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A review of structural resonance and the nature of long-range interactions in modulated mineral structures[1]

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Abstract

For some time now physicists have understood the general nature of the interactions in metallic crystals that lead to the development of modulated (incommensurate) structures. These structures result through interaction between displacement modes in the crystal and electrons with energies near the Fermi level. They are described as charge density wave structures. Until recently no corresponding explanation has been available for insulating crystals, and in particular minerals, which show comparable long-range modulation effects. Important mineralogical examples include the plagioclase feldspars, mullite and nepheline.

Theoretical study has now shown that certain basic symmetry principles are common to all incommensurate structures and that, in insulating crystals, the interactions producing long range modulation may comprise two physically distinct ordering schemes, or the combination of an ordering scheme with a system of lattice displacements of correct symmetry.

The objects of this paper are twofold. First, the symmetry principles which apply to modulated structures will be defined. Second, the nature of the physical interactions (resonance) in modulated structures will be discussed in terms of a simple example. The combination of resonance theory with experimental data from both X-ray single crystal diffraction study and high resolution electron microscopy provides new insights on the real structure of modulated mineral solutions. This insight is essential in modelling the thermodynamics of such solid solution systems.

Introduction

Recently physicists have been interested in explaining the origin of long period modulations in certain metallic compounds, of which $TaSe_2$ is a good example (DiSalvo and Rice, 1979; McMillan, 1977a,b). In these materials charge density wave modulations develop on cooling and are associated with an interaction between electrons with energies close to the Fermi level, and a system of local lattice displacements. One of the most striking features of these long period modulations is the fact that the wavelength of the lattice distortions is incommensurate with the primary lattice repeat periods of the crystal. It is for this reason that such structures may be described as incommensurate, a term which may be used without specific reference to their mode of origin. It is usual to find, in the case of these incommensurate charge density wave structures that, at some lower temperature, a lock-in transition occurs, at which point the period of the distortion wave becomes commensurate. The important features of the interaction between a charge density wave, and a system of local displacements, or distortions, can be explained quite simply as follows.

Fröhlich (1954) and Peierls (1955) were the first to show that a one-dimensional metallic system is unstable against the development of a charge density wave. This follows from the fact that, for such a system, the Fermi surface comprises two planar surfaces with separation 2 k_F as indicated in Figure 1. If we now introduce a displacement wave on the one-dimensional lattice with period such that it spans the Fermi surfaces, a band gap will be introduced in the electron energy level diagram leading to an overall reduction in the energy of the electron system, at least at low temperatures. Atomic displacements in this model system necessarily occur in quadrature with the charge density wave, *i.e.*,

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[1] This report and the four reports which follow were first presented at the M.S.A. Symposium entitled, "Real Behavior in Minerals: The Integration of Theory and Technique," held at the G.S.A. Annual Meeting in Cincinnati, on November 4, 1981.

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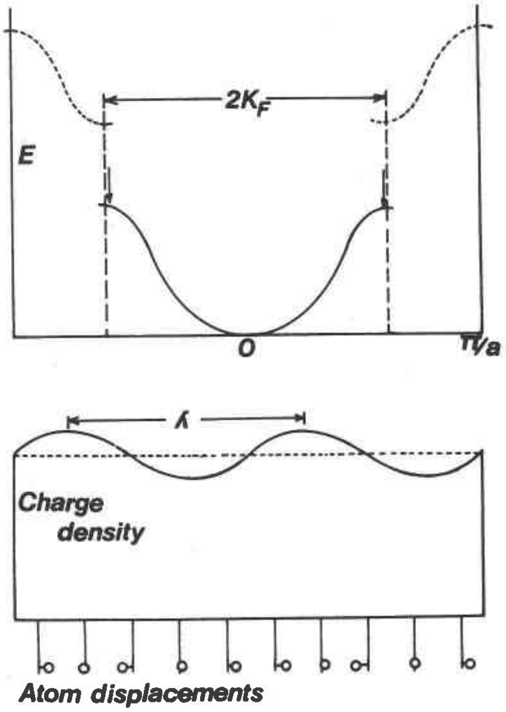

Fig. 1. The upper, k-space, diagram illustrates the presence of a band gap associated with the Fermi surface for a one-dimensional metal system. Notice that occupied energy levels (full line) have been substantially reduced in energy (E) just below the Fermi level. In the lower diagram the corresponding situation in real space is illustrated. This corresponds to a modulation in charge density in the crystal with related displacements of the positively charged atom cores.

they are related to grad ρ, where ρ is the charge density. The lowering of the electron energy levels at the Fermi surface is illustrated in Figure 1 together with a schematic model of the charge density wave and its associated displacement wave.

