but the results of a simulation are obtained in about 30 minutes.

If suitable indexes of efficiency are chosen then the same principles can be applied rigorously to other situations in X-ray crystallography with equal or greater profit.

References

BEZJAK, A. (1961). *Croat. Chem. Acta*, **33**, 197-200.

BUROVA, E. M. & ZHIDKOV, N. P. (1977). *Kristallografiya*, **22**, 1182-1190.

CHUNG, F. H. (1974). *Adv. X-ray Anal.* **17**, 106-115.

DRAPER, N. R. & SMITH, H. (1966). *Applied Regression Analysis.* New York: John Wiley.

ENGELHARDT, W. (1955). *Z. Kristallogr.* **106**, 430-459.

FIALA, J. (1972). *J. Phys. D*, **5**, 1874-1876.

FIALA, J. (1976). *J. Appl. Cryst.* **9**, 429-432.

FUENTES, L. (1982). Thesis. Havana.

GONZALEZ, C. R. (1981). *Rev. Cubana Fis.* **1**, 61-77.

GONZALEZ, C. R. (1987). *Acta Cryst.* In the press.

GONZALEZ, C. R. & ROQUE, R. (1983). *Kinam.* **5**, 67-74.

HARTMANN, U. (1972). *Haerterei-Tech. Mitt.* **27**, 271-278.

KARLAK, R. F. & BURNETT, D. S. (1966). *Anal. Chem.* **38**, 1741-1745.

LEROUX, J., LENNOX, D. H. & KAY, K. (1953). *Anal. Chem.* **25**, 740-743.

NARAY-SZABO, I. & PETER, E. (1964). *Chimia*, **18**, 275-277.

PETER, E. & KALMAN, A. (1964). *Acta Chim. Acad. Sci. Hung.* **41**, 244-248.

VLASOV, V. V. & VOLKOVA, S. A. (1974). *Rentgenogr. Miner. Syr'ya*, **10**, 25-34.

ZAVYALOVA, L. L., IVOILOV, A. S. & DENISOVA, E. K. (1964). *Rentgenogr. Miner. Syr'ya*, **4**, 190-206.

ZEVIN, L. S. (1977). *J. Appl. Cryst.* **10**, 147-150.

Acta Cryst. (1987). A**43**, 626-635

Deriving the Two-Component Description of Incommensurate Structures From the Superspace Group

BY E. H. SIMMONS* AND VOLKER HEINE

Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, England

(*Received* 17 *July* 1986; *accepted* 5 *January* 1987)

Abstract

McConnell & Heine [*Acta Cryst.* (1984), A**40**, 473-482] have shown that an incommensurate (IC) structure may be fully described as an average structure plus two pure component difference structures C_1 and C_2 modulated by $\cos(\mathbf{Q}.\mathbf{r})$ and $\sin(\mathbf{Q}.\mathbf{r})$ respectively, where the symmetries of C_1 and C_2 are related in a precise way. This result was derived from the conventional Landau theory where the symmetry is specified by an irreducible representation of the space group of the average or disordered structure. It has also been shown by de Wolff, Janssen & Janner [*Acta Cryst.* (1981), A**37**, 625-636] that an IC crystal has the symmetry of a four-dimensional space group; the papers discussing these superspace groups describe the modulation in terms of only a single component. It is proved here that the two descriptions are identical in content, showing that the structure of a superspace group implicitly requires the existence of both C_1 and C_2, and that their symmetries are uniquely related in this formulation as in the McConnell-Heine theory. Two one-dimensional examples are discussed and $NaNO_2$ is considered in detail. Although the McConnell-Heine theory was formulated in terms of the sinusoidal modulation which occurs just below the transition temperature, it is shown that the symmetry properties derived in that theory continue to be valid as the modulation 'squares up' at lower temperatures.

1. Introduction

In recent years it has become recognized that incommensurate (IC) modulated structures have very precisely definable symmetry. Since the IC modulation destroys the regular lattice periodicity, it had at one time been felt that the symmetry was essentially lost. But this is now seen not to be the case. Given the lattice structure and the modulation, the structure is determined throughout all space, implying a correlation of essentially infinite range. This situation is quite

* Present address: Physics Department, Harvard University, Cambridge, MA 02138, USA.

0108-7673/87/050626-10$01.50

different from the case of an amorphous solid where, in spite of local order, all long-range correlation is lost.

Broadly speaking, two approaches have been published to describe the symmetry precisely. One of these involves the use of one (or more) extra coordinates, τ, to describe the phase of the modulation as a fourth dimension in what is termed superspace. Since shifting the modulation by one wavelength (phase of 2π) leaves the material unchanged, it is invariant under all translations by $2\pi n$ (n an integer) in the τ direction, giving a four-dimensional space group. A table of the four-dimensional superspace groups has been given by de Wolff, Janssen & Janner (1981). The alternative description writes the structure as (McConnell & Heine, 1984)

$$\text{average structure} + C_1 \cos(\mathbf{Q}\,.\,\mathbf{r}) + C_2 \sin(\mathbf{Q}\,.\,\mathbf{r}), \tag{1.1}$$

where C_1 and C_2 are pure component difference structures, *i.e.* differences from the average structure. They are periodic in the lattice, the modulation being provided purely by the cosine and sine factors. Thus [average $+ C_1$] is the notional periodic crystal structure observed at phase $\mathbf{Q}\,.\,\mathbf{r} = 2n\pi$ and [average $- C_1$] at $\mathbf{Q}\,.\,\mathbf{r} = 2(n+1)\pi$, where n is an integer. Similarly we have [average $\pm C_2$] at the $(1+4n)\pi/2$ and $(3+4n)\pi/2$ positions. It is important to note here that C_1 and C_2 have different, but uniquely related, spatial symmetries. When the modulation wave vector $\mathbf{q}_{IC}$ is near half a reciprocal-lattice vector, *e.g.*

$$\mathbf{q}_{IC} = \tfrac{1}{2}\mathbf{a}^* + \mathbf{Q}, \tag{1.2}$$

then the $\frac{1}{2}\mathbf{a}^*$ is absorbed into C_1 and C_2 which become superlattice structures (in this example, $2\times1\times1$ superstructures). The same is done in the superspace description.

The relationship between the two descriptions has never previously been fully worked out, although it has been supposed that they must be equivalent. In particular, the superspace-group approach is formulated purely in terms of one modulated component, C_1 say, with no mention of the existence of C_2. In deriving the superspace-group symbol for the IC phase of $NaNO_2$, for instance, one considers the effect of the generators of the basic space group *Immm* only on the ferroelectric ordered structure which we describe as [average $+ C_1$]: no mention need be made of the shear which is C_2. We shall show that the two approaches are completely equivalent, and that the symmetry of C_2 is in fact contained within the superspace group when one uses the effect of the basic space-group generators on C_1 or *vice versa*.

