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Incommensurate Structures [and Discussion]

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Incommensurate structures

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Incommensurate structures occur in a very wide range of crystalline materials and illustrate a number of interesting aspects of the physics of atomic interaction in the context of crystal structure and bonding. Formal theories that deal with the origin of these phases are reviewed and shown to have a great deal in common. Several important examples of incommensurate structures in simple compounds are described and these include the minerals quartz and nepheline. Nepheline, which has not been analysed previously shows an interaction between oxygen displacements associated with the loss of a triad axis, a three-state Potts model, and potassium-vacancy ordering. The important role of incommensurate structures in mineral solid solutions is discussed and illustrated with reference to the plagioclase feldspar solid solution.

1. Introduction

Incommensurate structures are characterized by the existence of a modulation, or system of modulations, which are incommensurate with the underlying lattice repeats of the crystal. Evidence of such behaviour is generally obtained from single crystal diffraction data where the presence of the modulation is associated with the existence of additional closely paired intensity maxima that are convoluted with either the normal reciprocal lattice points, or with high symmetry points on the Brillouin zone boundary. This distribution of intensity may be specified formally by defining a small reciprocal vector Q as measured from the nearest symmetry point. This vector characterizes the wavelength and wave vector for the modulation, it normally has high symmetry and usually defines a wavelength of the order of several unit cell, or supercell, repeats. To date a large number of incommensurate structures have been studied. Examples include simple compounds such as biphenyl, $NaNO_2$ and quartz but there is also a large class of mineral examples where incommensurate behaviour may be directly associated with ordering behaviour in solid solutions. This article deals initially with the theory of the origin of incommensurate structures in simple compounds and then proceeds to the special problems associated with incommensurate behaviour in solid solutions. Problems in the latter category have not been discussed in a general way previously. Sections 3 and 4 provide examples of incommensurate structures in simple compounds and solid solutions respectively.

2. General theory

In attempting to provide a completely general theory for the origin of incommensurate crystal structures it is necessary to establish the nature of interactions within the single crystal that can lead to a minimum of free energy for some arbitrary wavelength associated with the observed modulation. It is usual in

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the case of simple ordering events in single crystals to find that positive gradient energy terms associated with modulation (non-zero values of Q) lead to an increase in enthalpy and free energy. Thus it is usual to find energy minima located at the symmetry points where, by definition, Q is zero. A mechanism or interaction which acts to reduce the free energy of the system for non-zero Q may be anticipated where there are competing local interactions, as in the ANNNI model. However, a phenomenological approach based on local neighbour interactions is not particularly helpful in developing a general theory of incommensurate behaviour.

To provide a sufficiently abstract theory it is useful to begin by discussing the formal symmetry aspects of the problem. Symmetry arguments have been used by a number of workers and it is possible to show that all the theories proposed have a great deal in common although this may not be apparent at first sight. The earliest recorded reference to symmetry in the development of incommensurate structures is contained in Axe *et al.* (1970). These authors presented a theory of anomalous acoustic dispersion associated with interaction between two phonon bands of the same reduced symmetry, and comparable frequency, leading to an energy minimum in the lower band at a non-zero value of Q. The same principle was evoked somewhat later (McConnell 1978) in defining the selection rules for the interaction of modulated structures based on ordering schemes of different symmetry. It was noted there that it is possible to chose two ordering schemes of appropriate symmetry for a symmetry point vector such that they have the same reduced symmetry at Q. Thus the ordering structures may interact with advantage at non-zero Q to produce a complex modulation and hence reduce the free energy of the system. It was also noted that, within the complex modulation thus formed, the two modulation components must be in quadrature and hence may be written:

$$\eta \cos Qr \pm \xi \sin Qr, \tag{1}$$

where η and ξ are order parameters associated with the two original ordering schemes (group representations) and the choice of sign relates to the choice of the lower of two free energies. This concept of the interaction of two component structures within the modulation has been particularly useful in establishing the structure of incommensurate phases in insulators (Heine & McConnell 1981). It has led directly to the development of the so-called gradient ploy (Heine & McConnell 1981, 1984) which may be used both to determine the second structure, the nature of the interaction and the relevant phase relationships. In dealing with the component structures in a modulation in this way it is possible to demonstrate the precise symmetry properties which define the gradient concept and it will be convenient to illustrate these later in the context of the incommensurate structures of quartz and nepheline.