Given this accepted mechanism for the development of charge density waves it will be apparent that the wavelength of the associated atomic displacements need be related only to the position of the Fermi surface and hence may certainly be incommensurate.

The development of charge density waves in a single crystal may be studied by a number of physical techniques. The simplest way to demonstrate the existence of such an incommensurate structure is to use diffraction techniques which may employ X-rays, electrons or neutrons. In the corresponding single crystal diffraction patterns additional diffraction effects are associated with the displacement wave, and additional maxima of intensity occur other than at the normal reciprocal lattice points throughout reciprocal space. The incommensurate character of the modulations may be determined directly by measurement since the additional scattering occurs displaced from the Bragg positions by vectors which are irrational in relation to the basic reciprocal lattice repeats.

The presence of a transformation involving the appearance of a charge density wave may also be detected directly by making electrical conductivity measurements on the single crystal sample as a function of changing temperature across the transition. The introduction of the band gap associated with the development of the charge density wave system is associated with a dramatic decrease in the conductivity of the crystal. Direct electron-optical observation of charge density wave structures is also possible, and has recently been described (Chen *et al.*, 1981).

It appears from diffraction evidence that charge density waves are but one of a number of possible interactions in crystalline solids which yield long period structures that are incommensurate. Diffraction studies on the plagioclase feldspars (Bown and Gay, 1958), on nepheline (McConnell, 1962, 1981a), and on mullite (Agrell and Smith, 1960) all combine to show that additional diffraction maxima, which cannot be indexed rationally, and hence must be described as incommensurate, are a common feature of many mineral systems (McConnell, 1981b). In considering the possible origin of such incommensurate and modulated structures in minerals one is driven to consider the possibility of other kinds of interaction in the single crystals concerned since these materials are insulators, and the role of the Fermi surface and possible charge density wave modulations are quite inapplicable. In what follows an attempt will be made to demonstrate that the general theory on which the incommensurate charge density wave structures have already been explained may be expanded to include many other types of interaction in a single crystal, in particular in relation to several different ordering schemes.

In order to make this connection among incommensurate structures associated with a wide range of possible interactions, it will be necessary to discuss such interactions in very general terms, which in practice means in terms of fundamental symmetry rules (Heine and McConnell, 1981).

The advantage of approaching the problem of the origin of incommensurate mineral structures from this point of view is that the general theory can then be tested by direct reference to symmetry and structural data for a number of mineral systems. Apart from its current success in relation to the explanation of modulated mineral structures, the new general theory on the origin of incommensurate structures (McConnell, 1978a; Heine and McConnell, 1981) has been used to show that effects as diverse as Jahn–Teller distortions may be subsumed under the theory as now developed for insulators (McConnell and Heine, 1982).

The function of the following section of the paper is to develop the symmetry arguments necessary to the understanding of the origin of interactions, and resulting incommensurate structures, in insulating compounds including minerals.

Symmetry analysis of interactions between different transformation modes in single crystals

It is possible to develop the theory of interaction between different transformation modes in a single crystal in terms of symmetry arguments alone. Here it will be more meaningful to illustrate the operation of these symmetry rules by considering the example of ordering in a single crystal. The arguments that we employ in this case may equally well be used for other types of transformation mode in a single crystal, including displacive or soft mode transitions. Furthermore, the arguments may be applied to interaction between modes of entirely different physical origin.

Our analysis begins with a consideration of the possible interaction between different possible ordering schemes associated with the reciprocal vector 000 for the single crystal. For convenience we choose the space group *Pmm*2 and deal only with the possibilities of ordering an equal number of A and B atoms on a single general equivalent position (multiplicity four) in this space group. We assume that A and B atoms are initially completely disordered, *i.e.*, we presuppose a high temperature regime. The group representations of the vector 000 are simply the representations of the point group *mm*2 and these have been set out in Figure 2 together with the three possible ordering schemes for the crystal based on this point group. It is important here to note that the representations of the point group for the vector 000 imply that, if we choose a particular ordering scheme from this list of representations, this ordering scheme must apply throughout the entire crystal, *i.e.*, every unit cell is identically ordered.

We may now ask how, if at all, the different ordering schemes associated with the vector 000 may interact with each other. The answer here is simply that they may not interact in any way since they are orthogonal. In group theoretical language the direct product of any chosen pair of representations fails to yield the identity representation and consequently they are forbidden to interact.[2] This condition follows from the fact that the Hamiltonian for the system must have the full symmetry of the single crystal.

At this point we may note that the orthogonality condition will also apply to representations for vectors at the Brillouin zone boundary such as the vectors ½00 and 00½. In these cases we may set up a group representation table and list the possible space groups under which ordering of our A and B atoms may occur. Again we must reach the conclusion that there can be no interaction between different ordering schemes. We note here that care must be exercised in the case of non-symmorphic space groups when dealing with the representations for symmetry points on the Brillouin zone boundary. The presence of a screw axis or glide plane in such cases requires that certain of the representations become degenerate with each other (Bradley and Cracknell, 1972, p. 161).