How the symmetry of C_1 implies that of C_2 in the superspace group is suggested by Fig. 1. The figure can be used to describe the structure in superspace, and we prefer to draw it slightly differently from de Wolff, with the τ coordinate (which is $\mathbf{Q}\,.\,\mathbf{r}$, the phase) on the vertical axis. The line $\tau = 0$ in the figure becomes a 3D hyperplane in (3+1)D space containing the ideal structure C_1 or [average $+ C_1$]. Similarly, $\tau = \pi/2$, π, $3\pi/2$ define the 3D hyperplanes containing the structures C_2, $-C_1$ and $-C_2$ respectively. The actual modulated structure is represented by the diagonal line in the figure, which has slope Q and corresponds to a 3D hyperplane in 4D superspace. We shall demonstrate this explicitly in the (1+1)D examples of § 2. The point we wish to make here is that because the symmetry of the whole (3+1)D space is given by a superspace group, the hyperplanes $\tau = 0$, $\pi/2$, π, $3\pi/2$ are the hyperplanes of special symmetry exactly analogous to the planes of special symmetry in ordinary 3D space groups. With the latter, it is perfectly clear both that the full 3D space group implies the 2D symmetry on all planes of special symmetry within the structure and that those 2D symmetries are related to one another since they are part of the same overall space group. The same is true in superspace. Thus the superspace-group symbol contains within it both the C_1 and the C_2 sets of hyperplanes with their distinct symmetries and the relation between those symmetries. How this works out in practice is shown in the examples of §§ 2 and 3. Then, in § 4, we prove that the precise relation between the symmetries of C_1 and C_2 is the same from the superspace point of view as has already been derived by McConnell & Heine (1984) from the component approach.

The two approaches also differ in their relationship to the traditional Landau theory (Lifshitz & Pitaevskii, 1980), where the symmetry of the ordered phase is specified by an irreducible representation of the space group of the disordered (or average) structure. Basically the superspace approach has no connection with the Landau theory. It describes the

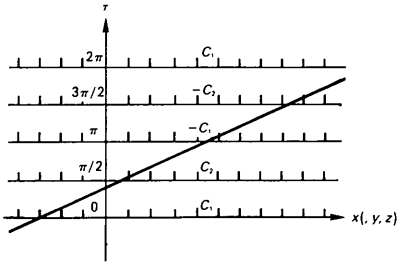


Fig. 1. Four-dimensional superspace τ, x, y, z (drawn here as τ, x) for describing incommensurate modulated structures. The diagonal line of (irrational) slope Q contains the actual structure. The horizontal lines become hyperplanes of special symmetry in superspace. These represent the pure 3D component difference structures $\pm C_1$ and $\pm C_2$. Alternatively one may add the average structure and label them as [average $\pm C_1$], [average $\pm C_2$]. From a mathematical point of view it is more convenient to work with the difference structures while adding the average structure gives a more easily visualized description of the material.

symmetry of the IC structure *per se* in terms of a four- (or higher) dimensional *group*, and is not concerned with phase transitions or the relationship between the ordered and disordered phases. Thus it is broader and can include the symmetry of vernier structures that have nothing to do with phase transitions. Of course one can graft the Landau requirement onto the superspace theory afterwards, *i.e.* one can restrict one's choice of superspace group to those which correspond to irreducible representations of the disordered space group. This has not always been done, resulting in what we see as inappropriate assignments, as discussed elsewhere (Heine & Simmons, 1987). On the other hand the approach of McConnell & Heine (1984) is a development of the Landau theory and hence incorporates the symmetry requirement automatically. Thus the symmetries of the components C_1 and C_2 are irreducible representations at $\mathbf{q}=0$ or other symmetry point such as $\frac{1}{2}\mathbf{a}^*$ in (1.2). This is a slightly different way of presenting the symmetry from the conventional one in that the modulation $\cos(\mathbf{Q}\,.\,\mathbf{r})$, $\sin(\mathbf{Q}\,.\,\mathbf{r})$ has been factored out in (1.1). The reason for preferring the form (1.1) is that the role of symmetry elements turning $\mathbf{Q}$ into $-\mathbf{Q}$ becomes much more explicit. One finds that regions of even and odd character under these elements are separated in space in the standing wave (1.1). Thus C_1 and C_2 transform as irreducible representations of the group $G_{\pm\mathbf{Q}}$ of elements which leave $\mathbf{Q}$ invariant or turn it into $-\mathbf{Q}$, taken from the Landau space group of the disordered or average structure.

The component description is not limited to purely sinusoidal modulations as in (1.1) and as previously discussed by McConnell & Heine (1984). As the temperature is lowered from the transition temperature, the modulation tends to square up in various ways (see *e.g.* Shaw & Heine, 1987) and one can insert such more general modulation functions into (1.1) in place of the sinusoids. If there is no further phase transformation, then the superspace-group symmetry cannot change and hence neither does that of the pure components C_1 and C_2 since they are the symmetries on the special hyperplanes of the superspace group. This is directly relevant when one is making the choice of superspace-group symbol for particular materials, as discussed in Heine & Simmons (1987).

The paired symmetries of C_1 and C_2 have been tabulated for each (3+1)-dimensional superspace group by Simmons (1987).

2. One-dimensional examples

In this section, we will use a pair of simple examples to demonstrate how the difference structures C_1 and C_2 fit into the supercrystal and how the symmetry of C_1 (C_2) within the context of the superspace group uniquely determines that of C_2 (C_1). We consider a one-dimensional crystal along $\mathbf{x}$ with a one-dimensional modulation also along $\mathbf{x}$: so this is not merely a line symmetry within a fundamentally two-dimensional pattern. Two 1D space groups are possible for the average structure of such a crystal. One ($P1$) contains only translations (see Fig. 2*a*). This is not very interesting as an average structure of an IC phase because the only possible symmetries of the 2D superspace denoted (x, τ) in the notation of de Wolff *et al.* (1981) are $(T_\mathbf{a})^n(\mathbf{x}, \tau)=(\mathbf{x}+n\mathbf{a},\ \tau-[\mathbf{Q}\,.\,n\mathbf{a}])$ (n being an integer). Since none of those turn $\mathbf{Q}$ into $-\mathbf{Q}$ (*i.e.* $G_{\pm\mathbf{Q}}=G_\mathbf{Q}$), an IC phase with such a basic structure falls into the category mentioned by McConnell & Heine (1984) of materials too simple to support separate modes C_1 and C_2; we shall not consider this case further. The other possible 1D space group (Fig. 2*b*) has pairs of reflections (r, r') which are the 1D equivalents of what could be twofold rotation axes, inversion centres or mirror planes in a higher-dimensional space. We shall call these 'reflections' so as not to prejudice our expectations of how they will function in the 2D superspace. The space group of such an average structure can be designated *Pr*. We shall take this as our average structure from here on.

Let us take as our first example a crystal undergoing displacive modulation with wave vector $\mathbf{Q}$. To begin, let us see how this structure looks in (1+1)-dimensional superspace. Since $\mathbf{Q}$ is being measured from the symmetry point $\mathbf{q}=0$, then C_1 and C_2 have the lattice periodicity a. The elements of the average structure's space group, besides translations, are E, r and r', which turn $\mathbf{Q}$ into $\mathbf{Q}$, $-\mathbf{Q}$ and $-\mathbf{Q}$, respectively. Then, according to McConnell & Heine (1984), C_1 and C_2 must behave in the same way under E and in opposite fashion under r and r'. Two displacive difference structures satisfying these requirements are the one shown in Fig. 3(*a*), which is even under E, r and r', and the one shown in Fig. 3(*b*), which is even under E, but odd under r and r'. If we lay out

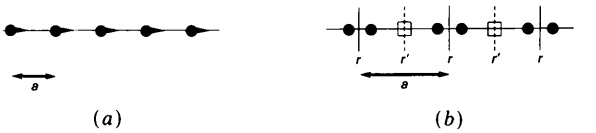


Fig. 2. Patterns illustrating the two possible 1D space groups. (*a*) Space group $P1$. (*b*) Space group Pr; r and r' are 'reflections' which are the 1D equivalent of mirrors, inversion centres or twofold axes.

