in cell zero where the extra phase $\mathbf{q} \cdot \mathbf{r}$ is small.

It is now easy to show what the real IC modulation (2.2) actually looks like. Using (2.7) we can express it as

$$\psi_{1C}(\mathbf{r}) = \cos(\mathbf{q} \cdot \mathbf{r} + \varphi)\Psi_1(\mathbf{r}) + \sin(\mathbf{q} \cdot \mathbf{r} + \varphi)\Psi_2(\mathbf{r}). \quad (2.8a)$$

This clearly shows that the modulated structure is approximately the pure periodic component C_1 in cells where the phase $\mathbf{q} \cdot \mathbf{r} + \varphi$ is near a multiple of 180° , and is like C_2 in cells where the phase is near an odd multiple of 90° , as we set out to prove (see discussion in § 1). There is no approximation involved about \mathbf{q} needing to be small.

It may seem unsatisfactory to use continuous phase factors in (2.3), (2.6) since group theory only defines the discrete ones (2.4). We have therefore verified that an entirely parallel treatment can be given in terms

of the discrete phase factor $\exp i\mathbf{q} \cdot \mathbf{l}$ for cell \mathbf{l} leading to a result equivalent to (2.8a):

$$\begin{aligned} \psi_{1C}(\mathbf{l} + \boldsymbol{\rho}) &= \cos(\mathbf{q} \cdot \mathbf{l} + \varphi)\Psi'_1(\boldsymbol{\rho}) \\ &\quad + \sin(\mathbf{q} \cdot \mathbf{l} + \varphi)\Psi'_2(\boldsymbol{\rho}). \end{aligned} \quad (2.8b)$$

Here $\boldsymbol{\rho}$ is the position variable confined to within cell zero so that points in cell \mathbf{l} are given by $\mathbf{r} = \mathbf{l} + \boldsymbol{\rho}$. It is easy to relate Ψ'_1 , Ψ'_2 to Ψ_1 , Ψ_2 from a comparison of (2.8a), (2.8b):

$$\begin{aligned} \Psi'_1(\boldsymbol{\rho}) &= \Psi_1(\boldsymbol{\rho}) \cos \mathbf{q} \cdot \boldsymbol{\rho} + \Psi_2(\boldsymbol{\rho}) \sin \mathbf{q} \cdot \boldsymbol{\rho}, \\ \Psi'_2(\boldsymbol{\rho}) &= \Psi_2(\boldsymbol{\rho}) \cos \mathbf{q} \cdot \boldsymbol{\rho} - \Psi_1(\boldsymbol{\rho}) \sin \mathbf{q} \cdot \boldsymbol{\rho}. \end{aligned} \quad (2.9)$$

3. The symmetry relationship theorem

We now prove the theorem (1.3), supposing that the space group \mathcal{G} of the average structure contains an element S (1.2) which turns \mathbf{q} into $-\mathbf{q}$. We have

$$S^2\psi_{\mathbf{q}} = \psi_{\mathbf{q}}, \quad S^2\psi_{-\mathbf{q}} = \psi_{-\mathbf{q}} \quad (3.1)$$

as is obvious if S is an inversion, twofold rotation or reflection since S^2 is then the unit operator. But it remains true when S is a twofold screw axis or glide plane, in which case S^2 is a pure translation l_1 which from (1.2) must be perpendicular to \mathbf{q} : hence, $\mathbf{q} \cdot l_1 = 0$ and (3.1) follows from (2.4). We use S in a standard argument to define the phase of $\psi_{\mathbf{q}}$ by combining it with the time reversal operator T (2.1) which also turns \mathbf{q} to $-\mathbf{q}$ and *vice versa*. We have that $ST\psi_{\mathbf{q}}$ also has wave vector \mathbf{q} and is a multiple of $\psi_{\mathbf{q}}$ (or can be so chosen), the multiplier being a phase factor $\exp 2i\gamma$ with modulus unity by normalization. We have

$$ST\psi_{\mathbf{q}} = \exp(2i\gamma)\psi_{\mathbf{q}}, \quad (3.2)$$

i.e.