Having failed to establish the possibility of interaction between different ordering schemes in the single crystal for the symmetry points (points of high symmetry such as 000, ½00, ½½½ *etc.*), we now turn to considering ordering on the basis of other vectors in the Brillouin zone. If we choose to use a vector displaced somewhat from the position 000, and label it k_i, in general we will have to include with this vector the vector $-k_i$, hence defining a two-dimensional representation (E_k) similar to that written out in Figure 3. The representations associated with $\pm k_i$ are complex conjugates and we may combine them to yield real terms: 2, 2Cos

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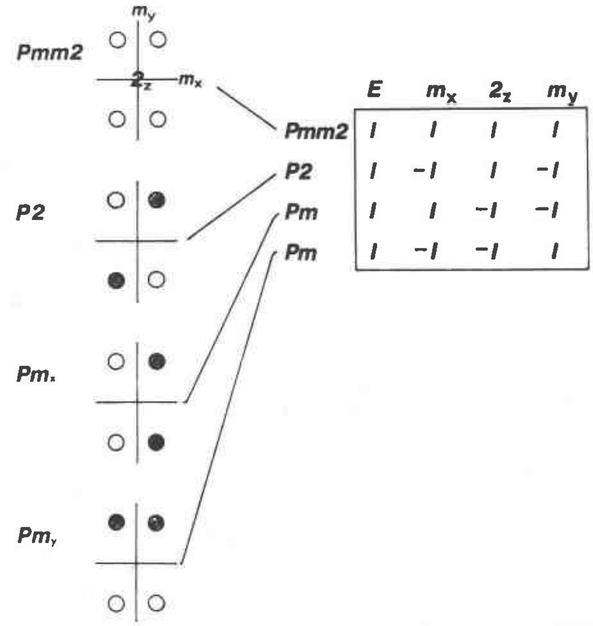
[2] This condition is imposed by the physics of the problem since it is inevitable that the energy of the system, and particularly the energy of interaction in the present case, must be invariant under the operation of the symmetry elements. In the matrix elements which define this energy of interaction we are required to integrate over the product of the functions which define the two ordering states. It follows that this integral will be identically equal to zero if this product function or a component of this product function is not invariant under the symmetry operations. In the case of the product of two functions an invariant can only result where both functions transform according to the same irreducible representation of the group. This theorem and several examples of its application are discussed in detail by Cotton (1971, p. 98–104).



	E	m_x	2_z	m_y
Pmm2	1	1	1	1
P2	1	−1	1	−1
Pm	1	1	−1	−1
Pm	1	−1	−1	1

Fig. 2. Group representation table for the vector 000 of the space group *Pmm*2. We consider here the role of the four irreducible representations in relation to possible ordering schemes for two A atoms and two B atoms on the fourfold general equivalent positions in this space group. The first representation is fully symmetrical and we associate it with the average situation. Thus the four symbols in the first diagram on the left all have equal weights (A+B)/2 in a distribution which is invariant under all the symmetry elements of the group. The other three irreducible representations and their associated diagrams illustrate possible ordering schemes. The weightings are now ±(A−B)/2 and the sign of this function is chosen locally on the basis of the relevant irreducible representation. Open and filled circles may be identified with the characters +1 and −1 respectively. Note that a completely ordered state for A and B atoms must be described in terms of the fully symmetrical representation and one of the three remaining irreducible representations.

$k_i \cdot t$. . . . *etc.*, at the same time noting that a single discrete character (cosine term) is multiplied on the complete contents of a unit cell on translation t. This operation, involving discrete translation and subsequent multiplication by a single character, must not be confused with the operation of multiplication by a continuous (cosine) function since that is not what the translation group representations imply. The formula for defining ordered states based on vectors $\pm k_i$ will now be apparent and amounts simply to an initial choice of ordering scheme from the point group table for 000, and then operation with the representation of the chosen vectors $\pm k_i$. By choosing all possible values of k_i, in this way we may define an effectively continuous ordering band in the single crystal for each one of the permitted representations, *i.e.*, ordering schemes, for 000. In general these bands can be drawn out to show the energy associated with individual representations k_i (McConnell, 1978b).