Fig. 3. Two displacive difference structures in one dimension for a 1D IC crystal with $\mathbf{q}_{IC}=\mathbf{Q}$. (*a*) Structure C_1 which is even under both r and r'. (*b*) Structure C_2 which is odd under both r and r'.

a (1+1)-dimensional supercrystal in the manner of Fig. 1, the result looks like Fig. 4. The diagonal line represents the modulated crystal: because its slope (Q) is irrational only one 'atom' (shown here at the origin) lies precisely on a hyperplane of special symmetry.

Now, we shall turn from structure to symmetry and see how consideration of the symmetry of C_1 in the superspace context determines that of C_2. Since C_1 is even under both r and r', we can represent its symmetry properties as indicated in Fig. 5(a). Extending this to superspace, we can fill in the $\tau=\pi$ and $\tau=2\pi$ hyperplanes as $-C_1$ ('− −') and C_1('+ +'), respectively. The result, shown in Fig. 6(a), clearly has twofold rotation axes as marked. But notice that between the pairs of '+ +' and '− −' twofold axes lie what one might call anti-twofold axes, $\tilde{2}$, which turn '+ +' into '− −' (see Fig. 6b). Then on the hyperplane $\tau=\pi/2$, the C_2 *must* have the antisymmetry '+ −' (Fig. 5b) so that where C_1 is even under r and r', C_2 will be odd - exactly as required by McConnell-Heine theory. Alternatively we may discover the symmetry of C_2 without reference to the anti-twofold axes. In Fig. 6(c) we have inserted a plus sign in a square on the hyperplane $\tau=\pi/2$, and then propagated it by using (a) the twofold axes shown in Fig. 6(a), and (b) the fact that the structure on the hyperplane $\tau=3\pi/2$ has an extra phase factor of -1 relative to that on $\tau=\pi/2$. These plus and minus signs could indicate positive and negative electron density for X-ray scattering in the difference structure. Now looking along the line (hyperplane) $\tau=\pi/2$ we see that the pure C_2 component is odd under the reflection r at $\mathbf{x}=\mathbf{a}$ and odd under r' at $\mathbf{x}=\mathbf{a}/2$. So we again reach the symmetry pattern of Fig. 5(b). The 2D space group containing the symmetries of Fig. 6(b) is $P2$; using notation analogous to that of de Wolff *et al.* (1981), we can also write it as the (1+1)-dimensional superspace

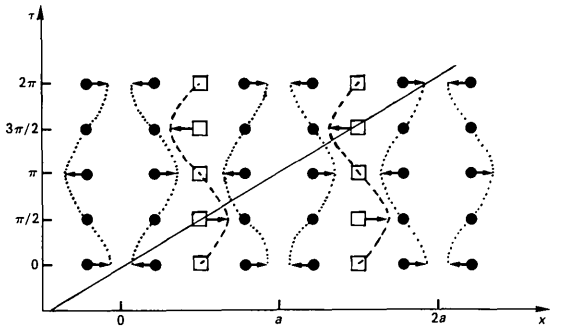


Fig. 4. (1+1)-dimensional supercrystal encompassing the displacive difference structures of Fig. 3 in the manner indicated by Fig. 1. The diagonal line of (irrational) slope Q represents the modulated 1D crystal. Atomic positions in superspace are indicated by the dotted and dashed lines.

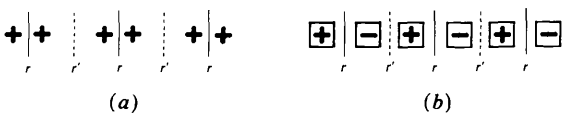


Fig. 5. Symmetries of the difference structures of Fig. 3. (a) Symmetry of C_1, even under both sets of reflections. (b) Symmetry of C_2, odd under both sets of reflections.

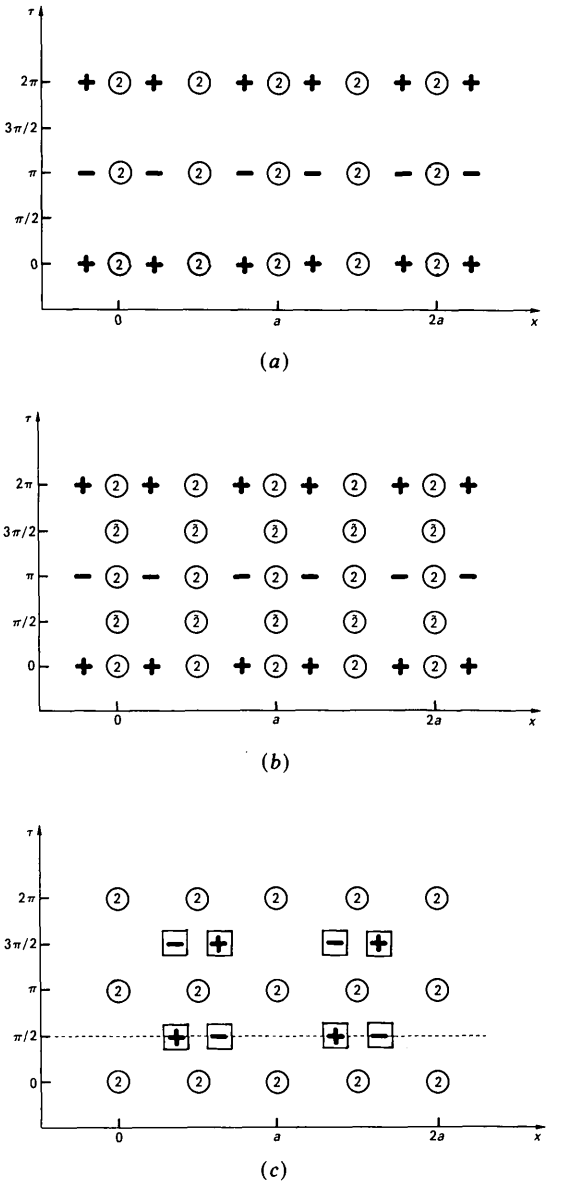


Fig. 6. The symmetries of the supercrystal with $\mathbf{q}_{1C}=Q$. (a) Extending the known symmetries of C_1 (Fig. 5a) into superspace produces this pattern of twofold rotation axes. But these axes imply the existence of other 'anti-twofold' axes, denoted $\tilde{2}$, between them as shown in (b). From (b) we deduce that the symmetries of C_2 must be as shown in Fig. 5(b). In (c) we derive the symmetries of C_2 by an alternative route, starting with a 'plus sign in a square' on the $\pi/2$ hyperplane and propagating it *via* the twofold axes while remembering that the $\pi/2$ and $3\pi/2$ hyperplanes are in antiphase with respect to one another.

group $P_{\bar{1}}^{Pr}$ (P means $\mathbf{q}_{IC}=\mathbf{Q}$, Pr is $G_{\pm Q}$ of the average structure, and $\bar{1}$ means r sends $\mathbf{Q}$ to $-\mathbf{Q}$ and τ to $-\tau$). For simplicity we shall be writing superspace-group symbols all on one line with colons separating the parts written by de Wolff *et al.* (1981) as superscripts and subscripts; for example, the group we have just mentioned above would be designated $P:Pr:\bar{1}$ in our notation.