$$ST[\exp(i\gamma)\psi_{\mathbf{q}}] = [\exp(i\gamma)\psi_{\mathbf{q}}], \quad (3.3)$$

from which we redefine $\psi_{\mathbf{q}}$ to absorb the phase factor so that in future we write

$$ST\psi_{\mathbf{q}} = TS\psi_{\mathbf{q}} = \psi_{\mathbf{q}}, \quad ST\psi_{-\mathbf{q}} = TS\psi_{-\mathbf{q}} = \psi_{-\mathbf{q}}. \quad (3.4)$$

This defines $\psi_{\mathbf{q}}$ with a definite phase, with the property from (2.1) and (3.4)

$$S\psi_{\mathbf{q}} = \psi_{-\mathbf{q}}, \quad S\psi_{-\mathbf{q}} = \psi_{\mathbf{q}}. \quad (3.5)$$

We also have

$$\begin{aligned} S[\exp(i\mathbf{q} \cdot \mathbf{r})] &= \exp(-i\mathbf{q} \cdot \mathbf{r}), \\ S[\exp(-i\mathbf{q} \cdot \mathbf{r})] &= \exp(i\mathbf{q} \cdot \mathbf{r}) \end{aligned} \quad (3.6)$$

as follows from the fact that S reverses the component of \mathbf{r} parallel to \mathbf{q} and other components are irrelevant in (3.6). The symmetries of Ψ_1 , Ψ_2 now follow from (2.3), (2.6), (3.5), (3.6):

$$S\Psi_1 = \Psi_1, \quad S\Psi_2 = -\Psi_2, \quad (3.7)$$

and the same symmetries apply to Ψ'_1 , Ψ'_2 in (2.8b), which proves the theorem (1.3).

This mathematical result (3.7) combined with (2.8a, b) specifies precisely what the symmetry-relationship theorem (1.3), (1.4) is, and shows that it holds true without any approximation about \mathbf{q} being small. We have used one element S with the property (1.2) to define the phases and hence the symmetries (3.7); we may ask what will be the effect on Ψ_1 , Ψ_2 of other elements $S^{(i)} = S', S'', \dots$ also with the property (1.2)? As always in group theory the answer lies in the complete irreducible representations by which Ψ_1 and Ψ_2 transform under $\mathcal{G}_{\pm\mathbf{q}}$. If these irreducible representations are one dimensional then Ψ_1 and Ψ_2 must be even or odd under each $S^{(i)}$ because all characters are ± 1 . With irreducible representations of higher dimension the situation can be more complicated but we reiterate that one S suffices to establish the result (1.4) that the relative phases of different aspects (§ 1) must be 0 or 90°.

In view of the centrality of the symmetry-relationship theorem we sketch an alternative proof based on building up the IC structure from all possible aspects in the sense of § 1. It leads directly to the form (1.4) of the theorem relevant to structural analysis, namely relating the phases of the aspects to one another at non-zero \mathbf{q} . Let the χ_n , $n = 1, 2, \dots$, represent all possible aspects defined in the unit cell of the average structure, chosen real and with intrinsic symmetry under S :

$$S\chi_n = s_n\chi_n \quad s_n = \pm 1 \quad (\text{for even/odd}). \quad (3.8)$$

The corresponding Bloch waves are defined in the usual way:

$$\chi_{n\mathbf{q}} = \sum_{\mathbf{l}} \exp(i\mathbf{q} \cdot \mathbf{l}) \chi_n(\mathbf{l}). \quad (3.9)$$

The Landau theory of phase transitions revolves around an instability (soft mode in the generalized sense including ordering) of the second-order terms in the free energy which we write as

$$G_2 = \sum_{\mathbf{q}} \sum_n A_{nn}(\mathbf{q}) \chi_{n\mathbf{q}}^* \chi_{n\mathbf{q}} + \sum_{\mathbf{q}} \sum_{n \neq m} [H_{nm}(\mathbf{q}) \chi_{n\mathbf{q}}^* \chi_{m\mathbf{q}} + H_{nm}(\mathbf{q})^* \chi_{n\mathbf{q}} \chi_{m\mathbf{q}}^*]. \quad (3.10)$$

