

## Correct Choice of Superspace Group for an Incommensurate Phase Transition

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### Abstract

The Landau theory of second-order phase transitions imposes a precise symmetry requirement on the phase at lower temperature. It is shown how this affects the assignment of superspace groups for incommensurate phases reached by one second-order transition from a disordered state. It is noted that the symmetry requirement appears to have been overlooked in several cases when superspace groups were assigned by other authors. For those materials, namely  $\text{NaNO}_2$ , biphenyl and  $\text{Rb}_2\text{ZnBr}_4(\text{Cl}_4)$ , the correct choice of superspace group is discussed.

### 1. Introduction

It has been shown by a group of authors that the symmetry of incommensurate (IC) materials may be specified by a four-dimensional superspace group (de Wolff, 1974; de Wolff, Janssen & Janner, 1981). The fourth dimension comes from the phase ( $\tau$ ) of the modulation along the wave: since  $\tau \rightarrow \tau + 2\pi$  is clearly a symmetry, including  $\tau$  as a dimension along with the three spatial ones leads to a 4D space group. As has been discussed by the aforementioned authors, the superspace groups provide a straightforward interpretation of diffraction data. However, in order to use them to analyse accurately the structure of a particular IC material, one needs to know how to determine which of the many 4D superspace groups describes that material's symmetry properties. This is a point which has not been dealt with very systematically in the literature. On the one hand, some authors like Janner & Janssen (1980) have just postulated or stated part of the answer and derived the remainder from that beginning. On the other, a number of experimentalists (Baudour & Sanquer, 1983; Paciorek & Kucharczyk, 1984) have sought to determine the superspace group from the observation of extinctions and symmetry in intensities among the satellite reflections. Neither approach has been entirely satisfactory.

The main point of this paper is that the Landau theory of second-order (and nearly second-order) phase transitions also imposes a symmetry require-

ment on the IC phase, a requirement which seems never to have been mentioned explicitly in previous discussions of the superspace groups. Accordingly, some superspace groups which have been suggested for certain materials directly violate this law of physics, in particular:  $\text{NaNO}_2$  (Paciorek & Kucharczyk, 1984), biphenyl (Baudour & Sanquer, 1983) and  $\text{RbZnBr}_4(\text{Cl}_4)$  (Janner, Rasing, Bennema & van den Linden, 1980). We shall argue below that this symmetry requirement, which we call the Landau symmetry theorem, reduces to a simple and useful rule of thumb. This is that the 3D space group  $G_{\pm\mathbf{q}}$  (the 'basic group') appearing in the upper part of the superspace-group symbol consists of all elements of the full space group  $G$  of the disordered phase which turn the modulation wave vector  $\mathbf{q}$  either to  $+\mathbf{q}$  or  $-\mathbf{q}$ . That the rule is simple to apply may be seen by example: if the disordered phase has space group  $G = 4/mmm$  and  $\mathbf{q}$  does not point along the 4 axis, then  $G_{\pm\mathbf{q}}$  is  $mmm$ ; the elements 4 and  $4^2$  cannot, by definition, belong to  $G_{\pm\mathbf{q}}$ . That it is useful may be seen from the fact that  $G$  and  $\mathbf{q}$  are readily found:  $G$  from the symmetry and extinctions of the main Bragg reflections and  $\mathbf{q}$  from the axis on which the satellites lie. It should be noted that the better known (and applied) but weaker requirement—also stemming from Landau theory (Liftshitz & Pitaevskii, 1980, pp. 462–463)—that the symmetry group of the low-temperature structure be a subgroup of  $G$  is not sufficient. In particular, it would allow the incorrect superspace-group assignments for the three materials mentioned above.