An alternative but closely related analysis of the origin of incommensurate phases arose originally from considering the implications of the so-called Lifshitz invariant. This was originally discussed in the context of the selection rules associated with second-order phase transformations. Lifshitz (1942) was the first to point out that the presence of an invariant of the form:

$$\eta\, \mathrm{d}\xi/\mathrm{d}x - \xi\, \mathrm{d}\eta/\mathrm{d}x, \tag{2}$$

in the Landau free energy expansion would lead to a spatial instability in the transforming single crystal, and thus preclude the occurrence of a normal second-order phase transition. Here η and ξ are order parameters associated with two degenerate one-dimensional representations and the spatial derivatives relate to a chosen direction in the crystal. The Lifshitz invariant arises naturally for representations associated with vectors on the Brillouin zone boundary under conditions where the symmetry includes glide or screw operations. Later it was appreciated that the presence of this invariant must lead to the development of a modulated or incommensurate structure (Levanyuk & Sannikov, 1976). It is possible† to prove that the ordering selection rules defined by the Lifshitz gradient invariant are equivalent to those already discussed in the two component structure theory in (1) above, and that the gradient invariant is simply a formal description of their symmetry relationships.

In discussing gradient invariants in general Sannikov & Golovko (1989) distinguishes two possibilities relating to the origin of incommensurate phases. The first of these they identified with a true Lifshitz invariant where the two representations (and related order parameters) were combined in a two-dimensional irreducible representation, and were therefore necessarily degenerate in energy. In the second case, which they describe as a Lifshitz-type invariant, the two representations are initially independent and, consequently, need be merely comparable in energy to interact. This distinction, which we here describe as the Sannikov condition, is important physically for the following reasons. In the case of a true, or what we will here call a proper Lifshitz invariant the basis structures to be considered in the incommensurate structure are necessarily identical physically and must transform into one another under the symmetry operations of the vector associated with the relevant symmetry point. In the case of incommensurate structures associated with the Lifshitz-type invariant, however, the component structures, which are now defined in terms of initially independent one-dimensional irreducible representations, certainly need not transform into one another physically. They may well relate to totally different physical ordering events or to an ordering mode combined with a soft mode.

In the present article I use the term 'improper Lifshitz invariant' to describe this more general situation. Thus we use the term to describe the situation where certain symmetry criteria and phase relationships are satisfied but the structural phenomena to which they relate are not degenerate. Examples of both types of incommensurate structure are described in the literature. In biphenyl, for example, the incommensurate structure designated phase III by Baudour & Sanquer (1983) stable below 20 K, must be associated with the existence of a proper Lifshitz invariant. This follows since the high-temperature space group of biphenyl is $P2_1/a$, and modulation wave vector in phase III is associated with the symmetry point vector $0, \frac{1}{2}, 0$ where all representations are necessarily doubly degenerate through the presence of the screw diad axis. In studying the nature of the incommensurate structure in this case it is only necessary to establish one component structure or structural event since the second is identical and must be phase related within the modulation to the first. There are many examples in the literature of structures associated with improper Lifshitz invariants. Sodium nitrite is an important example in this class and shows

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† The operative condition for the Lifshitz invariant is that the anti-symmetrized square of the chosen irreducible two-dimensional representation for the crystal should contain a representation that transforms as a vector. Now for appropriate pairs of full space group representations in the two component structure theory which have the name symmetry at Q the symmetry elements that turn Q into $-Q$ must have opposite sign since the representations are orthogonal. Thus the product of all pairs of characters in the two representations in the subset of elements that turn Q into $-Q$ must yield the character -1. This condition in turn dictates that the product representation is itself a vector representation.

incommensurate behaviour in a narrow temperature interval around 163 °C (McConnell 1981*a*; Heine & McConnell 1981). At temperatures above 163 °C sodium nitrite is paraelectric with space group *Immm*. The incommensurate structure is modulated parallel to the *a* axis and two-component structure theory indicates that one of the structures is ferroelectric with space group *Im*2*m*, while the other is ferroelastic with space group $I2/m_z$.