Reality and reciprocity in \mathbf{l} , \mathbf{l}' require $A_{nn}(\mathbf{q})$ to be real and even in \mathbf{q} . From (3.9) the term $\chi_{n\mathbf{q}} \chi_{m\mathbf{q}}^*$ is identical to $\chi_{n-\mathbf{q}}^* \chi_{m-\mathbf{q}}$ and there is no point in having it twice with different coefficients, so that without loss of generality we have

$$H_{nm}(\mathbf{q})^* = H_{nm}(-\mathbf{q}). \quad (3.11)$$

The free energy (3.10) has to be invariant under the symmetry S , *i.e.* it has to be the same for two crystals one with aspects having some arbitrary set of values $\chi_{n\mathbf{q}}^{(1)}$ and the other with values given by

$$\chi_{n\mathbf{q}}^{(2)} = s_n \chi_{n-\mathbf{q}}^{(1)}. \quad (3.12)$$

The energies obtained from substituting the $\chi_{n\mathbf{q}}^{(1)}$ and $\chi_{n\mathbf{q}}^{(2)}$ [in the form (3.12)] into (3.10) have to be equal. Equating the coefficient of $\chi_{n\mathbf{q}}^{(1)*} \chi_{m\mathbf{q}}^{(1)}$ in the two expressions gives

$$\begin{aligned} H_{nm}(\mathbf{q}) &= s_n s_m H_{nm}(-\mathbf{q}) \\ &= s_n s_m H_{nm}(\mathbf{q})^*, \end{aligned} \quad (3.13)$$

where the last step follows from (3.11). Rephrased, we have

$$\begin{aligned} H_{nm}(\mathbf{q}) &= \text{real} && \text{if } s_n = s_m, \\ &= \text{imaginary} && \text{if } s_n = -s_m. \end{aligned} \quad (3.14)$$

All the H_{nm} become real if we absorb a factor i to define new variables $\chi'_{n\mathbf{q}}$ for all aspects which have $s_n = -1$. The mode going soft is then given by a real transformation to diagonalize the now real matrix A_{nn} plus H_{mn} , *i.e.* with all aspects in phase in terms of the new variables. In terms of the original $\chi_{n\mathbf{q}}$ all aspects even under S are in phase and all aspects odd under S are 90° out of phase with the former. *Q.E.D.*

4. Difference Patterson functions

Cochran (1968) has defined a complex Patterson function for a phonon, which may be extended to an arbitrary IC structure. Picking out its real and imaginary components we will define the plus and minus difference Patterson functions (DPFs) and express them in terms of the components C_1 , C_2 . Their application has already been discussed in § 1.

In accordance with (1.1) and (2.9) we write the electron density as

$$\rho(\mathbf{r}) = \rho_{av}(\mathbf{r}) + \rho_1(\mathbf{r}) \cos \mathbf{q} \cdot \mathbf{r} + \rho_2(\mathbf{r}) \sin \mathbf{q} \cdot \mathbf{r}. \quad (4.1)$$

The scattering amplitude per unit cell in the satellite reflections is proportional to

$$A(\mathbf{g} \pm \mathbf{q}) = N^{-1} \int \rho(\mathbf{r}) \exp i(\mathbf{g} \pm \mathbf{q}) \cdot \mathbf{r} d^3\mathbf{r}, \quad (4.2)$$

where the integration is over all N cells of the crystal. Substitution of (4.1) into (4.2) yields

$$A(\mathbf{g} \pm \mathbf{q}) = \frac{1}{2} A_1(\mathbf{g}) \pm \frac{1}{2} i A_2(\mathbf{g}), \quad (4.3)$$