Once the Landau symmetry theorem has been used to find the basic group for a given IC material, the lower part of the 4D space-group symbol is readily determined. In discussing this, it is useful to use the alternative way of describing the symmetry of IC structures (McConnell & Heine, 1984):

structure = average structure

$$+ C_1 \cos(\mathbf{q} \cdot \mathbf{r}) + C_2 \sin(\mathbf{q} \cdot \mathbf{r}), \quad (1)$$

where  $C_1$  and  $C_2$  are component difference structures with periodicity in the unit cell or in the twofold superlattice cell if  $\mathbf{q}$  is measured from  $\frac{1}{2}\mathbf{g}$ . Note that (1) can be directly generalized to a more 'squared-up' modulation at lower temperature. That this

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Table 1. *The space groups of the components  $C_1$  and  $C_2$  (to be precise, of the average structure plus  $C_1$  or  $C_2$ ) for incommensurate materials with given superspace-group symmetry*

Superspace group	$C_1$ ( $\tau=0$ )	$C_2$ ( $\tau=\pi/2$ )
$P:Immm:\bar{1}11$	$Immm$	$Imm2$
$P:Immm:\bar{1}s1$	$I2/m$	$I2/m$
$P:Immm:\bar{1}1s$	$Im2m$	$I2/m_x$
$P:Immm:\bar{1}ss$	$I2/m_z$	$I222$
$P:Pcmm:11\bar{1}$	$Pcmm$	$P2_1am$
$P:Pcmm:s1\bar{1}$	$P2_1/mn$	$P2_1/m$
$P:Pcmm:1s\bar{1}$	$P2_1/cn$	$P2_1/c$
$P:Pcmm:ss\bar{1}$	$P2_1/n$	$P2_12_12_1$

description and the accompanying symmetry description are completely equivalent to the superspace-group method is shown elsewhere (Simmons & Heine, 1987). Starting from (1), McConnell & Heine (1984) have shown how, for a given  $G_{\pm q}$ , one can enumerate the possible symmetries of the modulated structure in terms of pairs of related symmetries for  $C_1$  and  $C_2$ . Each such pair corresponds to a different superspace group, though all share the basic group  $G_{\pm q}$  (see Fig. 1). Alternatively, one may express the symmetries purely in terms of groups by considering the structures [average +  $C_1$ ] and [average +  $C_2$ ] which occur at phases 0 and  $\pi/2$  along the modulation wave. It is shown in Simmons & Heine (1987) that the 3D space groups  $G_1$  and  $G_2$  of those structures are uniquely related to the superspace group of the IC crystal and the relationships have been tabulated by Simmons (1987). Then, once  $G_{\pm q}$  is known for a material, one may look in the tables to find the possible superspace groups together with the symmetries of the difference structures. A little information about the symmetry of  $C_1$  or  $C_2$  will then suffice to fix the superspace group from among those alternatives. As an example, consider the case of IC  $\text{NaNO}_2$ , for which  $G_{\pm q}$  is simply  $G = Immm$  and  $q$  is along  $a^*$ . Table 1 gives the lower portion of the superspace

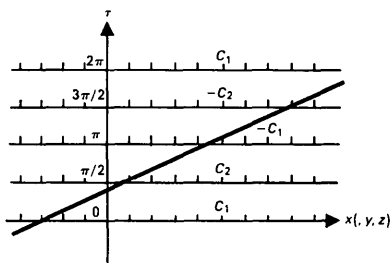


Fig. 1. Four-dimensional superspace  $\tau, x, y, z$  (drawn here as  $\tau, x$ ) for describing incommensurate modulated structures. The diagonal line of slope  $|q|$  contains the actual structure. The horizontal lines become hyperplanes of special symmetry in superspace. These represent the pure 3D 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.

group as either  $\bar{1}11$ ,  $\bar{1}s1$ ,  $\bar{1}1s$  or  $\bar{1}ss$ . Since one expects the ferroelectric ordering along  $b$  of the  $\text{NO}_2$  ions to be one of the component difference structures, one writes down the 3D space group of [average + ferroelectric ordering on  $b$ ] which is  $Im2m$  and finds in Table 1 that the superspace group must be  $P:Immm:\bar{1}s1$ .