The distinction, originally created by Sannikov, between what are here described as proper and improper Lifshitz invariants is very important when one considers the potential stability of incommensurate structures over a range of temperatures. Where the origin of the incommensurate phase is associated with a proper Lifshitz invariant there need be no reason in symmetry to seek a low-temperature commensurate phase and the IC structure, or something very closely related to it, may well exist down to 0 K. However, where the incommensurate structure, at least in a simple compound, is associated with an improper Lifshitz invariant it is usual to find the incommensurate phase restricted to a narrow temperature interval above a first-order transformation to a commensurate structure related to the dominant-component structure. These conclusions accord well the actual behaviour of incommensurate structures in simple compounds such as that in quartz and sodium nitrite. Up to this point the theory of incommensurate behaviour has revolved around the possibilities associated with the proper and improper Lifshitz invariants, and the existence of incommensurate structures that can be analysed on strict symmetry principles.

There is in addition a large and important class of incommensurate structures that occur in binary solid solutions and here the appropriate theory is less well developed. While the two-component theory has been used (McConnell 1978) and is often applicable, it is also clear that the rigidity of the symmetry rules must be substantially relaxed in the interests of variable chemistry. The phenomena are illustrated in the case of the incommensurate structure of wustite, $Fe_{(1-x)}O$ (Garstein *et al*. 1986) and also in one of the most important mineral solid solution systems, namely the plagioclase feldspars. In both these materials the incommensurate mechanism is complicated by the fact that it is necessary to consider ordering characteristics as a function of composition as well as temperature. It is at this point that the simple physical picture associated with the mixing and splitting of phonon bands, which appeared at the beginning of this section, proves to be inadequate.

It has proved helpful in practice to develop a theory of incommensurate structures in binary solid solutions by first establishing possible ordered structures for specific end member phases, or for intermediate compounds, in the relevant binary system. Where the symmetry of these ordered structures satisfy the Lifshitz invariant condition the structures may combine in an incommensurate modulation with appropriate phase and a substantial reduction in free energy. The refractory phase mullite provides a good example of the application of these principles.

Mullite is the most important refractory phase in the system SiO_2–Al_2O_3 and develops an incommensurate structure on crystallization at 1500 °C (McConnell, 1981*a*; McConnell & Heine 1985*b*). In terms of possible end members it can be considered as a member of a solid solution series between end member compounds $Al_8Si_4O_{20}$ (sillimanite) and iota alumina, with the corresponding formula unit written as $Al_{12}O_{18}[\ ]_2$, where the symbol [ ] indicates the presence of oxygen vacancies. When disordered both these compounds are isostructural with space group Pbam. On ordering each develops a simple superlattice involving doubling of the *c* axis but with space groups *Pbnm* (ordering of Al and Si as in sillimanite) and *Pnnm* (ordering of vacancies as in iota alumina). It is easy to show that these two space groups are related in an improper Lifshitz invariant for modulation parallel to the *a* crystallographic axis, which accords with the experimental diffraction observations (Cameron 1977). Within the incommensurate structure Si/Al ordering and the ordering of vacancies combine to reduce the free energy of the system. Clearly the real component structures present must depart appreciably from the idealized end member structures for sillimanite and iota alumina.

A comparable approach may be used in the study of the incommensurate structure in the plagioclase feldspar solid solution although, since these materials are triclinic the symmetry aspects are by no means so clear cut. The details will be discussed later in this article.

Recent direct calorimetric studies (Carpenter *et al.* 1986) indicate that incommensurate behaviour in mineral solid solutions is generally associated with large stabilization enthalpies. Calorimetric data for the plagioclase structures indicate stabilization enthalpies of the order of kilocalories per mole and in the case of mullite the stabilization enthalpy may be estimated at approximately 10 kilocalories per mole. Clearly incommensurate behaviour is of pivotal importance in rendering these phases stable with respect to disordered solid solutions. We note that these stabilization enthalpies are vastly in excess of those observed in simple compounds such as quartz and sodium nitrite and reflect the role of chemical variables on the ordering behaviour of these materials.