where

$$A_j(\mathbf{g}) = \int \rho_j(\mathbf{r}) \exp(i\mathbf{g} \cdot \mathbf{r}) d^3\mathbf{r} \quad (j = 1, 2) \quad (4.4)$$

and the integration is over one cell, and the intensities $I(\mathbf{g} \pm \mathbf{q})$ are of course $|A(\mathbf{g} \pm \mathbf{q})|^2$. We now define

$$I_+(\mathbf{g}) = 2[I(\mathbf{g} + \mathbf{q}) + I(\mathbf{g} - \mathbf{q})] \quad (4.5a)$$

$$I_-(\mathbf{g}) = 2[I(\mathbf{g} + \mathbf{q}) - I(\mathbf{g} - \mathbf{q})] \quad (4.5b)$$

from the summed and differenced intensities. Use of (4.3) gives

$$\begin{aligned} I_+(\mathbf{g}) &= \frac{1}{2} [A_1^* - iA_2^*] (A_1 + iA_2) \\ &\quad + (A_1^* + iA_2^*) (A_1 - iA_2) \\ &= A_1^* A_1 + A_2^* A_2 \end{aligned} \quad (4.6a)$$

$$I_-(\mathbf{g}) = i(A_1^* A_2 - A_1 A_2^*) \quad (4.6b)$$

and we substitute for the $A_j = A_j(\mathbf{g})$ the expression (4.4) to obtain

$$\begin{aligned} I_+(\mathbf{g}) &= \iint \exp i\mathbf{g} \cdot (\mathbf{r}' - \mathbf{r}) [\rho_1(\mathbf{r})\rho_1(\mathbf{r}') \\ &\quad + \rho_2(\mathbf{r})\rho_2(\mathbf{r}')] d^3\mathbf{r} d^3\mathbf{r}' \\ &= \int d^3\mathbf{R} \exp(i\mathbf{g} \cdot \mathbf{R}) \int [\rho_1(\mathbf{r})\rho_1(\mathbf{r} + \mathbf{R}) \\ &\quad + \rho_2(\mathbf{r})\rho_2(\mathbf{r} + \mathbf{R})] d^3\mathbf{r} \end{aligned} \quad (4.7a)$$

$$\begin{aligned} I_-(\mathbf{g}) &= \int d^3\mathbf{R} \exp(i\mathbf{g} \cdot \mathbf{R}) \int i[\rho_1(\mathbf{r})\rho_2(\mathbf{r} + \mathbf{R}) \\ &\quad - \rho_2(\mathbf{r})\rho_1(\mathbf{r} + \mathbf{R})] d^3\mathbf{r}. \end{aligned} \quad (4.7b)$$

By making the substitution $-\mathbf{r} - \mathbf{R}$ for \mathbf{r} in the second term of (4.7a), (4.7b), we find the square bracket in (4.7a) and (4.7b) to be an even and odd function of \mathbf{R} respectively. The plus and minus difference Patterson functions $P_+(\mathbf{R})$, $P_-(\mathbf{R})$ are obtained by Fourier inversion of the experimental intensities $I_+(\mathbf{g})$, $I_-(\mathbf{g})$ and dropping a factor i from P_- . Since $I_+(-\mathbf{g}) = I_+(\mathbf{g})$ and $I_-(-\mathbf{g}) = -I_-(\mathbf{g})$ by Friedel's law, the P_+ and P_- become cosine and sine transforms, respectively. Comparison with (4.7) therefore gives

$$\begin{aligned} P_+(\mathbf{R}) &= (\text{constant}) \\ &\quad \int [\rho_1(\mathbf{r})\rho_1(\mathbf{r} + \mathbf{R}) + \rho_2(\mathbf{r})\rho_2(\mathbf{r} + \mathbf{R})] d^3\mathbf{r} \end{aligned} \quad (4.8a)$$

$$\begin{aligned} P_-(\mathbf{R}) &= (\text{constant}) \\ &\quad \int [\rho_1(\mathbf{r})\rho_2(\mathbf{r} + \mathbf{R}) - \rho_2(\mathbf{r})\rho_1(\mathbf{r} + \mathbf{R})] d^3\mathbf{r}. \end{aligned} \quad (4.8b)$$