A few comments on the limits of the applicability of the Landau symmetry theorem are in order here. Firstly, while most of our discussion will deal specifically with IC phases whose modulation wave vectors have but two arms in their stars ('one-dimensional' modulated structures), we shall briefly outline how our results may be extended to cases in which the star has more arms. Secondly, in our discussion, we are consciously limiting ourselves to IC phases resulting from second-order or nearly second-order phase transitions to which the concept of a Landau order parameter is applicable. We believe the theorem is not invalidated by the critical fluctuations near  $T_{IC}$  which cause the Landau expansion of the free energy to be not strictly correct. Similarly we believe the theorem is not invalidated by some weak higher-order coupling terms in the free energy which make the transitions sometimes weakly first order. Likewise, it should hold in a case like mullite in which we are clearly dealing with an ordering process on a disordered average structure but in which that structure is never physically realized because the material melts below the disordering temperature.

As stated already, the application of the Landau symmetry theorem reduces to a rule of thumb as far as the choice of superspace group is concerned. This will occupy § 2. In § 3 we will consider the application to  $\text{NaNO}_2$ , biphenyl and  $\text{Rb}_2\text{ZnBr}_4(\text{Cl}_4)$ .

## 2. The Landau symmetry theorem and the choice of 'basic space group'

The symmetry theorem of Landau theory is that in a second- (or nearly second-) order phase transition the order parameter describing the low-temperature phase must have the symmetry of an irreducible representation of the space group  $G$  of the high-temperature (disordered) structure (Lifshitz & Pitaevskii, 1980, p. 460). This theorem is discussed by these authors, but while their treatment may be regarded as sufficiently complete for someone well versed in the use of group theory, it can hardly be described as a satisfactory proof for anyone less initiated. Moreover, these authors apparently do not distinguish the theorem from the weaker result that the low-temperature phase has a subgroup symmetry: they state both, without discussion, whereas we have seen that there is a significant difference between them. We therefore start with a few remarks about the theorem before discussing its implications for superspace-group determination.

In Landau theory, the free energy  $F$  (the Gibbs free energy, but we reserve the symbol  $G$  for groups) is expanded in powers of all the coordinates of the system  $\chi_i$ . Above the transition temperature their mean value is zero, but they describe all possible fluctuations. The stability of the system depends on the quadratic terms in the expansion

$$F = \sum_{ij} \alpha_{ij} \chi_i \chi_j + \dots \quad (2)$$

We wish to diagonalize this quadratic form in terms of normal modes

$$\Psi_n = \sum_i \psi_{n,i} \chi_i \quad (3)$$

so that the second-order terms  $F_2$  become

$$F_2 = \sum_n A_n \Psi_n^* \Psi_n, \quad (4)$$

where the use of the complex conjugate  $\Psi_n^*$  includes cases where the  $\Psi_n$  are complex. The  $\Psi_n$  are the normal modes, including all phonons and also non-oscillatory 'ordering modes'; we shall always use the phrase 'normal modes' in this wider sense. The  $A_n$  are in general temperature dependent: they are all greater than zero for  $T$  above the transition temperature and the phase transition occurs when one of them hits zero—that is, when one normal mode goes soft. The  $A_n$  and  $\psi_{n,i}$  are determined as eigenvalues and eigenvectors of the matrix equation

$$\sum_{ij} \alpha_{ij} \psi_{n,j} = A_n \psi_{n,i} \quad (n \text{ fixed}) \quad (5)$$

which may be written symbolically as

$$\alpha \Psi_n = A_n \Psi_n \quad (n \text{ fixed}). \quad (6)$$

In (2) and (6) the matrix  $\alpha$  incorporates the full symmetry group  $G$  (here a 3D space group) of the system in the disordered phase above the transition temperature.