In the study of both crystal structure and stabilization enthalpies in incommensurate mineral solid solutions computer simulation is now a viable tool and such studies are likely to become even more important in the immediate future.

3. Incommensurate structure in compounds

(*a*) *Quartz*

The incommensurate behaviour of quartz has as long been the subject of detailed study (Aslanyan *et al.* 1983; Dolino *et al.* 1989). This occurs in a very narrow temperature interval at the β to α transition temperature at 573 °C (846 K). The incommensurate structure is associated with the existence of an improper Lifshitz invariant involving a soft optical and an acoustical mode. High quartz (the β form) is hexagonal with space group $P6_222$, and the low temperature commensurate structure (the α phase) is trigonal with space group $P3_221$. Both the β–α, and the incommensurate phase transition in quartz depend on the dynamic properties of the SiO_4 tetrahedra and their linkages which produce a fully three-dimensional framework structure. From data on the optical frequencies of quartz we know that the weakest forces in the structure relate to Si–O–Si bending. These tend to leave the individual SiO_4 tetrahedra undistorted (giving rise to the so-called rigid modes). Deformations of the individual tetrahedra involving O–Si–O bending are associated with somewhat higher frequencies, but with force constants some 6% of those associated with the Si–O stretching modes which define the highest optical frequencies. These bonding criteria provide the general constraints on transformation mechanisms in quartz, and serve, when taken together with a symmetry analysis of the problem, to establish the nature of the incommensurate behaviour.

First we consider the full symmetry of the components in the modulation and start by studying a single SiO_4 tetrahedron. In the β structure above 573 °C each tetrahedron is located on a site with site symmetry 222. The three diad axes may be chosen in directions x (parallel to the modulation wave vector and a^*), y, and with z parallel to the screw hexad axis. In the transformation to the α structure, which we must regard as the dominant structure in the incommensurate phase, a quasi-rigid-body rotation about the y axis occurs. Above the β–α transition this gives rise to a soft mode along ζ00. Thus in the transition the diad parallel to the y axis is retained but both the remaining diad axes parallel to x and z are lost.

We now apply the selection rules to establish the full symmetry of the additional components. Since the symmetry at Q must be retained the diad parallel to x must be odd. Opposite character for symmetry elements that take Q into $-Q$ implies that the diad parallel to y must be odd, and that the diad parallel to z must be even. For $Q = 0$ (the Γ point) this symmetry accords with full space group symmetry $P6_2$. In principle, therefore we are permitted to include on this basis translations parallel to z, rotations of the tetrahedra about z and an xy distortion of the tetrahedra (presumably with O–Si–O bending and minimal Si–O stretching). In the model of the incommensurate structure due to Valade (Heine 1988) the rotation about z is singled out and originates as the gradient of the transverse acoustical mode. Note that the related shear combines with the optical mode associated with the β to α rigid-body rotation to give an improper Lifshitz invariant. It is likely that the other contributions, from z translation and xy distortion, are also important in the relaxation processes which generate the incommensurate structure. The two-component structure theory, as outlined above, permits one to establish the nature of all the required eigenvectors that contribute to the incommensurate structure. Current computer simulation studies have provided important data on these eigenvectors (F. S. Tautz, personal communication 1990).

(*b*) *Nepheline*

Nepheline is a complex silicate mineral which shows an interesting incommensurate phase transformation at relatively low temperatures (180 °C). Its incommensurate behaviour has not previously been analysed in detail in spite of the fact that much is already known about its structure. It is of theoretical interest since the incommensurate structure involves interaction between two ordering processes both of which require the loss of threefold axes of symmetry and are thus necessarily described initially in terms of irreducible two-dimensional representations. In the incommensurate coupling interaction both degeneracies are split and a second-order phase transition results. This interaction constitutes a new type of improper Lifshitz invariant.