For our second example, we consider a 1D crystal modulated with $\mathbf{q}_{IC}=\mathbf{Q}+\frac{1}{2}\mathbf{a}^*$. This will have difference structures C_1 and C_2 with the periodicity $2a$ of a twofold superstructure. Starting from the symmetry point of view, we can choose C_1 to be odd under r and even under r' (see Fig. 7*a*). Then the symmetry picture of superspace is as shown in Fig. 8, where the symmetry points in parentheses are implied by the presence of those arising from C_1. So the symmetry of C_2 must have the form indicated in Fig. 7(*b*), which is even under r and odd under r' - again as predicted by McConnell-Heine theory. The 2D space group of Fig. 8 is again $P2$, though one could call it $C2$, and the (1+1)-dimensional superspace group is $C:P2:\bar{1}$ (where C tells us that $\mathbf{q}_{IC}=\mathbf{Q}+\frac{1}{2}\mathbf{a}^*$). Turning to structure, we consider an ordering modulation as a change. A pair of structures [average + C_1] and [average + C_2] with the required symmetries are depicted in Figs. 9(*a*) and (*b*); the '+' and '−' symmetries have become different atoms called '*A*' and '*B*'. The supercrystal will therefore have the structure of Fig. 10.

It should be noted that, in each of the examples, it would have been possible to start from the symmetry of C_2 and derive that of C_1. Similarly, either superspace group could equally well represent IC phases whose modulation resulted from displacive or ordering mechanisms.

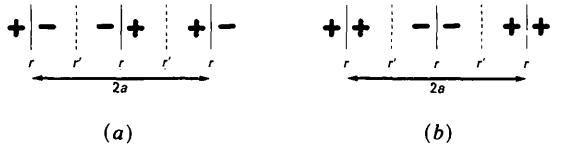


Fig. 7. Symmetries of the difference structures for a 1D IC crystal with $\mathbf{q}_{IC}=\mathbf{Q}+\frac{1}{2}\mathbf{a}^*$. (*a*) Symmetry of what we shall call C_1. This is odd under r and even under r'. (*b*) Symmetry of C_2: even under r and odd under r'. This symmetry is implied once the symmetry of C_1 is chosen.

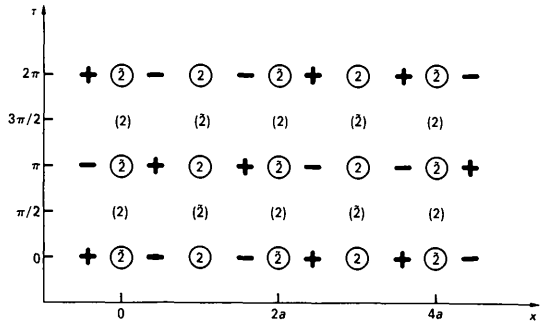


Fig. 8. The symmetries of the (1+1)D supercrystal of the 1D IC crystal with $\mathbf{q}_{IC}=\mathbf{Q}+\frac{1}{2}\mathbf{a}^*$. The twofold and 'anti-twofold' axes which arise directly from extending the symmetry pattern of C_1 through superspace imply the existence of the additional axes shown in parentheses.

3. Sodium nitrite

Since 3D crystals and their supercrystals are not as easy to draw on a flat page as are the 1D examples of the preceding section, we shall next demonstrate how to handle a 3D example: $NaNO_2$. The symmetry of IC $NaNO_2$ has already been dealt with both in the superspace approach (Janssen & Janner, 1980) and in the McConnell-Heine theory (Heine, Lynden-Bell, McConnell & McDonald, 1984). What we shall be focusing on is how the symmetry of C_1 determines that of C_2 in the superspace point of view. The way the symmetries of the difference structures fit into the superspace group will be presented in a slightly different format which relies less heavily on visualization.

To begin, we review the relevant facts about $NaNO_2$. First, the space group of the average high-temperature structure is *Immm*, and so the basic space group of the supercrystal, $G_{\pm Q}$ (see Heine & Simmons, 1987) is also *Immm*. Secondly, the modulation wavevector, $\mathbf{q}_{IC}=\mathbf{Q}$ is along the $\mathbf{a}^*$ axis. Finally, one of the component difference structures, call it C_1, is

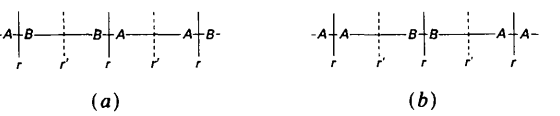


Fig. 9. Two possible ordering difference structures in one dimension with the symmetries indicated in Fig. 7. The letters *A* and *B* represent two different kinds of atoms. (*a*) Structure C_1 which is odd under r and even under r. (*b*) Structure C_2 which is even under r and odd under r'.

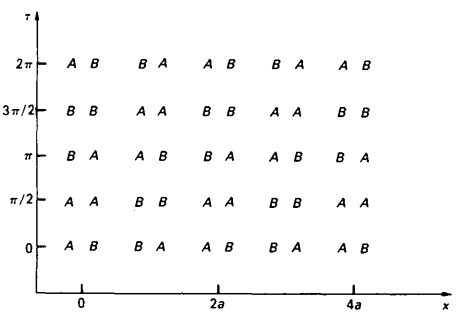


Fig. 10. (1+1)-dimensional supercrystal incorporating the ordering difference structures of Fig. 9 in the manner indicated by Fig. 1.

known to be the ferroelectric ordering of NO_2 groups along the **b** axis (see Fig. 11).

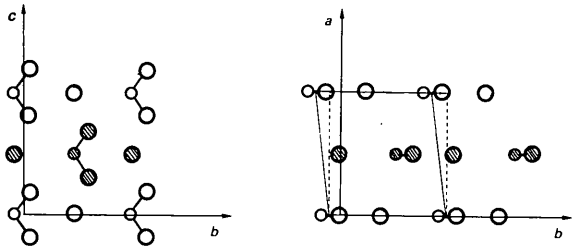
From these facts, we can extract the symmetry of C_1. All that is necessary is to consider how each generator of the basic space group acts on C_1 as drawn in Fig. 11. Elements E, m_x and m_z certainly leave it invariant. m_y on the other hand reverses the NO_2 polarization, in effect changing the modulation phase by π and changing C_1 to $-C_1$. So the effect of *Immm* on the structure [average + C_1] is

$$\begin{aligned} E:&\quad x\,y\,z\,C_1 \rightarrow x\ \ y\ \ z\ \ C_1\\ m_x:&\quad x\,y\,z\,C_1 \rightarrow -x\ \ y\ \ z\ \ C_1\\ m_y:&\quad x\,y\,z\,C_1 \rightarrow x\ \ -y\ \ z\ \ -C_1\\ m_z:&\quad x\,y\,z\,C_1 \rightarrow x\ \ y\ \ -z\ \ C_1. \end{aligned} \tag{3.1}$$

This structure has as symmetry elements E, m_x, m_z and, therefore, also 2_y; that is, it has space-group symmetry $Im2m$.