The proof that each of  $F_2$ 's normal modes  $\Psi_n$  belongs to an irreducible representation of  $G$  now follows in the usual way as for the classical normal modes of oscillation of a system or quantum-mechanical eigenstates of a system (Heine, 1960, p. 235). We sketch the proof briefly since it will be useful in some of the further discussion in this paper. We consider any symmetry element  $S$  of the group  $G$  and operate with it on (6): since  $\alpha$ , like  $F$ , is invariant under  $S$  (in fact, under all of  $G$ ), this generates a new normal mode  $S\Psi_n$  with the same eigenvalue  $A_n$ . In this way we generate with  $G$  a vector space of modes  $[\Psi_{n1}, \Psi_{n2}, \dots, \Psi_{ns}]$  all having identical eigenvalue  $A_n$  and transforming into one another under  $G$ ; the transformation matrices form a representation of  $G$ . If  $G$  contains all the symmetries of the system (and we assume the effects of time reversal to have been taken into account), then this representation is irreducible apart from accidental

degeneracies in the sense of Heine (1960, pp. 44, 278). To see that the set  $[\Psi_{n1}, \Psi_{n2}, \dots, \Psi_{ns}]$  of normal modes belonging to one  $A_n$  spans one irreducible vector space, let us start by assuming the opposite: *i.e.* that the vector space breaks up into two (or more) irreducible vector spaces  $[\Psi_{n1}, \Psi_{n2}, \dots, \Psi_{nr}]$  and  $[\Psi_{nr+1}, \dots, \Psi_{ns}]$ . Then on the one hand they have mathematically identical eigenvalues  $A_n$ , which implies some mathematical connection between them, and on the other hand no symmetry element of  $G$  connects one space with the other. This is a contradiction, since  $G$  was taken as the complete symmetry group of the system, apart from accidental degeneracy in the sense already referred to. Then the theorem is proven as stated.

Having proved a precise result about the symmetry requirements for all second-order phase transitions, we shall now specialize in incommensurates with a one-dimensional modulation (*i.e.* a single  $\mathbf{q}$  along a crystal axis). In talking about a single real crystal with a 1D modulation we are forced to differentiate between the modulation vector and other vectors (aside from the negative of that vector) which in the unmodulated crystal would be equivalent to it by symmetry. For example, in a cubic crystal with modulation along  $\mathbf{z}$ , the axes  $[100]$  and  $[001]$  are no longer equivalent; in choosing to look at one crystal, we have chosen to look at one particular modulation vector. This means that in order to discuss an IC crystal we must drop all elements of  $G$  which do not belong to  $G_{\pm\mathbf{q}}$  from the discussion; the order parameters are then constrained to transform as irreducible representations of  $G_{\pm\mathbf{q}}$ . McConnell & Heine (1984) have discussed this point with respect to the order parameters,  $\psi_{\mathbf{q}}$  and  $\varphi_{\mathbf{q}}$ , of the difference structures  $C_1$  and  $C_2$  of (1). They have shown that the order parameters, and hence the difference structures themselves, transform according to irreducible representations of  $G_{\pm\mathbf{q}}$  such that under elements sending  $\mathbf{q}$  to itself both representations are either even or odd while under the other elements of  $G_{\pm\mathbf{q}}$  one representation is even and the other odd.

The proof of our rule of thumb is now straightforward. We have seen that the language of irreducible representations is fundamentally the correct one for specifying the symmetries of the ordering patterns produced by second-order incommensurate phase transitions. However, as mentioned in §1, the language of the superspace groups of de Wolff *et al.* (1981) is a natural one in which to discuss diffraction data, so we shall now 'translate' our result. In essence, this means proving our rule of thumb: that the 3D space group  $G_{\pm\mathbf{q}}$  is the correct choice of 'basic space group' for the superspace-group symbol. The irreducible representation associated with an order parameter specifies whether the order parameter is even or odd under any symmetry element of  $G_{\pm\mathbf{q}}$ . Now consider any generator  $g_1$  of  $G_{\pm\mathbf{q}}$ . Either it leaves  $\mathbf{q}$