Nepheline is hexagonal with space group $P6_3$ and has been described as a stuffed derivative of the tridymite structure (SiO_2) with Al replacing Si in tetrahedral sites, and Na and K ions added to balance the electrostatic charge associated with the Al for Si substitution. The formula may be written as $K_x[\ ]_{1-x}Na_3\,Al_{4-x}Si_{4+x}O_{16}$, where x is usually about $\frac{1}{3}$ and the symbol [ ] corresponds to a vacancy on a K site. There are two formula units in the small, high-temperature unit cell. The earliest structural studies on natural nepheline by Hahn & Buerger (1955) showed that the oxygen atom O_1, which should lie on the triad axis in space group $P6_3$, is permanently displaced, and appears in X-ray structural analyses with weight one-third in triad related positions just off the threefold axis. Subsequent structural studies on a number of nephelines by Dollase (1970) and Parker (1972) and studies made at high temperature by Foreman & Peacor (1970) confirmed this interesting feature of the

Table 1. *Representations for the reciprocal vector* $\frac{1}{3}$, $\frac{1}{3}$, 0 *in space groups* $P6_3$, $\omega = \exp(2\pi i/3)$

	$\{E/0\}$	$\{E/t\}$	$\{E/t^2\}$	$\{C_3^+/0\}$	$\{C_3^+/t\}$	$\{C_3^+/t^2\}$	$\{C_3^-/0\}$	$\{C_3^-/t\}$	$C_3^-/t^2\}$
E_1	1	ω	ω^*	1	ω	ω^*	1	ω	ω^*
	1	ω^*	ω	1	ω^*	ω	1	ω^*	ω
E_2	1	ω	ω^*	ω	ω^*	1	ω^*	1	ω
	1	ω^*	ω	ω^*	ω	1	ω	1	ω^*
E_3	1	ω	ω^*	ω^*	1	ω	ω	ω^*	1
	1	ω^*	ω	ω	1	ω^*	ω^*	ω	1
η	2	-1	-1	2	-1	-1	2	-1	-1
ξ	0	-1	1	0	-1	1	0	-1	1

structure. Natural nepheline has a resulting incommensurate structure at low temperature associated with the ordering of the displaced O_1 atoms and shows satellite intensity maxima paired about the points $\pm(\frac{1}{3}, \frac{1}{3}, 0)$ in the hexagonal reciprocal cell at fractional coordinates of approximately ± 0.20 along c^* (McConnell 1962). These O_1 displacement vectors for the oxygen atom O_1 define a basis for a three-dimensional three-state Potts model that is rather closely related to the classical example of the adsorption of He on Grafoil since it requires a threefold increase in the volume of the unit cell on ordering.

It is possible to define the corresponding supercell and space group for O_1 ordering uniquely from the following argument. The vector $\frac{1}{3}$, $\frac{1}{3}$, 0 has threefold symmetry only and we are required to augment the point group symmetry of this vector with translations t and t^2 associated with the tripling of the unit cell volume. The relevant irreducible representations of the vector $\frac{1}{3}$, $\frac{1}{3}$, 0 comprise three two-dimensional representations which conform individually to retention of each of the three triad axes in the small $P6_3$ cell in turn as indicated in table 1. The observed pattern of displacements of O_1 imply that two of the two-dimensional irreducible representations (E_2 and E_3) are irrelevant and we are forced to conclude that the supercell must retain the triad axis at the cell origin. Hence it is inevitable that we describe the simple transformation associated with O_1 ordering in terms of the two-dimensional representation E_1. In describing this ordering it is necessary to write down two real representations which are derived from the appropriate complex conjugate representations as indicated in table 1. These real functions may be used to prepare difference functions which must be used in describing the ordered structure (McConnell & Heine 1984, 1985*a*). Note that the choice of the representation with order parameter η corresponds to normal ordering where complete order is achieved within a supercell with symmetry $P6_3$, and that the second representation ξ relates to a state of partial order only.