If we now consider C_1 to be some hyperplane $\tau =$ constant (since C_1 itself is a pure unmodulated structure) of a (3+1)-dimensional superspace, the behaviour of C_1 and **Q** under the generators of *Immm* will define the symmetries of the superspace and lead us, thereby, to C_2. We have just listed the effects of the generators on C_1; note that if C_1 corresponds to phase $\tau = \tau_0$, then $-C_1$ must correspond to phase $\tau = \tau_0 + \pi$. Thus m_y plus a phase shift of π becomes a symmetry element in 4D space. Of the four generators, the only one which sends **Q** to $-$**Q**, and hence τ to $-\tau$, is m_x: hence reversing **x** and going to phase $-\tau$ is a symmetry element in 4D. The other generators leave **Q** untouched. We can summarize these symmetry elements as

$$\begin{aligned} E:&\quad x\,y\,z\,\tau \rightarrow x\ \ y\ \ z\ \ \tau\\ m_x:&\quad x\,y\,z\,\tau \rightarrow -x\ \ y\ \ z\ \ -\tau\\ m_y:&\quad x\,y\,z\,\tau \rightarrow x\ \ -y\ \ z\ \ \tau+\pi\\ m_z:&\quad x\,y\,z\,\tau \rightarrow x\ \ y\ \ -z\ \ \tau, \end{aligned} \tag{3.2a}$$



(*a*) (*b*)

Fig. 11. The component structures of IC $NaNO_2$. (*a*) C_1: the ferroelectric ordering of the NO_2 groups along the *b* axis. The shaded atoms are on a **bc** plane which lies $\frac{1}{2}$**a** below the others. (*b*) C_2: shear in the **ab** plane. The dotted lines indicate how the shear affects the atomic positions. The shaded atoms correspond to those shaded in (*a*).

and the multiplication table of *Immm* easily yields the remaining symmetries:

$$\begin{aligned} I:&\quad x\,y\,z\,\tau \rightarrow -x-y-z-\tau+\pi\\ 2_x:&\quad x\,y\,z\,\tau \rightarrow\ \ x-y-z\ \ \tau+\pi\\ 2_y:&\quad x\,y\,z\,\tau \rightarrow -x\ \ y-z-\tau\\ 2_z:&\quad x\,y\,z\,\tau \rightarrow -x-y\ \ z-\tau+\pi. \end{aligned} \tag{3.2b}$$

Note that (3.2*a*) is another way of saying that the superspace group of IC $NaNO_2$ is $P{:}Immm{:}\bar{1}s1$; s is the shift along τ by π and $\bar{1}$ is the change of sign of τ, just as discussed in de Wolff *et al.* (1981). Since we know which elements of this superspace group are symmetry elements of C_1, it is easy to see that C_1 corresponds to the hyperplane $\tau = 0$. The hyperplane $\tau = \pi$ which we would expect to correspond to $-C_1$ has the same set of symmetries (since π and $-\pi$ are the same modulo 2π) just as it ought to. However, these are not the only hyperplanes of special symmetry. Consider $\tau = \pi/2$. This is left invariant by E, I, m_z and 2_z, so it has special symmetry as well. The same goes for $\tau = 3\pi/2$. There being no other planes $\tau =$ constant with higher symmetry than $\{E, m_z\}$, these two hyperplanes must correspond to C_2 and $-C_2$ and the symmetry of C_2 is uniquely determined.

In the course of the above discussion, we started by assuming C_1 to lie on an arbitrary hyperplane τ_0 and ended by seeing it fixed on the zero hyperplane. That fixing of the location of C_1 has two causes. First, we have represented moving from C_1 to $-C_1$ by a phase shift of π; this confines C_1 to one of the hyperplanes $\tau = 0$ or $\tau = \pi/2$, as is clear from (3.2). Second, in choosing between those two hyperplanes we have made a choice of origin, selecting the inversion operation to be represented as sending τ to $-\tau + \pi$ rather than to $-\tau$.

Clearly the identification of C_1 and C_2 with the hyperplanes of the superspace corresponds to what one would have expected from Fig. 1. However, the relation of C_1 and C_2 is also in accordance with McConnell-Heine theory. We have already discussed the effects of the generators of $G_{\pm\mathbf{Q}}$ on C_1; a quick look at (3.2*a*, *b*) for $\tau = \pi/2$ shows that any element of $G_{\pm\mathbf{Q}}$ sending **Q** to **Q** is a symmetry of both C_1 and C_2 or of neither, while any element sending **Q** to $-$**Q** is a symmetry of one but not of the other.

It is important to realize that one could equally well have started from C_2 and built up the same superspace group and, hence, the symmetry $Im2m$ for C_1. Heine *et al.* (1984) have shown that the structure C_2 corresponds to the shear of the unit cell in the **xy** plane. Of the generators of *Immm*, the only one leaving this invariant are E and m_z; both m_x and m_y change C_2 to what can only be described as $-C_2$. Knowing this, and knowing how the generators act on **Q** (still along **a***), we can take C_2 to lie on a hyperplane $\tau =$ constant of the superspace and write

down the symmetries of the supercrystal based on those of C_2:

$$\begin{aligned}
E:&\quad x\,y\,z\,\tau \rightarrow\ \ x\ \ y\ \ z\ \ \tau\\
m_x:&\quad x\,y\,z\,\tau \rightarrow -x\ \ y\ \ z\ -\tau+\pi\\
m_y:&\quad x\,y\,z\,\tau \rightarrow\ \ x\ -y\ \ z\ \ \tau+\pi\\
m_z:&\quad x\,y\,z\,\tau \rightarrow\ \ x\ \ y\ -z\ \ \tau\\
I:&\quad x\,y\,z\,\tau \rightarrow -x\ -y\ -z\ -\tau\\
2_x:&\quad x\,y\,z\,\tau \rightarrow\ \ x\ -y\ -z\ \ \tau+\pi\\
2_y:&\quad x\,y\,z\,\tau \rightarrow -x\ \ y\ -z\ -\tau+\pi\\
2_z:&\quad x\,y\,z\,\tau \rightarrow -x\ -y\ \ z\ -\tau.
\end{aligned} \tag{3.3}$$

In this description we see that C_2 lies along the hyperplane $\tau=0$, and the hyperplane $\tau=\pi/2$ may be seen to correspond to the symmetry of the ferroelectric ordering, C_1. The superspace group summarizing (3.3) is $P{:}\,Immm{:}\,\bar{s}s1$, which is equivalent to $P{:}\,Immm{:}\,\bar{1}s1$ since the only difference is a change by π of the origin to which the elements sending $\mathbf{Q}$ to $-\mathbf{Q}$ is referred. The symbol $\bar{s}$, meaning $\tau\rightarrow-\tau+\pi$, is a slight extension of the notation of de Wolff *et al.* (1981) who represent all elements involving inversion of τ by $\bar{1}$. Their argument is that one can always choose the origin such that the shift is zero for a given group element containing inversion. However, since there are some superspace groups which include both the symmetries $\tau\rightarrow-\tau$ and $\tau\rightarrow-\tau+\pi$, we find it less confusing to choose a single origin and denote the two types of elements by $\bar{1}$ and $\bar{s}$ respectively. In any case, we have seen that in determining the superspace group of an IC material from $G_{\pm\mathbf{Q}}$, $\mathbf{Q}$, and the symmetry of one difference structure, one obtains the same superspace group whether the symmetry of C_1 or of C_2 is considered.