invariant or it turns  $\mathbf{q}$  into  $-\mathbf{q}$ . In the latter case it must have character +1 for  $C_1$  (or  $C_2$ ) and -1 for  $C_2$  (or  $C_1$ ) as in McConnell & Heine (1984). Thus  $g_1$  combined with  $\tau \rightarrow -\tau$  is a symmetry in superspace since the latter leaves the hyperplane  $\tau = 0$  containing  $C_1$  ( $C_2$ ) invariant and changes the hyperplane  $\tau = \pi/2$  containing  $C_2$  ( $C_1$ ) to the hyperplane  $\tau = -\pi/2$  containing  $-C_2$  ( $-C_1$ ). Now consider another generator  $g_2$  which leaves  $\mathbf{q}$  invariant. By the McConnell & Heine analysis, both  $C_1$  and  $C_2$  have the same character +1 or -1, which in superspace become  $\tau \rightarrow \tau$  or  $\tau \rightarrow \tau + \pi$  respectively. Thus every generator  $g$  of  $G_{\pm\mathbf{q}}$  finds a place in the superspace group and the smallest group which can be the basic group must be  $G_{\pm\mathbf{q}}$ . Moreover the superspace-group element constructed from  $g$  incorporates whether  $C_1$  and  $C_2$  are even or odd under  $g$ . This proves our rule of thumb.

It is noted that the reduction of the largest candidate for the basic group from  $G$  to  $G_{\pm\mathbf{q}}$  also emerges from a discussion in the language of superspace groups by de Wolff *et al.* [(1981); see their equation (3.6)].

Having discussed the case of a one-dimensional modulation in detail, we shall now outline how the ideas may be applied to modulations whose wave vectors have more components. 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  $\cos[\mathbf{q} \cdot (\mathbf{a} + \mathbf{b})]$  or as  $\cos(\mathbf{q} \cdot \mathbf{x}) \cos(\mathbf{q} \cdot \mathbf{y})$ . 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  $\mathbf{q}_y$ , and with 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.

Those phases which make 'striped' patterns are not fundamentally different from the simple one-dimensional phases we have already discussed; for them our rule of thumb holds as stated. For the others, we need to extend the rule a bit, and to do so we must look carefully at what we mean by the 'star' of a wave vector in this context. The size of the star of the modulation vector is actually dependent on the current phase of the material. In the disordered phase, the star is, of course, determined by the symmetry group  $G$  of the material. But in an IC phase of a given crystal, directions which are symmetry equivalent in the disordered phase are distinguishable by virtue of the presence of the modulation. What remain equivalent are the independent components and their opposites: for example,  $\mathbf{q}_x + \mathbf{q}_y$  and  $-(\mathbf{q}_x + \mathbf{q}_y)$  in the striped phase,  $\mathbf{q}_x$  and  $-\mathbf{q}_x$ ,  $\mathbf{q}_y$  and  $-\mathbf{q}_y$  in the quilted phase. So the relevant star in an IC phase

consists of all vectors reached from the modulation vector by reversing the sign of one or more components. Then, following the arguments used in the discussion of the one-dimensional case, the basic space group of a higher-dimensional IC phase is that subgroup of the high-temperature symmetry group  $G$  which sends the wave vector of each independent modulation component of the phase either to itself or to minus itself. If the independent components are numbered as  $\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_n$  then one may designate this group as  $G_{\pm\mathbf{q}_1 \pm \mathbf{q}_2 \dots \pm \mathbf{q}_n}$ .