So far we have established one of the two possible component structures in the incommensurate structure. The nature of the second component structure was established (McConnell 1981*b*) from heating experiments in which the time–temperature dependence of the loss of incommensurate satellite intensity was monitored. These experiments showed that the disordering of the incommensurate structure had an associated activation energy of 0.84 eV. This was identified with the disordering of vacancies through the migration of potassium ions along the prominent channels in the nepheline structure, thus endorsing previous suggestions that potassium-vacancy ordering had some bearing on the development of the incommensurate structure (Foreman & Peacor 1970). Having established that

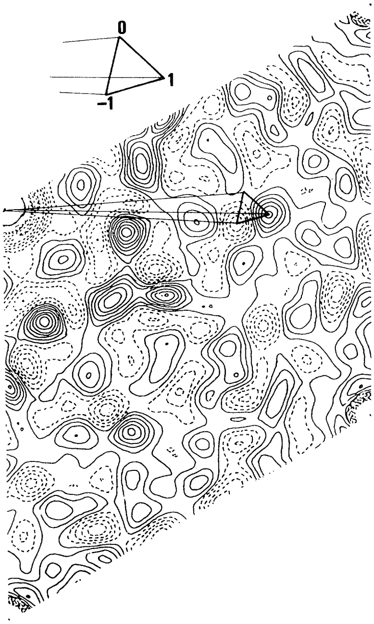

Figure 1. Difference Patterson projection on 0001 within the small $P6_3$ cell showing the vectors, with weights 1, -1 and 0, between the potassium-vacancy modulation and the O_1 displacements about the triad axis.

potassium-vacancy ordering as the second component structure in the modulation it remained to establish its full symmetry. Since there is only one acceptable irreducible representation for the vector $\frac{1}{3}$, $\frac{1}{3}$, 0 it is obvious that we must again use the two-dimensional representation E_1 of table 1 to describe the potassium-vacancy ordering.

Finally we establish the condition for interaction, and the phase relationships between the two ordering events. First we note that it would be possible to combine these two ordering events in phase to generate a simple $P6_3$ supercell with tripled unit cell volume. However, this is clearly not the correct solution. Since the interaction gives rise to an incommensurate structure we may use the gradient invariant concept to establish the necessary selection rules. There are two possibilities, and both necessarily involve the loss of degeneracy. In the first solution the real representation η can be used for the O_1 displacements, and the second real representation ξ, associated with partial order, can be used for the potassium-vacancy component. In the second acceptable solution this assignment is reversed. In either case we envisage that the two components of the modulation must exist in quadrature along the wave vector parallel to the c axis. Data from an experimentally derived difference Patterson function were used to establish the validity of this argument and these have been illustrated in figure 1. In this projection vectors labelled 1, -1 and 0 correspond to the products of difference functions for O_1 displacements and potassium-vacancy ordering and these characters, as described in McConnell & Heine (1985 *a*), are compatible with either of the two solutions deduced above.

This analysis of the nature of the incommensurate structure in nepheline is particularly interesting in that it represents a new type of interaction, illustrates the power of the methods available in component structure theory, and finally, that it illustrates the fact that an incommensurate interaction can be responsible for splitting degeneracies in a Potts model system to yield a second-order transition where the normal possibility relates to first-order transformation behaviour.

4. Incommensurate structure in solid solutions

In §2 dealing with the theory of incommensurate structures it was noted that the degree of rigour possible in the use of the two-component structure theory is dependent particularly on whether or not the system involves simple compounds or complex solid solutions. In the latter case it was noted that the ideal component structures may differ both in symmetry, and in ordering capability, as a function of chemical composition. Two such structural components with differing ordering characteristics may exist within an incommensurate modulation and interact favourably if the gradient invariant concept is also satisfied, i.e. if we can establish the existence of an improper Lifshitz invariant. In the case of mullite, which was used as an example of this phenomenon, the existence of space groups of appropriate symmetry, which order Al and Si in tetrahedral sites and vacancies respectively, leads to an extremely stable structure which orders with a very large reduction in enthalpy which provides a substantial stabilization energy.