Thus P_+ is the sum of the Pattersons of ρ_1 and ρ_2 , whereas P_- is a cross correlation function. Incidentally, there have been no symmetry assumptions used in these derivations. Note that in (4.5) the intensities at $\mathbf{g} \pm \mathbf{q}$ have in a sense been shrunk to the wave vector \mathbf{g} (or $\frac{1}{2}\mathbf{g}$ for a superlattice: see § 1), so that in forming the Patterson functions $P_+(\mathbf{R})$, $P_-(\mathbf{R})$ they are taken with phase factor $\exp i\mathbf{g} \cdot \mathbf{R}$, not $\exp i(\mathbf{g} \pm \mathbf{q}) \cdot \mathbf{R}$. Our Patterson functions, like our components C_1 and C_2 , are periodic in the unit cell of the average structure (or twofold superlattice): we avoid entirely any large supercell obtained by setting q approximately equal to some rational fraction.

One clarification is required concerning the point already raised in § 2 about whether to use a continuous phase factor as in (4.1) or a discrete one jumping from cell to cell. Formally either can be used. In reality the atomic positions and site probabilities tend to follow the continuous phase factor but one hardly expects the electron density inside one atom to have such a variation! Thus the scattering amplitudes and intensities at $\mathbf{g} \pm \mathbf{q}$ in reality will contain the atomic scattering factors at $\mathbf{g} \pm \mathbf{q}$ as in (1.6) but positional structure factors calculated for C_1 and C_2 with factors $\exp i\mathbf{g} \cdot \mathbf{R}$. Thus the relationship between real X-ray amplitudes $A(\mathbf{g} \pm \mathbf{q})$ implied by (4.3) applies only to zero order in \mathbf{q} , and so does the rest

of the analysis. Strictly one should use intensities in (4.5) and in the corresponding Pattersons which have been corrected for the variation of atomic scattering factors in letting $\mathbf{g} \pm \mathbf{q}$ tend to \mathbf{g} (Cochran, 1968).

5. Inclusion of full space-group symmetry

When we consider the full symmetry analysis of an IC material we have an interplay of two features. Firstly, we must incorporate the symmetry relationship theorem (1.3) into the full description under all symmetry elements. Secondly, as remarked in § 1, as long as we are dealing with first-order satellites only, the correct symmetry specification of a difference structure is an irreducible representation rather than a space group (Landau & Lifshitz, 1968). We will defer to the end of this section the full and formal analysis, proceeding first to some more straightforward points.

As already mentioned in § 1, it is clear from (4.3) that the satellites at $\mathbf{g} \pm \mathbf{q}$ (or $\frac{1}{2}\mathbf{g} \pm \mathbf{q}$ if appropriate: § 1) will have equal intensity when either C_1 or C_2 gives zero diffraction intensity at \mathbf{g} . One obtains 'systematic equalities' in satellite intensities, where equality means after correction for the atomic scattering factors as discussed at the end of § 4 so that in practice one may only be able to identify them with certainty in a case with moderately small \mathbf{q} . Such systematic extinctions in the reflections from one component of course imply the presence of certain symmetries as in the normal manner of space-group determination, and the symmetry relationship (1.3) can be useful in assigning which symmetries belong to the same component and which to the two different ones when several symmetry elements are evident. We wish to point to a couple of further ramifications of this line of thought.