### 3. Applications of the Landau symmetry theorem

In order to demonstrate the power of the rule of thumb arising from the Landau symmetry theorem, we shall show here how it specifies the superspace groups of three materials:  $\text{NaNO}_2$ , biphenyl and  $\text{Rb}_2\text{ZnBr}_4(\text{Cl}_4)$ . These examples have been chosen because, as mentioned earlier, other authors have previously made what we believe to be some incorrect suggestions for the superspace group in analysing the symmetry of these compounds. We discuss the determination of the correct superspace group, taking into account both the requirements of the Landau symmetry theorem and the evidence cited by the authors in support of their suggestions. For simplicity we shall write superspace group symbols all on one line with colons separating the parts written by de Wolff *et al.* (1981) as superscripts and subscripts, e.g.  $P_{\bar{1} \ 1 \ 1}^{Immm}$  is written here as  $P:Immm:\bar{1}s1$ .

The determination of the superspace group of  $\text{NaNO}_2$  as  $P:Immm:\bar{1}s1$  has already been sketched in §1; this agrees with the analysis of Janner & Janssen (1980). Paciorek & Kucharczyk (1984) and Kucharczyk & Paciorek (1985) imply in their discussions that  $Immm$  and  $I2mm$  are equally acceptable choices of space groups; in fact, since  $mmm$  is its own  $G_{\pm\mathbf{q}}$  and  $2mm$  is a subgroup,  $2mm$  cannot possibly be the basic space group. Thus, according to the Landau symmetry theorem, Paciorek & Kucharczyk's assigned superspace group  $P:2mm:ss1$  could only be assigned to  $\text{NaNO}_2$  if an additional phase transformation were assumed to have occurred; no evidence is adduced for such a transition at the temperature concerned.

Paciorek & Kucharczyk base their choice of superspace group on X-ray structure analyses of  $\text{NaNO}_2$  in terms of the two superspace groups  $P:Immm:\bar{1}s1$  and  $P:I2mm:ss1$ . In their 1984 work, they find for  $P:I2mm:ss1$  a minimum  $R$  factor of  $R = 0.0822$  for the satellite reflections with a phase shift of  $22^\circ$  between the occupational and displacive modulation waves; for  $P:Immm:\bar{1}s1$ , i.e. without a phase difference, they find  $R = 0.0908$ . In their 1985 paper (Kucharczyk & Paciorek, 1985) they reanalyse the data and find 'practically no phase shifts' between the occupational and displacive modulation (the

actual figures are  $9^\circ$  for  $\text{Na}^+$  and  $2^\circ$  for  $\text{NO}_2^-$ ) but larger phase shifts between the modulation waves of  $\text{Na}^+$  and  $\text{NO}_2^-$  ( $12.5^\circ$  for occupational and  $22^\circ$  for displacive). The difference in the  $R$  factors is the same as before (0.08 compared with 0.09).

We suggest that the differences in the  $R$  factors are not significant and that the non-zero values of the phase shifts arise from small errors in the data. That the phase shifts must, by symmetry, be zero is explained quite extensively in Heine, Lynden-Bell, McConnell & McDonald (1984); however, we shall add a few remarks on this point here. Suppose for the moment that the  $\text{NO}_2^-$  ordering modulation and the displacement modulations are out of phase by  $22^\circ$ , as illustrated in Fig. 2. Then if we operate with the mirror  $m_x$  as indicated in Fig. 2, the ordering wave clearly is left invariant, while the displacive one is not. A real IC difference structure is a linear combination  $\Psi = \beta\psi_q + \beta^*\psi_{-q}$ ; and if we choose  $\beta$  such that  $m_x\Psi = \Psi$  for a particular mirror plane  $m_x$  (shown in Fig. 2) of the disordered space group, then the whole of  $\Psi$  must be invariant under  $m_x$  and not just part of  $\Psi$ . So we have a contradiction, and our initial assumption that the difference components could be  $22^\circ$  out of phase must be wrong. It should be mentioned that Böhm (1984, private communication) has reanalysed his diffraction data (Böhm, 1978) including a displacive modulation, and finds a sharp minimum at the  $R$  factor for zero phase difference from the occupational modulation, as we would expect.