We now turn to considering the possibility of interaction between different ordering schemes, *i.e.*, different bands, at points k_i other than the primary symmetry points in the Brillouin zone. Here we must determine and use the symmetry of the chosen vector k_i, *i.e.* the symmetry group of k_i, and establish its representations. Determination of the symmetry group of the chosen vector k_i proceeds exactly as though the chosen vector were in direct space. Thus in reciprocal space we must mark in the relevant symmetry elements as has been done in Figure 4. In this reciprocal plot the chosen position for the little vector k_i has symmetry E and m_x only. It follows that the vector k_i has only two irreducible representations, one even and one odd under the mirror plane m_x, as indicated in the inset in Figure 4. It should be apparent now that, while there were four independent ordering bands at k_i based on the four different irreducible representations of the point group *mm*2 (000), these four representations at k_i become equivalent in pairs. Thus ordering bands based on *P*2 and Pm_y are both

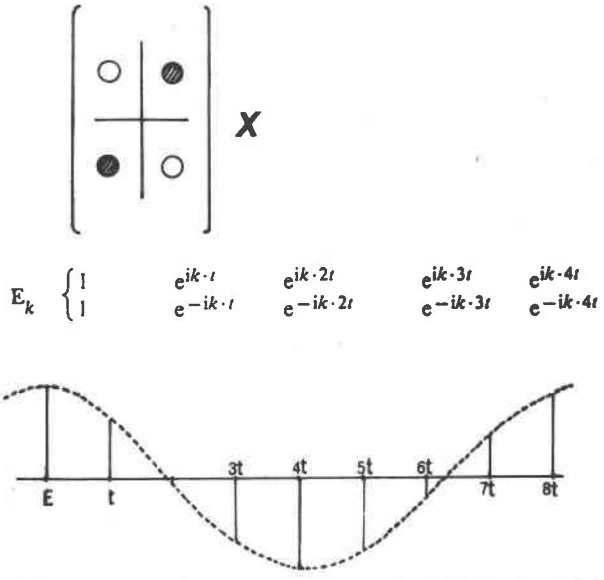
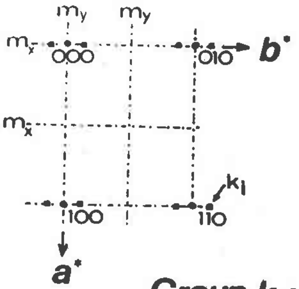


Fig. 3. Schematic representation of the development of a modulated structure based on one of the irreducible representations of the vector 000 as defined in Fig. 2. Note that the modulated structure is derived by selecting a basis function associated with a single lattice point. This function is modified, after translation by a lattice vector (t), by multiplication by the character ($2\cos k \cdot t$) of the chosen two-dimensional representation (E_k) of the translation group of the crystal.

odd under the mirror plane m_x. It follows directly that interaction between these two ordering schemes is possible at k_i where this was quite impossible at the original point 000. This condition, under which independent ordering bands in a single crystal may interact, has been described as a structural resonance (McConnell, 1978a). Reduction of the energy due to the interaction in resonance means that it may be more favorable for the crystal to order by utilizing both ordering schemes than to order singly at the symmetry point 000 on either (Heine and McConnell, 1981). In effect the resonance between two ordering schemes produces a local free energy minimum away from the symmetry point. Clearly there is no difficulty in accepting, in this case, as in the case of the charge density wave systems, that the minimum of free energy in the lowest band may occur at an incommensurate value of k_i. Further it is to be expected that, since the position of this minimum is dependent on the interaction of two ordering schemes, it may move as a function of temperature, pressure and chemical composition.



NB
The group of k_i has symmetry elements E and m_x only.

Group k_i;	E	m_x
	1	1
	1	−1

	E	m_x	2_z	m_y
$Pmm2$	1	1	1	1
$P2$	1	−1	1	−1
Pm	1	1	−1	−1
Pm	1	−1	−1	1

Fig. 4. The use of symmetry in reciprocal space to define the symmetry group of the vector k_i. Note that at points of high symmetry in the Brillouin zone such as 000 the group of the corresponding vector is of order four. At the point chosen in the diagram for the vector k_i the symmetry elements comprise only the identity E and the mirror plane m_x. This means that the group of k_i is of order two and that modulated structures based on the four different space groups associated with the vector 000 must become equivalent in pairs at k_i as indicated by the dashed boxes in the final table.

Finally we note here that if a resonance interaction is postulated it may be tested directly from a knowledge of the symmetry changes which must be associated with the proposed structural changes. In many cases at least one of the two ordering schemes is likely to be known. These symmetry data may be used to determine the group of the vector k_i and the relevant representation. This symmetry may then be used to explore the possibilities for the second transformation mode present in the structural resonance which has the same symmetry and representation.