Firstly, we note that if certain satellite reflections arise from one component only, then it may be possible to obtain from them a Patterson projection solely of that component. A good example occurs in the mineral mullite where the relevant symmetry point for the IC modulations is $\frac{1}{2}C^* = 00\frac{1}{2}$. The space group \mathcal{G} of the high-temperature average structure is $Pbam$, and the two-component twofold superlattice structures C_1 , C_2 have been inferred as $Pbnm$ and $Pnnm$ from an analysis of all the available information (McConnell, 1981a, 1984b). If one defines difference structure factors for the two-component structures $Pnnm$ and $Pbnm$ at the symmetry point $00\frac{1}{2}$ and in the reciprocal-lattice plane containing reflections of the set $0kl + \frac{1}{2}$, one finds that systematic absences occur for k even for the space group $Pnnm$ and for k odd for $Pbnm$, leading to systematic equalities for both sets of k 's. In practice the modulation vector in mullite is parallel to \mathbf{a}^* so that the intensities at the satellites of $0kl + \frac{1}{2}$ must be equal in any case. However, the systematic equalities may be used to

Table 1. Representations for mullite at the symmetry point vector $00\frac{1}{2}$

		$\{E 000\}$	$\{C_{2x} \frac{1}{2}0\}$	$\{m_x \frac{1}{2}0\}$	$\{m_z 000\}$	$\{E 001\}$	$\{C_{2x} \frac{1}{2}1\}$	$\{m_x \frac{1}{2}1\}$	$\{m_z 001\}$	$\{i 000\}$	$\{m_x \frac{1}{2}0\}$	$\{C_{2x} \frac{1}{2}0\}$	$\{C_{2z} 000\}$	$\{i 001\}$	$\{m_x \frac{1}{2}1\}$	$\{C_{2x} \frac{1}{2}1\}$	$\{C_{2z} 001\}$
X_1	<i>Pbam</i>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
X_2	<i>Pnam</i>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
X_3	<i>Pbnm</i>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
X_4	<i>Pnnm</i>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
X_5	<i>Pnam</i>	1	-1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
X_6	<i>Pbam</i>	1	-1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
X_7	<i>Pnnm</i>	1	-1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
X_8	<i>Pbnm</i>	1	-1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

derive difference Patterson projections on the (100) plane for the two components separately using the even- k and odd- k reflections, respectively.

The fact that the symmetries of C_1 , C_2 are irreducible representations means that they are richer in their symmetry than space groups. For example, they can be odd under some symmetry elements which can lead to new extinction rules compared with those for normal space groups. Note again that C_1 and C_2 are difference structures, and it is only these differences from the average structure that diffract into the satellites. Fig. 6 gives a simple example with two sites at \mathbf{R}_1 , \mathbf{R}_2 in the unit cell connected by a screw axis in the average structure. In the difference structure these may have positive and negative weights corresponding to a character -1 for the screw axis in the irreducible representation. Such a component structure clearly has zero structure factor

$$S(\mathbf{g}) = (+1) \exp(i\mathbf{g} \cdot \mathbf{R}_1) + (-1) \exp(i\mathbf{g} \cdot \mathbf{R}_2) \quad (5.1)$$

for reflections $h00$ with h even which is different from any of the usual extinction rules for symmetry elements in space groups.

We turn now to a more complete and precise statement of the symmetry specification of IC structures. As noted in § 1 the IC structure transforms as one component of an irreducible representation of the space group \mathcal{G} of the average structure (Bradley & Cracknell, 1972) if we confine ourselves to the sinusoidally modulated structure defined by the first-order satellites. The irreducible representation involves a 'star' of all symmetry-related \mathbf{q} vectors of which we shall only consider one pair to be denoted as $\pm\mathbf{q}$, the mixing with other members of the star (if present) having been considered thoroughly, for example, by Cowley & Bruce (1978) and Jacobs & Walker (1982). The modulation with $\pm\mathbf{q}$, viewed as a difference structure from the average structure, trans-

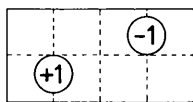


Fig. 6. Simple difference structure with odd symmetry under a twofold screw axis in the x direction. The two equivalent sites with opposite weights are at $\mathbf{R}_1 = (\frac{1}{4}, y, z)$ and $\mathbf{R}_2 = (\frac{3}{4}, -y, -z)$.

forms as one component of an irreducible representation of $\mathcal{G}_{\pm\mathbf{q}}$, the subgroup of \mathcal{G} which turns \mathbf{q} into $\pm\mathbf{q}$. It follows from (2.3), (2.6) and the arguments leading to (3.7) that Ψ_1 and Ψ_2 also transform under the space group $\mathcal{G}_{\pm\mathbf{q}}$ according to irreducible representations, now with wave vector zero or $\frac{1}{2}\mathbf{g}$ as the case may be (see § 1) since Ψ_1 , Ψ_2 are periodic in the lattice (or superlattice). These then are the symmetries of the two components C_1 and C_2 which formally completes the symmetry specification of the IC structure. Since the two components are linked by the theorem (1.3) the symmetry of one determines the other.