The case of phase III of biphenyl is equally straightforward. Here the high-temperature average structure has space group  $P2_1/a$  and since  $\mathbf{q}$  is parallel to  $\mathbf{b}^*$  both  $2_1$  and the glide plane belong to  $G_{\pm\mathbf{q}}$ . Accordingly, the superspace group is (only a two-dimensional irreducible representation exists at  $\frac{1}{2}\mathbf{b}^*$ )  $P:P2_1/a:1\bar{1}$ . Baudour & Sanquer (1983) have

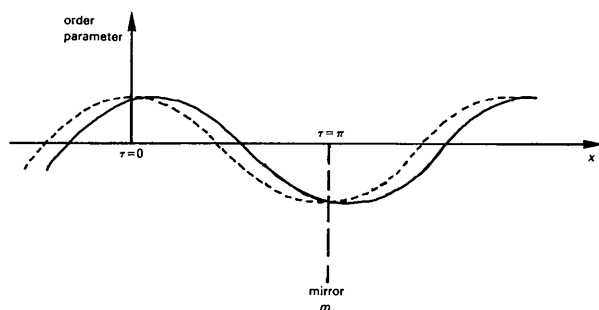


Fig. 2. Modulation of the  $\text{NO}_2^-$  ordering amplitude (broken line) and of the atomic displacements (full line) in  $\text{NaNO}_2$  with a supposed phase difference between them. While the ordering modulation is invariant under the mirror plane  $m_x$ , the displacement wave is not. Thus the structure shown cannot form an irreducible representation of the space group  $G$  of the disordered phase.

maintained that  $P:Pa:\bar{1}$  is the superspace group, but this would clearly violate the Landau symmetry theorem since  $Pa$  is merely a subgroup of  $G_{\pm\mathbf{q}}$ . The arguments of Baudour & Sanquer supporting  $P:Pa:\bar{1}$  on the basis of diffraction and spectroscopy experiments have been answered in Heine & Price (1985) so there is no need to repeat them here. This argument assumes that phase III results simply from a lock on of phase II onto  $q_a = q_c = 0$ , without any additional symmetry breaking for which no real evidence or argument has been produced.

$\text{Rb}_2\text{ZnBr}_4(\text{Cl}_4)$  is also quickly handled by the Landau symmetry theorem. The space group of the disordered phase is  $Pcmn$  and since  $\mathbf{q}$  is parallel to  $\mathbf{c}^*$  this is also  $G_{\pm\mathbf{q}}$ . From Table 1, we see that there are four possibilities for the lower portion of the space-group symbol:  $11\bar{1}$ ,  $1s\bar{1}$ ,  $s1\bar{1}$  and  $ss\bar{1}$ .  $\text{K}_2\text{SeO}_4$ , which is isomorphic to  $\text{Rb}_2\text{ZnBr}_4(\text{Cl}_4)$ , is known (Iizumi, Axe, Shirane & Shimaoka, 1977) to make the incommensurate phase transition *via* a soft mode of symmetry  $\Sigma_2$ ; unfortunately, the available neutron scattering data (de Pater & van Dijk, 1978) on  $\text{Rb}_2\text{ZnBr}_4$  merely show that the analogous mode is overdamped so no firm conclusions about the transition mechanism have been drawn. However, if we assume that  $\text{Rb}_2\text{ZnBr}_4(\text{Cl}_4)$  behaves similarly to  $\text{K}_2\text{SeO}_4$ , we see from Table 1 that  $P:Pcmn:ss\bar{1}$  is the correct superspace symbol. No matter which mode actually causes the transition, the group put forward by Janner *et al.* (1980),  $P:Pc2_1n:s\bar{1}\bar{1}$ , is clearly incompatible with our rule of thumb for the symmetry requirements. The experimental evidence cited by Janner *et al.* in support of their superspace assignment is at best inconclusive. While they state that 'a better interpretation' of their data (the orientation of satellite faces on single crystals of the IC phase) can be obtained by assuming the superspace group of  $\text{Rb}_2\text{ZnCl}_4$  to be  $P:Pc2_1n:s\bar{1}\bar{1}$ , they also say that the data for the isomorphic  $\text{Rb}_2\text{ZnBr}_4$  are 'compatible with both superspace groups'. Since they acknowledge that the satellite faces on the  $\text{Rb}_2\text{ZnBr}_4$  were 'much larger in size' than those on  $\text{Rb}_2\text{ZnCl}_4$  because the experimental temperature was well below  $T_{\text{IC}}$  of the former and near  $T_{\text{IC}}$  of the latter, the variations on which their superspace-group assignment of  $\text{Rb}_2\text{ZnCl}_4$  are based may not be significant (they are not quoted in the paper). The only way for their superspace group to be correct for  $\text{Rb}_2\text{ZnCl}_4$  is for another phase transition to precede arrival at the observed IC phase. Similarly, the suggestion by Dam, Janner, Bennema, van den Linden & Rasing (1983) that the superspace group of IC  $\text{Rb}_2\text{ZnBr}_4$  may have 3D point-group symmetry 222 (implying a basic group of lower symmetry than  $G_{\pm\mathbf{q}}$ ) would violate the Landau symmetry theorem unless an extra intermediate phase transition were postulated, a transition for which there is no experimental evidence quoted.