In the section which immediately follows an attempt will be made to demonstrate the physical significance of this resonance theory using $NaNO_2$ as an example. $NaNO_2$ is a simple chemical compound which has a ferroelectric transition at approximately 163°C. At the same temperature a thermodynamically stable resonance structure develops which is incommensurate. In this case it is possible to use symmetry criteria alone to determine uniquely the second transformation mode present in the resonance structure. It is also possible to demonstrate in this case why there should be a substantial reduction in the free energy of the system due to the combined effects of the two transformation modes which are present in the resonance, *i.e.*, it is possible to explore the purely physical origin of the resonance structure in $NaNO_2$.

The nature of the physical interaction in a structural resonance: the incommensurate structure of $NaNO_2$

It is possible to demonstrate in a particularly simple and convincing manner that the resonance structure observed in $NaNO_2$ close to 163°C involves a favorable interaction between two transformation modes in the single crystal. At high temperature (well above 163°C) the compound $NaNO_2$ has disordered NO_2 groups, is thus paraelectric, and belongs to the centered space group *Immm*. Well below 163°C the individual NO_2 groups, which lie in the plane (100), order with dipole vectors parallel to the *b* crystallographic axis, and the structure then belongs to the space group *Im*2*m* which lacks a center of symmetry, as is necessary in the case of a simple ferroelectric compound. In a very small temperature interval around 163°C, and prior to the paraelectric–ferroelectric transition in $NaNO_2$, an incommensurate structure develops. The incommensurate wave vector (k_i of our previous discussion) is situated close to 000 and along the *a** direction. Experimental study (Böhm, 1978) shows that the vector changes with temperature along *a** in the temperature interval over which the incommensurate structure exists. We now apply the symmetry theory of the previous section to determine the symmetry (little group) of the vector k_i and its appropriate irreducible representations.

In the case of the incommensurate structure in $NaNO_2$ the symmetry analysis is particularly straightforward since it is known, *a priori*, that the low temperature transformation relates to a simple ferroelectric mode associated with the change in space group symmetry to *Im*2*m*. This is a change associated with the vector 000. The group representation table for 000 in this case is simply the representation table for the point group *mmm*, which is shown in Table 1. In this table the space groups associated with seven different transformation modes have been indicated in parentheses, and the representation for the observed derivative space group *Im*2*m* has been underlined. In order to determine the symmetry appropriate to the space group *Im*2*m* at the position of the vector k_i for the incommensurate structure, we now select from the eight symmetry elements of the full point group those which are contained in the group of the vector k_i (at Δa^*). The reduced symmetry for the vector k_i comprises only the elements E, C_{2x}, m_y and m_z. These four symmetry elements therefore form the little group of k_i and we may immediately define its representations which include also the representation for the space group *Im*2*m* at k_i. This one-dimensional representation is even for both the identity E and the mirror plane parallel to (001) (m_z). It is odd for the elements comprising the diad parallel to x (C_{2x}), and the mirror plane parallel to (010) (m_y). The task of determining the second space group in the full representation table for the point group *mmm* which has the same representation for the chosen vector k_i is now straightforward. This second space group must have the same reduced representation as the space group *Im*2*m* in the group of k_i. It may be determined uniquely by simple inspection of the full point-group representation table for *mmm*, Table 1. Having doubly underlined the elements of symmetry associated with k_i in the representation of *Im*2*m* it will be apparent that precisely the same characters for all four of these elements occur in the representation of the space group *I*2/m_z, which is a centrosymmetric space group in the monoclinic system. What we have just done, from inspection of the character table, is to prove that for the vector k_i, the space groups *Im*2*m* and *I*2/m_z share exactly the same irreducible representation. Their associated bands may therefore interact to produce a resonance structure. It is of course also necessary that this is possible energetically, a condition which group theory alone does not permit us to comment on. However, since an incommensurate structure is observed in practice, it follows that the necessary energetic conditions must also be fulfilled, at least in the narrow temperature interval where the incommensurate structure is observed.

At this point we have established unequivocally that a resonance interaction in $NaNO_2$ is possible

Table 1. Group table showing the origin of the structural resonance in $NaNO_2$ for wave vectors at 000 $\pm\Delta a^*$ (underlined)

	{E/000}	$\{C_{2z}/000\}$	$\{C_{2y}/000\}$	$\{C_{2x}/000\}$	{i/000}	$\{m_z/000\}$	$\{m_y/000\}$	$\{m_x/000\}$
(I mmm)	1	1	1	1	1	1	1	1
(I $2/m_y$)	1	-1	1	-1	1	-1	1	-1
(I $2/m_z$)	$\underline{1}$	1	-1	$\underline{-1}$	1	$\underline{1}$	$\underline{-1}$	-1
(I $2/m_x$)	1	-1	-1	1	1	-1	-1	1
(I 222)	1	1	1	1	-1	-1	-1	-1
$\underline{\text{(I m2m)}}$	$\underline{\underline{1}}$	$\underline{-1}$	$\underline{1}$	$\underline{\underline{-1}}$	$\underline{-1}$	$\underline{\underline{1}}$	$\underline{\underline{-1}}$	$\underline{1}$
(I mm2)	1	1	-1	-1	-1	-1	1	1
(I 2mm)	1	-1	-1	1	-1	1	1	-1