4. The general proof

Having demonstrated the equivalence of the two-component and superspace descriptions of IC materials by example in the preceding sections, we now prove it more generally. Specifically, we shall prove that the superspace group must contain within itself the symmetries of both C_1 and C_2 and that the relation between those symmetries is exactly as given by McConnell-Heine theory. This implies that if the superspace group and the symmetry of one difference structure, say C_1, are known, then the symmetry of the other difference structure, C_2, is completely and uniquely determined.

We shall begin by assuming that the superspace group, the direction of the modulation wave vector $\mathbf{Q}$ and the symmetry properties of one difference structure are known, but that nothing is known about any possible second difference structure. The first step must be clarification of the relationship between the pieces of information we do have. The superspace group is given by a symbol containing a 3D space group (the basic space group) on the upper right, a group to which the $(3+1)$-dimensional superspace group is isomorphic apart from increments of 2π in the fourth dimension, τ (de Wolff *et al.*, 1981). As proven by Heine & Simmons (1987), this basic group must be the subgroup $G_{\pm\mathbf{Q}}$ of the full symmetry group G of the average high-temperature structure, as long as the IC phase has been reached from the disordered one by a single second- (or nearly second) order phase transition. Further, according to the Landau symmetry theorem also discussed in that paper, the difference structure (and order parameter) C_1 of the IC phase must transform according to an irreducible representation of $G_{\pm\mathbf{Q}}$. So from the symmetry point of view the superspace group, $\mathbf{Q}$ and the symmetry of C_1 are closely and precisely related. From the point of view of structure, this relationship can be expressed in a slightly different way. The structure of the IC material can be divided into an average (unmodulated) portion and the difference structure C_1 which is modulated by a periodic function $f(\mathbf{Q}\,.\,\mathbf{r})$. This modulation function may be expressed as a Fourier series:

$$f(\mathbf{Q}\,.\,\mathbf{r})=\sum_n f_n \exp\,(in\mathbf{Q}\,.\,\mathbf{r})/\sum_n f_n \qquad (n \text{ an odd integer}), \tag{4.1}$$

which is normalized simply so that pure ordering in terms of C_1 will always be represented by a modulation factor of unity, no matter what the form of $f(\mathbf{Q}\,.\,\mathbf{r})$. For T not too far below the transition temperature, only the fundamental is present so (4.1) reduces to

$$f(\mathbf{Q}\,.\,\mathbf{r})=\cos\,(\mathbf{Q}\,.\,\mathbf{r}), \tag{4.2}$$

which is familiar from (1.1). As mentioned in § 1, the distance along the modulation wave, $\mathbf{Q}\,.\,\mathbf{r}=\tau$, forms the fourth dimension of the supercrystal. The 3D unmodulated structure [average$+C_1$] lies on the hyperplane $\tau=0$ of superspace; C_1 therefore has the symmetry properties of that hyperplane. We shall explore the link between these two points of view in order to derive the existence and symmetry of C_2. The full proof will be worked on the assumption that the irreducible representation by which C_1 transforms is one-dimensional; the continuation of the proof to the higher-dimensional case will also be discussed.

Since the superspace group of the IC phase is $(3+1)$-reducible and isomorphic to the basic group $G_{\pm\mathbf{Q}}$ (de Wolff *et al.*, 1981), we can explore the symmetry of superspace by considering the effects of the elements of $G_{\pm\mathbf{Q}}$ on the coordinate τ. As τ is single-dimensional, it may be inverted, shifted or a combination of the two. So the possible actions of elements

of $G_{\pm\mathbf{Q}}$ on τ are

$$\begin{aligned} &\tau \to \tau \\ &\tau \to \tau + \varphi \\ &\tau \to -\tau \\ &\tau \to -\tau + \varphi. \end{aligned} \tag{4.3}$$

Clearly the elements involving an inversion of τ are those which send $\mathbf{Q}$ to $-\mathbf{Q}$; the others belong to $G_{\mathbf{Q}}$. But what limits, if any, are there on the phase shifts φ? Here it is crucial that the hyperplane at $\tau = 0$ (C_1) transforms according to an irreducible representation of $G_{\pm\mathbf{Q}}$, for an element of $G_{\pm\mathbf{Q}}$ can therefore only turn C_1 into another member of the same invariant subspace. Since we are considering one-dimensional irreducible representations, $G_{\pm\mathbf{Q}}$ can only turn C_1 into $\pm C_1$. As C_1 exists at phase 0 along the modulation wave in the IC phase, we must find $-C_1$ at phase π. Thus φ in (4.3) can only have the value π.

Now let us consider which of the operations (4.3) can be symmetries of a general hyperplane $\tau = \tau_0$. Of those resulting from $G_{\mathbf{Q}}$, the operation $\tau_0 \to \tau_0$ is always a symmetry and $\tau_0 \to \tau_0 + \pi$ never is, no matter what the value of τ_0. The other two cases are more restricted: $\tau_0 \to -\tau_0$ is a symmetry only of the hyperplanes $\tau_0 = 0$ and $\tau_0 = \pi$, while $\tau_0 \to -\tau_0 + \pi$ is a symmetry only for $\tau_0 = \pi/2$ or $3\pi/2$. So $\tau_0 = 0$, $\pi/2$, π, $3\pi/2$ are hyperplanes of special symmetry within superspace.

We have already noted that the pair of special hyperplanes $\tau = 0, \pi$ correspond to C_1 and $-C_1$ respectively, but we still need to account for the second pair. At $\tau = \pi/2$ we have $f(\mathbf{Q} \cdot \mathbf{r}) = 0$, so that the IC structure contains no C_1 ordering at this phase along the modulation wave. However, the hyperplane $\pi/2$ has as symmetries all elements of $G_{\pm\mathbf{Q}}$ which send $\tau \to \tau$ or $\tau \to -\tau + \pi$. This group of elements may clearly be either $G_{\pm\mathbf{Q}}$ or a subgroup thereof; in any case, it is necessarily different from the symmetry group of C_1. The (commensurate) structure of the IC material at phase $\tau = \pi/2$ must have the symmetry of the $\tau = \pi/2$ hyperplane. Then as long as the symmetry at $\pi/2$ is lower than that of $G_{\pm\mathbf{Q}}$, there must be a second difference structure, call it C_2, of lower symmetry than $G_{\pm\mathbf{Q}}$ such that the full structure of the material at $\tau = \pi/2$ is [average + C_2] which has the (lower) symmetry of C_2. The only exceptions are materials whose structures are too simple to support any ordering or displacive structure of symmetry C_2. Likewise, if the symmetry at $\tau = \pi/2$ is $G_{\pm\mathbf{Q}}$, there will be a second difference structure of symmetry $G_{\pm\mathbf{Q}}$ except in the case of materials with very simple structures. In order for this C_2 to be present throughout the IC crystal wherever $\mathbf{Q} \cdot \mathbf{r} = \pi/2$ (and hence for $-C_2$ to appear at $3\pi/2$) but not at the points 0 and π, which we know to have the different symmetry of pure C_1, the difference structure C_2 must be modulated by a periodic function $g(\mathbf{Q} \cdot \mathbf{r} + \pi/2)$. We could expand this function g as a Fourier series as we did with f, and just below T_c, it would have the form $\cos(\mathbf{Q} \cdot \mathbf{r} + \pi/2) = \sin(\mathbf{Q} \cdot \mathbf{r})$. Thus in an IC material described by a (3+1)-dimensional superspace group there must exist two difference components C_1 and C_2 modulated 90° out of phase, just as stated in McConnell–Heine theory.