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### Crystallography, Geometry and Physics in Higher Dimensions. III. Geometrical Symbols for the 227 Crystallographic Point Groups in Four-Dimensional Space

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#### Abstract

A geometrical 'WPV' notation for crystallographic point symmetry groups (PSG) in four-dimensional space is proposed. This simple notation generalizes the Hermann-Mauguin notation and makes it possible to retrieve the PSG elements easily. Tables classifying all elements of each PSG for systems 1 to 28 are presented. For higher systems, from 29 up to 33 inclusive, the results of the work are not reported owing to the space required, but they are at the disposal of the reader upon request.

#### Introduction

The present article is the continuation of two previous papers; we first defined the crystallographic point symmetry operations (PSOs) as elements of crystallographic point symmetry groups (PSGs) in  $E^4$ ,  $E^5$  and  $E^6$  (Weigel, Veysseyre, Phan, Effantin & Billiet, 1984), then we gave an extensive description of the 384 elements of the crystallographic PSG for the holohedry of the primitive hypercubic crystal system in  $E^4$  (Veysseyre, Weigel, Phan & Effantin, 1984). For some PSGs in  $E^4$  we proposed geometric symbols which were generalizations of Hermann-Mauguin

symbols but we did not give a listing of all PSOs of these PSGs (Weigel, Phan & Veysseyre, 1984; Veysseyre, Phan & Weigel, 1985).

By means of a completely different approach, Whittaker (1984) recently published a list of rather complicated symbols for the 227 groups but did not propose any list of PSOs. Furthermore his symbolism is far from the Hermann-Mauguin notation except for some polar groups.

In this paper we propose simple geometric symbols for each of the 227 crystallographic PSGs of  $E^4$ ; then we give the entire listing of all PSOs, elements of each of 161 crystallographic PSGs among the total of 227. It should be pointed out that for each PSG of  $E^4$  our geometric symbol is a generalization of a Hermann-Mauguin symbol for physical space  $E^3$  and makes it possible to retrieve any symbol of any PSO, an element of the PSG.

We recall that Wondratschek, Bülow & Neubüser (1971) determined the number of crystallographic PSGs of  $E^4$ . There are 227 belonging to 33 crystallographic systems which in turn are grouped into 23 families, indicated by a Roman numeral. The 227 PSGs of  $E^4$  are all subgroups of at least one of the four following PSGs: 20–22; 30–13; 31–07 and 33–16: here the first number characterizes the system (*cf.* Table 1, fourth column), the second number the PSG