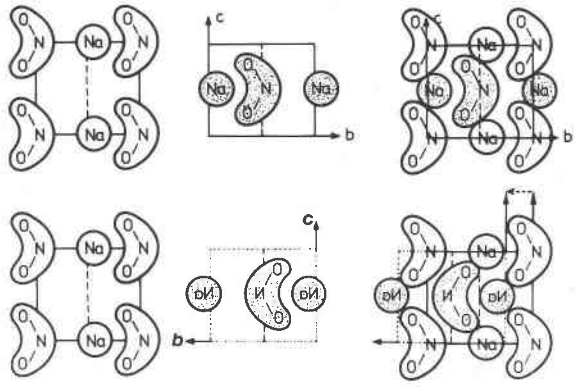


Fig. 5. Diagram illustrating the effect of introducing an antiphase boundary into the ferroelectric sequence in $NaNO_2$. In the upper set of diagrams the development of the normal $Im2m$ structure is illustrated. In the lower sequence the introduction of a layer of structure with reversed polarity is shown to lead to offset of the layers parallel to b in the final diagram. This shift accommodates the structural misfit.

between a ferroelectric transformation mode ($Im2m$), and what is effectively a shear transformation mode associated with the monoclinic structure ($I2/m_Z$). We now approach the problem of demonstrating that these two structures may with advantage be combined to produce a resonance and hence reduce the free energy of the system. In order to demonstrate that the ferroelectric and shear modes of transformation can be combined with advantage, we proceed by considering a simple ferroelectric sequence and introduce a single antiphase boundary parallel to (100). This involves the rotation of a NO_2 group about the c axis and across the antiphase boundary and we now model this juxtaposition of NO_2 groups across the antiphase boundary. The characteristics of the normal structural sequence of ordered NO_2 groups, and the situation across the antiphase boundary, are combined in Figure 5. It is clearly necessary in modelling the antiphase boundary to introduce a shear parallel to the b axis. This shear is exactly that which is implied by the transformation mode $I2/m_Z$. It will now be clear that there is a particular advantage in including a section of sheared structure in a simple antiferroelectric domain sequence. A very schematic model of the way in which the two transformation modes in the incommensurate structure of $NaNO_2$ are thus combined is provided in Figure 6. This diagram should not be interpreted too literally. It is primarily a thinking device which illustrates the basic symmetry aspects of the resonance structure. In the complete structural sequence within the resonance structure the component transformation modes have here been combined in quadrature, *i.e.*, the shear mode is in phase with the gradient of the ferroelectric mode, a point which was also made earlier with regard to the phase relationships between the charge density wave and associated displacements. This in-quadrature characteristic of the resonance structure has also been discussed in relation to the structure factor for the component transformation modes (McConnell, 1978a). Since the ferroelectric transformation mode is non-centrosymmetric, the character associated with the center of symmetry in the representation table (I) is -1, implying an anticenter. The shear transformation mode, however, is centrosymmetric with character $+1$ in the Table. It follows that their respective difference structure factors are necessarily also in quadrature. Thus if the difference structure factor associated with the ferroelectric mode is defined as purely imaginary, then the structure factor associated with the shear mode is necessarily totally real. Further discussion of this point is contained in McConnell (1978a), where the origin of the resonance structure itself is discussed in terms of the

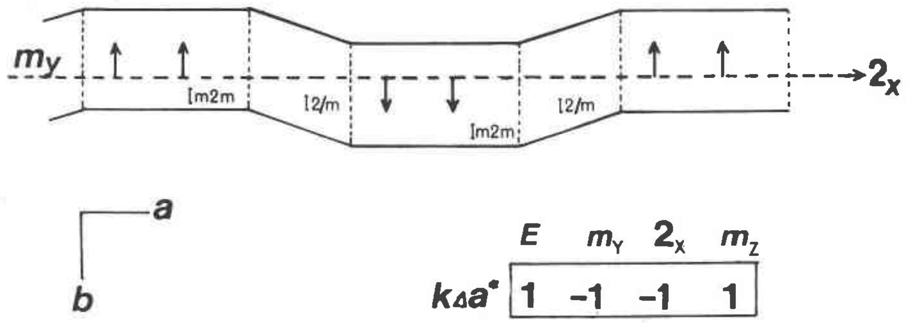


Fig. 6. Schematic diagram illustrating the sequence of structure types ($Im2m$ and $I2/m_Z$) in the modulated structure of $NaNO_2$. Note that the irreducible representation given is applicable to both components of the modulation.

choice which necessarily exists in combining the two component transformation modes in quadrature, *i.e.*, as (a ± ib). The physical nature of this choice of phase is clearly demonstrated in the case of $NaNO_2$ where, at a chosen antiphase boundary, shear in one sense is acceptable and in the other is not, and two different energy states are clearly involved.