Table 1. *Effect of τ transformations on pure components C_1 and C_2*

	$\tau \to \tau$	$\tau \to \tau + \pi$	$\tau \to -\tau$	$\tau \to -\tau + \pi$
$C_1(\tau = 0)$	1	−1	1	−1
$C_2(\tau = \pi/2)$	1	−1	−1	1

Having discovered C_2, we need to examine its symmetry properties more closely; we shall use the symmetry properties of C_1 as a guide. Since C_1 transforms like a one-dimensional irreducible representation of $G_{\pm\mathbf{Q}}$, we can construct the representation by considering whether a given element of $G_{\pm\mathbf{Q}}$ sends C_1 to C_1 ($\chi = 1$) or $-C_1$ ($\chi = -1$). However, C_1 has the same symmetry as the hyperplane $\tau = 0$, and $G_{\pm\mathbf{Q}}$ is isomorphic to the superspace group with τ, so it is possible to construct an equivalent representation of $G_{\pm\mathbf{Q}}$ by considering whether an element of $G_{\pm\mathbf{Q}}$ sends $\tau = 0$ to itself ($\chi = 1$) or to $\tau = \pi$ ($\chi = -1$). The hyperplane $\tau = \pi/2$ is likewise even or odd under any element of $G_{\pm\mathbf{Q}}$, so another 1D representation of $G_{\pm\mathbf{Q}}$ can be made by considering whether an element of $G_{\pm\mathbf{Q}}$ sends $\tau = \pi/2$ to itself ($\chi = 1$) or to $\tau = 3\pi/2$ ($\chi = -1$). The result is clearly not merely an equivalent representation to the one given by $\tau = 0$. Since the hyperplane $\tau = \pi/2$ has been shown to be related to a difference structure, C_2, just as $\tau = 0$ is to C_1, this C_2 also transforms according to an irreducible representation of $G_{\pm\mathbf{Q}}$, a representation equivalent to that given by the action of $G_{\pm\mathbf{Q}}$ on $\tau = \pi/2$. The character table for these two representations is shown in Table 1. From the table we observe that the symmetry relation of C_1 and C_2 is exactly that given by McConnell–Heine theory: they behave the same under elements of $G_{\mathbf{Q}}$ and oppositely under elements sending $\mathbf{Q}$ to $-\mathbf{Q}$. This can also be seen if one labels each element sending τ_0 to τ_f by

$$\exp[i(\tau_f - \tau_0)]; \tag{4.4}$$

the representation based on $\tau_0 = \pi/2$ has an extra factor of $\exp(-i\pi)$ relative to that based on $\tau_0 = 0$ for elements of $G_{\pm\mathbf{Q}}$ sending $\mathbf{Q}$ to $-\mathbf{Q}$. The desired results have now been proven for the case of 1D irreducible representations.

Next we shall extend our proof to cover the cases where C_1 transforms according to an irreducible representation of $G_{\pm\mathbf{Q}}$ which is not one-dimensional. For the basic space groups of crystals with a 1D modulation, the most common other kinds of irreducible representations existing are 2D real representations

and 2D representations composed of paired complex-conjugate 1D representations; there are also a few cases (*e.g.* hexagonal) of 4D real representations and paired complex-conjugate 2D and 4D representations (see de Wolff *et al.*, 1981; Bradley & Cracknell, 1972; Heine, 1960). Then if we look at one basis vector of this 2D invariant vector space, $G_{\pm\mathbf{Q}}$ can clearly mix it with the other basis vector as well as with itself. Where for the 1D case C_1 corresponded to the unit vector of a 1D space, C_1 now corresponds to the unit circle of a 2D vector space and $G_{\pm\mathbf{Q}}$ can rotate that circle by amounts which need not be restricted to 0 or π. Thus φ in (4.3) is no longer forced to take the sole value of π. The possible values are, however, restricted by the requirements of group multiplication; then n repetitions of an 'n-fold' element (counting mirrors as twofold) must return τ to its starting point. Since only two-, three-, four- and sixfold crystallographic elements exist, φ must be one of π, $2\pi/3$, $\pi/2$ or $\pi/3$.

Having loosened the restrictions on φ, one now proceeds as before with the derivation of the existence and symmetries of C_2. C_1 still corresponds to $\tau=0$ and $\tau=\pi/2$ must contain C_2 for the same reasons adduced earlier. The main change from the 1D case is that extra planes of special symmetry now exist wherever $\tau=-\tau+\varphi$ has a solution other than $\tau=n\pi/2$ (n an integer). These do not require the existence of further order parameters, however, since there are no points where $f(\mathbf{Q}\,.\,\mathbf{r})=g(\mathbf{Q}\,.\,\mathbf{r}+\pi/2)=0$. Moreover, the action of $G_{\pm\mathbf{Q}}$ on these planes $\tau=\varphi/2$ does not give rise to irreducible representations of $G_{\pm\mathbf{Q}}$; as long as the Landau symmetry theorem is deemed to apply, this means that these planes cannot correspond to order parameters.

One can again construct irreducible representation for $G_{\pm\mathbf{Q}}$ from its actions on $\tau=0$ and $\pi/2$. The appropriate generalization of the procedure used before is labelling an element of $G_{\pm\mathbf{Q}}$ which sends $\tau_0\rightarrow\tau_f$ by

$$\begin{cases}\exp[i(\tau_f-\tau_0)]\\ \exp[-i(\tau_f-\tau_0)]\end{cases} \qquad (4.5a)$$

if C_1 transforms according to a pair of 1D complex-conjugate representations or, equivalently, by

$$\exp[i(\tau_f-\tau_0)]+\exp[-i(\tau_f-\tau_0)]=2\cos(\tau_f-\tau_0) \qquad (4.5b)$$

if C_1 transforms according to a real 2D representation. Expression (4.5a) essentially gives the separate components D_{11} and D_{22} of the trace of the representation matrix D, while (4.5b) gives the whole trace, $D_{11}+D_{22}$. The relationship between the symmetries of C_1 and C_2 is the same as in the 1D case; this may be seen by the essential similarity of (4.4) and (4.5a, b).