Not all of the known incommensurate solid solutions have the simplicity of the mullite example and it is now apparent that real incommensurate solid solutions range from those like mullite to examples where the concept of component structures is less easy to justify. The incommensurate structure of the plagioclase feldspars is of the latter type and we have chosen to discuss it here for two reasons. Firstly the incommensurate behaviour of the plagioclases has been known since the 1950s (Bown & Gay 1958) and there have been numerous attempts, both theoretical and practical, to establish the structure of the incommensurate phase, and the *raison d'etre* of the phenomena. The feldspars are also extremely common rock forming minerals and make up a very large fraction of the Earth's crust.

The plagioclase feldspars comprise triclinic solid solutions with the general formula $Na_xCa_{1-x}Al_{2-x}Si_{2+x}O_8$ with end member structures $NaAlSi_3O_8$ (albite) and $CaAl_2Si_2O_8$ (anorthite). They are framework structures like quartz and nepheline, with Si and Al in tetrahedrally coordinated sites. The ordering of Al and Si dominates the transformation behaviour of the feldspars. It is convenient to illustrate the structure and Al/Si ordering of both feldspar end members by drawing out a section parallel to the $\bar{2}01$ plane, as shown in figure 2, which shows the fourfold rings of tetrahedra that are characteristic of all feldspar structures. The planes of fourfold rings are stacked one above the other with counter rotation of the fourfold rings in such a way that a fully dimensionally linked framework structure results. Since the feldspars are triclinic in structure the incommensurate wave vector is not restricted in orientation and it is known to change its orientation and wavelength continuously as a function of composition between the sodium and calcium ends of this binary system (Bown & Gay 1958). Near the sodium end of the system the wave vector is approximately parallel to the *c* axis, it has a short wavelength and the intensity maxima are always diffuse. At the calcium end of the system the satellite intensity maxima are paired about the position of a simple superlattice, the reduced wave vector Q is approximately parallel to the *b* crystallographic axis and the maxima are extremely sharp defining a wavelength of the order of 60 Å (6 nm). The incommensurate structure itself exsolves into two incommensurate structures in a narrow com-

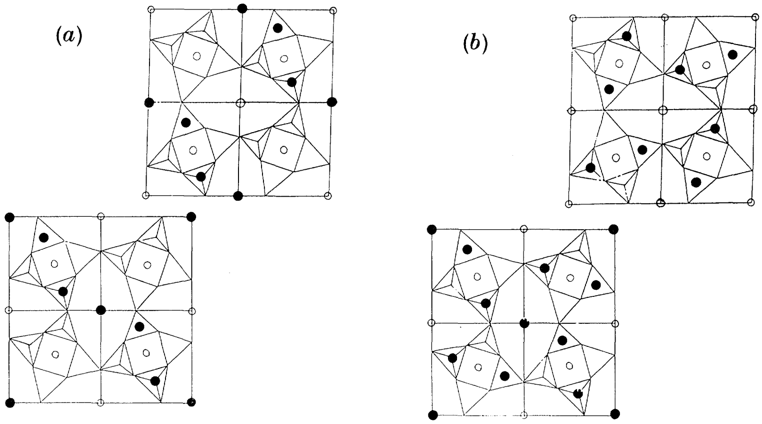

Figure 2. Diagrams illustrating the Si/Al ordering schemes in the end-member structures for (*a*) albite and (*b*) anorthite. In each case the tetrahedra containing Al are shown with black dots. Each diagram shows two adjacent $\bar{2}01$ layers of the structure. In the albite structure such pairs of layers are identical and lattice points occur in both. In the anorthite sequence the ordering pattern renders successive layers inequivalent and this leads to a doubling of the unit cell volume for anorthite.

positional interval in the middle of this binary system and the equilibrium microstructures in this compositional range have a fixed period and produce a very distinctive iridescence or schiller that was first studied seriously by Lord Rayleigh in 1923.

We now attempt an analysis of the origin of incommensurate structure in these materials. We first establish the ordering and transformation behaviour for the system. Here the most important factor to note is that the end member compounds albite and anorthite both have ordered Si/Al distributions but that these are not isostructural. The details are illustrated in figure 2. Since the Al/Si ratio in anorthite is one to one there is effectively only one possible scheme for ordering which requires that each Al containing tetrahedron in the framework is surrounded by four neighbouring tetrahedra containing Si atoms. This ordering scheme results in a doubling of the unit cell volume in anorthite and takes place at temperatures at or near to the melting point at 1500 °C.