While it is possible to make a complete analysis both in symmetry and in purely physical terms, for the resonance structure in $NaNO_2$, a similar complete analysis is not yet possible in the cases of some of the very complex resonance structures which are observed in minerals. Future structural work must aim, for example, at determining the exact advantages, in energy terms, of combining Al/Si ordering with Na/Ca ordering in the resonance structure in the intermediate plagioclase feldspars (McConnell, 1978a); or of combining K/□ ordering with a system of atom displacements in the case of nepheline (McConnell, 1981a). A detailed analysis of the specific implications of the new resonance theory in the context of structure analysis is in preparation.

Thermodynamic aspects of the origin of incommensurate phases

It is convenient in discussing the stability relationships of incommensurate phases, and the thermodynamics of the transformations in which they appear, to use an approach originally developed by Landau (Landau and Lifshitz, 1968). This has recently been revised and considerably simplified by Birman (1966). The Landau treatment of phase transformations is based on a group theoretical approach which assumes that the free energy function for the transforming phase close to the transition temperature may be expanded in a power series of η, and order parameter which describes the amplitude of a structural change which occurs at and below the transformation temperature.

$$G(PT\eta) = G_O + \alpha\eta + A\eta^2 + B\eta^3 + C\eta^4 \ldots \quad (1)$$

This structural change, in Landau theory, is necessarily associated with the appearance at the transformation temperature of a state of lower symmetry, *i.e.*, a subgroup irreducible representation of the high symmetry group which existed above the transformation temperature. Landau was particularly concerned with defining the conditions necessary for a second order phase transformation. A second order phase transformation requires that the order parameter η increases smoothly from zero as temperature falls below the transformation temperature. For this to be true it is necessary that no invariants occur in the linear or third order terms in the free energy expansion (1). The presence or absence of invariants in any of the terms of the free energy expansion may be demonstrated by deriving space group reduction coefficients as shown by Birman (1962, 1966). Thus in order to prove that there is no invariant of third order present in the expansion (1) it is only necessary to show that the symmetrized cube $[R]_3$ of the chosen subgroup irreducible representation does not contain the identity representation of the high symmetry group. A second condition necessary for a second order transformation in Landau theory requires that the antisymmetrized square $\{R\}_2$ of the chosen subgroup representation should not contain the representation of a polar vector. Finally, since the subgroup irreducible representation cannot in any case provide a linear invariant in (1), the relevant free energy expansion appropriate to a second order transformation may be written, up to terms of fourth order, as:

$$G(PT\eta) = G_O + A\eta^2 + C\eta^4 \ldots\ldots\ldots \quad (2)$$

We now consider the importance of the coefficient A in the second order term of the Landau expansion (2). Above the transformation temperature T_c the crystal has high symmetry which ensures that the equilibrium value of η is identically zero. This is possible only if the coefficient A for the quadratic term in the expansion of the free energy (2) is positive. For a transformation involving a change in symmetry the coefficient A must become negative below the transformation temperature. Hence the condition for the transformation is simply that A goes to zero at the transformation temperature T_c. Here we may assume that C, the coefficient of the fourth order term, remains constant and positive both above and below the transformation temperature. The nature of the free energy plot as a function of the order parameter η is shown, both above and below the transformation temperature, in Figure 7. Here we may assume that A varies with temperature as:

$$A(T) = a(T - T_c) \ldots\ldots\ldots\ldots \quad (3)$$

where a is a constant and hence

$$\eta^2 = a/2C(T_c - T) \ldots\ldots\ldots \quad (4)$$

We may now consider the application of Landau theory to transformations involving the appearance of certain incommensurate phases (Heine and

McConnell, 1981). The space group irreducible representation associated with the development of these incommensurate phases is the two-dimensional, physically irreducible, representation that is based, as discussed earlier, on the representations for $+k_i$ and $-k_i$. This two-dimensional representation we will refer to hereafter simply as E_k. From the point of view of Landau theory we must first establish the translation group reduction coefficients for the power series expansion of the free energy in terms of this representation E_k. Calculation shows that, for even order terms in the expansion, translation group invariants occur; for example, the second order term in the expansion contains both the identity representation of the translation group and the representation E_{2k} thus:

$$[E_k]_2 = A_1 + E_{2k}$$

Odd order terms in the expansion do not contain the identity representation provided that the incommensurate wavelength is really irrational. The symmetrized cube of the representation E, for example, contains only E_k and the representation E_{3k}. Thus no third order invariant can exist since the incommensurate wavelength is certainly not equal to three times the lattice repeat;

$$[E_k]_3 = E_k + E_{3k}\ .$$

Generally similar conditions attach to higher even and odd terms in the free energy expansion, implying that the incommensurate transformation should be of second order.