It should be noted that C_1 and C_2 may either belong to the same 2D irreducible representation of $G_{\pm\mathbf{Q}}$ at $\mathbf{Q}=0$ or to separate ones. In the first case, the structures C_1 and C_2 must arise from the same physical mechanism since they are mixed by $G_{\pm\mathbf{Q}}$. One example may be found in phase III biphenyl, where C_1 and C_2 both belong to the single 2D irreducible representation of $G_{\pm\mathbf{Q}}=P2_1/a$ at $\frac{1}{2}\mathbf{b}^*$; both ordering modes are based on combinations of the translations, librations and internal torsion of two pairs of molecules within the unit cell (Heine & Price, 1985). In the second case, C_1 and C_2 may involve physically different kinds of ordering as observed, for example, in mullite (McConnell & Heine, 1985).

Having discussed the case of a simple one-dimensional modulation in detail, we shall now outline how the ideas may be applied to modulations whose wave vectors have more than one component. Within this group of IC phases, there are several distinct possibilities to be considered. Starting with the example of a phase whose wave vector points along an arbitrary direction in the $\mathbf{a}^*\mathbf{b}^*$ plane, we see that the modulation may act either as $\cos[\mathbf{q}\,.\,(\mathbf{a}+\mathbf{b})]$ or as $\cos(\mathbf{q}\,.\,\mathbf{a})\cos(\mathbf{q}\,.\,\mathbf{b})$. The first corresponds to a one-dimensional modulation in an arbitrary direction (making a 'striped' pattern in the $\mathbf{ab}$ plane) and the second to a truly two-dimensional modulation with independent vectors $\mathbf{q}_x$ and $\mathbf{q}_y$ with four symmetry-inequivalent McConnell–Heine difference structures C_{1x}, C_{2x}, C_{1y} and C_{2y} (making a 'quilted' pattern). Similar distinctions may be drawn among the several kinds of IC phases possible when the wave vector has components along all three crystal axes.

Once that distinction has been made, the extension of our discussion about the relationship between the superspace and McConnell–Heine descriptions of IC phases is simple. The choice of the basic space group of the superspace group for the cases in which the wave vector has more than one component has been discussed in Heine & Simmons (1987). In essence, the basic space group is the subgroup of the high-temperature space group G which sends each independent component of $\mathbf{q}$ (each component corresponding to a separate pair of difference structures) to itself or minus itself. Thus, the phases which make 'striped' patterns are not fundamentally different from the simple one-dimensional phases we have already discussed; they have only one pair of difference structures C_1 and C_2 and a $(3+1)$D superspace group. Those which make any sort of 'quilted' pattern, *i.e.* those with more than one pair of symmetry-inequivalent difference structures, must be described by a $(3+n)$D superspace group where n is the number of pairs of difference structures. The extra n coordinates of the superspace group may be labelled τ_n and the difference structures C_{1n} and C_{2n} correspond to the hyperplanes of special symmetry located at $\tau_n=0$ and $\tau_n=\pi/2$.

References

BRADLEY, C. J. & CRACKNELL, A. P. (1972). *The Mathematical Theory of Symmetry in Solids.* Oxford: Clarendon Press.

HEINE, V. (1960). *Group Theory in Quantum Mechanics.* Oxford: Pergamon.

HEINE, V., LYNDEN-BELL, R. M., MCCONNELL, J. D. C. & MCDONALD, I. R. (1984). *Z. Phys. B*, **56**, 229-239.

HEINE, V. & PRICE, S. L. (1985). *J. Phys. C*, **18**, 5259-5278.

HEINE, V. & SIMMONS, E. H. (1987). *Acta Cryst.* A**43**, 289-294.

JANSSEN, T. & JANNER, A. (1980). *Ferroelectrics*, **24**, 11-22.

LIFSHITZ, E. M. & PITAEVSKII, L. P. (1980). *Statistical Physics*, 3rd ed., Part 1. Oxford: Pergamon.

MCCONNELL, J. D. C. & HEINE, V. (1984). *Acta Cryst.* A**40**, 473-482.

MCCONNELL, J. D. C. & HEINE, V. (1985). *Phys. Rev. B*, **31**, 6140-6142.

SHAW, J. J. A. & HEINE, V. (1987). In preparation.

SIMMONS, E. H. (1987). In preparation.

WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* A**37**, 625-636.

Acta Cryst. (1987). A**43**, 635-638

Determining Skewness in Atomic Probability Density Functions for Non-centrosymmetric Structures

BY R. J. NELMES AND Z. TUN

Department of Physics, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, Scotland

(*Received* 4 *July* 1986; *accepted* 19 *March* 1987)

Abstract

Skewness in atomic probability density functions can be represented by odd-order cumulants in the Edgeworth expansion about a Gaussian distribution, or by odd-order quasi-moments in the Gram–Charlier expansion. In the case of the Edgeworth expansion it is known that the absolute values of some odd-order cumulants cannot be determined from Bragg reflection data for non-centrosymmetric structures – because these cumulants affect only the phases of the calculated structure factors and not their magnitudes. It is shown that, in general, this problem is imposed by the form of the Edgeworth expansion and can be avoided by using the Gram–Charlier expansion instead. An example is given of the refinement of third-order quasi-moments for the non-centrosymmetric phase of $PbTiO_3$, using neutron-diffraction data collected at the Institut Laue–Langevin, Grenoble.

Many interesting phenomena are manifested in departures of atomic probability density functions (p.d.f.'s) from a purely harmonic form; and the anharmonicity of p.d.f.'s can be investigated with accurate high-resolution X-ray or neutron diffraction data. A widely used method of modelling anharmonicity in least-squares structure refinements is based on the Edgeworth expansion of the p.d.f. (Johnson & Levy, 1974), which gives the following form for the structure factor up to sixth-order terms (Kuhs, 1983):

$$F_{EW}(\mathbf{h}) = \sum_i b_i \exp\,[i(2\pi x_i h_j - K_i^{jkl} h_j h_k h_l + K_i^{jklmn} h_j h_k h_l h_m h_n) - (\beta_i^{jk} h_j h_k - K_i^{jklm} h_j h_k h_l h_m + K_i^{jklmno} h_j h_k h_l h_m h_n h_o)], \quad (1)$$

where the summation is over the atoms in the unit cell (the repeated-index summation convention is assumed for the indices $j, k, l, \ldots$), b_i are the atomic scattering lengths (form factors for X-rays), x_i^j and β_i^{jk} are the positional parameters and the harmonic thermal parameters, and $K_i^{jkl\ldots}$ are the anharmonic parameters. These last are known as cumulants. The odd-order cumulants model antisymmetric anharmonicity, or 'skewness', in the p.d.f.; and the even-order cumulants model symmetric anharmonicity, or 'kurtosis'. In practice, it is usually sufficient to include only the third- and fourth-order cumulants in a structure refinement, and it is rarely, if ever, warranted to attempt to refine terms higher than sixth order. Though generally effective, this approach to anharmonicity suffers the serious limitation that it is possible to determine only the *relative* magnitudes of odd-order cumulants whose signs are not reversed by the space-group operations (Hazell & Willis, 1978). This is because increasing or decreasing such a cumulant by the same amount for all atoms – as the symmetry then permits – alters the phase but not the magnitude of the calculated structure factors [see (1)].

0108-7673/87/050635-04$01.50