Although this scheme is acceptable for ordering in the sodium end member albite with a ratio of Al to Si of one to three, it is not the ordering pattern observed. Ordering in albite takes place in such a way that the cell volume remains the same as for the disordered solid solution, and occurs at a temperature of *ca*. 675 °C. In discussing the ordering schemes for anorthite and albite there is one additional factor which turns out to be of crucial importance. In the energetics of ordering Si and Al in the feldspars it is a long-established principle that the primary contribution to disorder enthalpy derives from the existence of Al neighbours in adjacent tetrahedra. It is also very easy to show that any addition of calcium feldspar to the ordered albite structure (with substitution of Al for Si) inevitably violates this principle. These several facts serve to establish the origin of the incommensurate structure in the plagioclase feldspars since we must consider the ordering behaviour within the solid solution in terms of the two radically different ordering schemes associated with the end-member structures. For compositions close to albite in composition the extra Al atoms are incorporated by creating a local ordering defect that is compatible with the anorthite ordering scheme. This requires that Al be displaced from its normal site in the ordered albite structure, and structural data provide concrete evidence for this effect (Ribbe 1983). Incommensurate wavelength depends on the fact that the defects have a tendency to cluster in planes in an effort to minimize the overall strain energy. A similar analysis may be used to elucidate the nature of the incommensurate structures in binary solid solution members rich in anorthite. Here the predominant structural influence relates to the development of the anorthite ordering scheme. The gradient ploy may be used to demonstrate that Na and Ca ions, and the extra Si atoms, are ordered in quadrature with the primary anorthite ordering scheme (McConnell 1978). Calorimetric data from Carpenter *et al.* (1985) demonstrate that, in this compositional range, and at 65% anorthite, the enthalpy of the incommensurate structure is close to that of a mechanical mixture of the ordered plagioclase end members implying that an extremely high degree of order exists in the incommensurate structure.

This brief review of incommensurate behaviour in solid solutions confirms that this is an extremely important class of behaviour leading to very substantial ordering, and related enthalpy stabilization in solid solutions.

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Discussion

P. W. Anderson (*Princeton, U.S.A.*) Is there not a close relation to the ‘blue phases’ of cholesteric liquid crystals? Here there are two possible directions of twist and they combine to make a lattice of defects, over a small temperature range near the cholesteric–isotropic transition.

J. D. C. McConnell. This seems quite likely but might be difficult to prove.

J. N. Murrell (*University of Sussex, U.K.*). Are there any aspects of the Jahn–Teller effect which enter the formation of incommensurate structures?

J. D. C. McConnell. Yes, we have studied an incommensurate complex copper nitrate phase in which the Jahn–Teller effect forms the basis of its incommensurate behaviour.

J. M. Lynden-Bell (*Cambridge University Chemical Laboratories, U.K.*). In the last example the relevant irreducible representation is two dimensional. Couldn’t there have been a proper Lifschitz invariant and, if so, why wasn’t this important?

J. D. McConnell. The representation E_1 has a third-order invariant and thus leads to first-order transformation which splits the degeneracy. The Lifshitz invariant is not relevant.

A. O. E. Animalu (*University of Nigeria, Nsukka, Nigeria*). Is the transition from commensurate to incommensurate structure always continuous? Professor McConnell’s answer for getting ‘order’ out of ‘chaos’ in natural selection implies that the emergence of a new species that is incommensurate with the old species may be spontaneous (i.e. discontinuous) rather than smooth (i.e. continuous) contrary to what second-order phase transition would predict.

J. D. C. McConnell. All known examples appear to be second order.

B. Coles (*Imperial College, London, U.K.*). A category of incommensurate structures perhaps closer to Professor McConnell's minerals are the long-period stacking fault structures in certain metallic alloys. Even metallic samarium can be treated as nine-layer close-packed structure produced by stacking faults every third layer in the simpler close-packed structures.

J. D. C. McConnell. Where the period is incommensurate this is likely to be true, as in CuAu.