Our remaining points are best made with respect to a specific example for which we choose mullite $\text{Al}_{8+2x}\text{Si}_{4-2x}\text{O}_{20-x}\square_x$ with modulation wave vector $\mathbf{q} = Q\mathbf{a}^* + \frac{1}{2}\mathbf{c}^*$ where $Q \ll 1$. The space group $\mathcal{G}_{\pm\mathbf{q}}$ is given in Table 1 with character table for all irreducible representations at the symmetry-point wave vector $00\frac{1}{2}$ labelled X_1 to X_8 . Our first point is to note that X_1 and X_2 have the same symmetry (even or odd) under the space-group elements on the left of the table which leave \mathbf{q} invariant, and opposite symmetries under elements which turn \mathbf{q} into $-\mathbf{q}$ on the right half of the table. Thus X_1 , X_2 are a pair of irreducible representations satisfying the symmetry relation (1.3) and can apply to a pair of components C_1 , C_2 . Similarly, X_3 , X_4 and X_5 , X_6 etc. form related pairs. The actual pair relevant to mullite is X_7 , X_8 .

Our second point about Table 1 is applicable to any real one-dimensional irreducible representation, in this case all of them. Its characters consist purely of plus ones and minus ones, the irreducible representation being completely determined if we know which group elements have character $+1$, the remaining then having character -1 . Now for any given irreducible representation the group elements with character $+1$ form a subgroup so that a specification of this subgroup determines the representation uniquely. In our case such a subgroup is again a space group as listed in the second column of the table. Each space-group symbol actually occurs twice in the column but relating to different origins with respect to the original so that they are different symmetries for our purposes. This therefore explains the use of space-group symbols occasionally in this paper where irreducible representations are referred to. Such a

notation has the following utility. The irreducible representation with even and odd behaviour under various group elements refers to the difference structure C_1 or C_2 . Now the average structure is of course invariant under all group elements, so that when we add it to C_1 or C_2 to give the actual structure of the material at OO' etc. or NN' etc. in Fig. 1, the group elements with character -1 for C_1 or C_2 are lost. Our subgroup symbol therefore remains as the space group of the material in the pure component form. This will remain unchanged if at lower temperatures the modulation wave squares up and we move out of the realm of sinusoidal modulation described by an irreducible representation.

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An Experimental Determination of the Anomalous Dispersion Factor f'' for Sulfur

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Abstract

The anomalous dispersion factor, f'' , of sulfur for Cu $K\alpha$ radiation has been determined to be 0.60 (3) using measurements of Bijvoet differences of 175 selected reflections for a 6-(4-nitrobenzyl)thioinosine crystal.

Introduction

During the course of our study on the structure and absolute configuration of 6-(4-nitrobenzyl)-

thioinosine, a potent inhibitor of nucleoside transport, we discovered that crystals of this compound exhibited pronounced Bijvoet differences ($\Delta I = I_H - I_{\bar{H}}$) for Cu $K\alpha$ radiation. From the measured values of selected Bijvoet differences and using the method reported earlier by one of us (Parthasarathy, 1962), we have determined experimentally the absorption part of the anomalous scattering factor f'' for the sulfur atom.

Direct experimental determinations of f'' have been carried out only for a few atoms (see Table 1) by careful measurements of selected Bijvoet differences. The availability of synchrotron radiation of tunable wavelengths has led to accurate determinations of f'' (Phillips, Templeton, Templeton & Hodgson, 1978).

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