Reduction of the complete space group irreducible representation based on the translation group representation E_k involves taking the direct product of the characters of the chosen irreducible representations for the group of the vector k_i (Birman, 1962). Here we note simply that if the two transformation modes which interact to produce the incommensurate structure have the same symmetry, *i.e.*, belong to the same irreducible representation of the group of k_i, then three quadratic invariants will appear, two associated with the symmetrized square of each of the chosen representations, and a third associated with their direct product.

If, therefore, we restrict attention solely to the quadratic terms present in the Landau expansion we may write:

$$G = \Sigma_k\{A_k\psi_k^2 + 2H_k\psi_k\phi_k + B_k\phi_k^2\} \ldots\ldots (5)$$

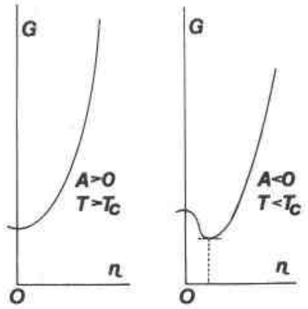


Fig. 7. Diagrams illustrating the behavior of the free energy (G) in terms of the Landau quadratic coefficient (A), both above and below the transition temperature, T_c.

Here ψ and ϕ are the order parameters associated with the two chosen irreducible representations, with quadratic coefficients A and B respectively and H is the coefficient of the interaction term. Since it is quite unlikely that both of the coefficients A and B will tend independently to zero at the same temperature, we will assume that the main transformation is associated with the order parameter ψ and the coefficient A, and that the coefficient B does not vary markedly with temperature in the temperature range of interest. Where this is so it is permissible to rewrite the three second order terms as:

$$[A_k + 2H_k\phi_k/\psi_k + B_k(\phi_k/\psi_k)^2]\psi_k^2 \ldots\ldots (6)$$

On mixing the two chosen transformation modes in the optimum ratio such that $\phi_k/\psi_k = -H_k/B_k$ we derive a single coefficient of the main mode ψ_k:

$$[A_k - H_k^2/B_k]\psi_k^2 \ldots\ldots (7)$$

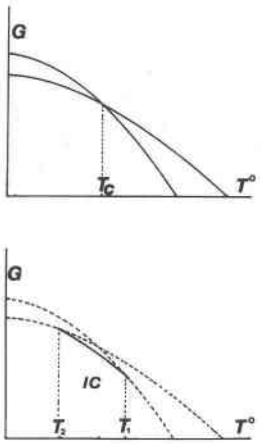


Fig. 8. The thermodynamics of incommensurate structures. In the upper of the two diagrams the free energy curves associated with a normal transition are shown, with a normal transition temperature at T_c. The stability range of an incommensurate structure between temperatures T_1 and T_2 is shown in the lower diagram. Note that the entropy of the incommensurate phase is lower than that of the normal completely disordered phase.

This compound coefficient implies that the transformation associated with the combined or resonance ordering system will occur at higher temperature than that based on the ordering scheme for ψ alone. In short the interaction between the two transformation modes will lead to a reduction in free energy, and stabilization of the associated resonance structure, at a temperature somewhat above that for the normal transformation based on ψ alone.

Finally, it is of some interest to define the essential form of the free energy–temperature plots associated with the development of an incommensurate phase. In the first of the plots shown in Figure 8 it has been assumed that there is a simple phase transformation at T_c based on a single transformation mode. In the second of the two plots the presence of a resonance structure must involve a reduction of free energy in the immediate temperature range of the main transformation. It must also have a lower entropy than the completely disordered phase ($\partial G/\partial T = -S$) in order to exist in this temperature range. It is thus clear that resonance stabilization involves a very substantial decrease in the enthalpy of the system.

In the treatment presented above it has been assumed, as in the simple case of $NaNO_2$, that there is one major transformation mode, and that the second mode is important only in combination, leading to the existence of a resonance structure over a limited temperature range. It is apparent, however, in several mineral systems, particularly where one is dealing with incommensurate behavior in solid solutions as in the case of mullite (McConnell, 1981b) and the intermediate plagioclase feldspars (McConnell, 1978a), that both transformation modes may be equally important. In this case the incommensurate structure may be stable over a very wide temperature range, and indeed may be the only stable single-phase state possible for the system at low temperatures.

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