

The Application of the ANNNI Model to Polytypic Behaviour

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Abstract

We show that many of the important features of polytypism are reproduced by a simple spin model, the axial next-nearest-neighbour Ising (ANNNI) model. The phase diagram of the ANNNI model contains sequences of long-wavelength-modulated phases. These correspond to the long stacking sequences developed in polytypic series, and are stabilized by a subtle balance between energy and entropy which results from short-range competing interactions. We discuss the extent to which this mechanism can describe polytypism in the spinelloids, pyroxenes, silicon carbide and other mineral phases.

1. Introduction

In any close-packed structure each layer of atoms may occupy one of three positions, conventionally denoted *A*, *B* and *C*. No two successive layers, however, may occupy the same state. The two most commonly observed stacking sequences are those which result in hexagonal (... *ABAB*...) and cubic (... *ABCABC*...) close-packed structures. In some compounds a large number of other stacking sequences are also observed, many of which have remarkably long periodicities. These phases are known as polytypes. Polytypism is a special form of polymorphism, in which the polymorphs are derived simply by varying the way in which structurally compatible units are arranged. This definition of polytypism, proposed by Thompson (1981), is slightly less demanding than most conventional definitions, which require that the compatible units or modules are structurally and chemically identical. In our analysis of polytypism, we shall not enforce these conditions. However, for structures to be considered truly polymorphic, it is necessary that different stacking arrangements should not affect the chemistry of the phase as a whole.

Examples of stoichiometric, non-metallic materials which exhibit polytypism include the mica minerals, and the classic polytypes with *MX* or *MX*₂

stoichiometry, characterized by SiC, ZnS, CdI₂ and MoS₂. Also included within the wider definition of polytypism, being composed of structurally compatible modules, are a range of minerals which include the pyroxenes, pyroxenoids, perovskites, spinelloids, zoisites, chlorites, sappharine and MnO₂ oxides.

The relative stability of two or more polymorphs is determined by the free energies of the phases considered. Because polytypes are composed of virtually identical modular units, however, it is to be expected that their free energy will differ less than for polymorphs of other kinds. As a consequence, the kinetics of transformations between different polytypes are often sluggish, and it is frequently difficult to establish that the system is in true thermodynamic equilibrium. Theories which have been advanced to explain polytypic behaviour have, therefore, invoked non-equilibrium, kinetically dominated processes [such as dislocation-controlled crystal growth (Frank, 1951)], as well as equilibrium thermodynamic arguments (Jagodzinski, 1954; Smith, Yeomans & Heine, 1984; Price, 1983).

Frank's (1951) theory of polytypism assumes that the crystal initially grows from a screw dislocation in the stacking planes, so that the period of the polytype is determined by the step height of the growth spiral. Using this mechanism, it is possible to generate almost any polytype from shorter-period structures, especially if the theory is modified to include growth resulting from interweaving spirals with different step heights (Trigunayat & Chadha, 1971). However, these mechanisms are not universally applicable, as many examples of long-period polytypes show no evidence of growth spirals. Moreover, the theory is unable to predict which polytypes will occur.

In contrast, equilibrium theories assume that polytypes may exist as thermodynamically stable phases, the structure adopted being determined by external conditions. It is, however, difficult to test such a theory because the polytypic structures obtained are often found to depend strongly upon impurity concentrations, thus obscuring any correlation of structure with

more easily controlled variables such as temperature and pressure. In addition, since transformations between polytypes may be extremely slow, metastable phases or assemblages may persist even on the geological time scales. Recently, however, a number of reversible transformations between shorter-period SiC polytypes have been observed (Jepps & Page, 1983), providing strong evidence that at least these phases are equilibrium structures.

An early equilibrium theory of polytypism was developed by Jagodzinski (1954), who argued that long-period polytypes are stabilized by their vibrational entropy. However, it has now been shown (Weltner, 1969) that the vibrational entropy differences between polytypes are too small to contribute significantly towards their stabilization. Another approach to developing an equilibrium theory was adopted by Hazen & Finger (1981) and by Price (1983). These workers explained the stability of polytypes in terms of the energy of interaction between component polytypic units. In this paper, we also adopt the approach of using the energy of interaction between units to model polytypic behaviour, but, in contrast to previous work, we do so by considering the statistical mechanical ANNNI or axial next-nearest-neighbour Ising model. This model was originally studied in the context of magnetic phase transitions (Elliott, 1961), and was first applied to polytypic problems by Smith *et al.* (1984). The model not only predicts the large number of equilibrium structures characteristic of polytypic behaviour, but also reproduces their very-long-range periodicities.

In § 2, we describe in greater detail the structures of the spinelloid polytypic family. The ANNNI model and its phase diagram are discussed in §§ 3 and 4. We then illustrate the relevance of the model to polytypic behaviour (§ 5), and finally we present a brief discussion of the advantages and shortcomings of the ANNNI model as a description of polytypism (§ 6).

2. The structure of spinelloid polytypes

The spinelloid structural family was first recognized by Horiuchi, Horioka & Morimoto (1980), and was named after the common member of the family, the spinel structure. Spinelloids are based upon an approximately cubic close-packed O framework, and have an ideal stoichiometry of AB_2O_4 . Two-thirds of the cations occupy octahedrally coordinated sites within the O framework, while the remaining one-third are tetrahedrally coordinated. The cations define a 'basic structural unit' (Horiuchi, Akaogi & Sawamoto, 1982) within the O framework, as shown in Fig. 1(a). All spinelloid structures can be constructed from this unit. In the vast majority of spinelloids, the arrangement of the basic structural units is invariant in two orthogonal directions, and generates an infinite sheet, part of which is shown in Fig. 1(b).

It is the variation in the packing of these sheets in the third dimension which gives rise to the observed range of spinelloid structures, the details of which will be described below.

The spinel structure may be viewed as having the component spinelloid sheets, shown in Fig. 1(b), packed normal to [110]. Adjacent sheets are related by a glide operator, having a displacement $\frac{1}{4}[1\bar{1}2]$ on (110), which when regularly repeated generates the structure shown in Fig. 1(c) (Price, 1983; Hyde, White, O'Keeffe & Johnson, 1982). This operation produces a sequence of basic structural units along [110], in which adjacent units are inverted relative to one another. If the basic structural unit shown in Fig. 1(a) is represented by the arrow illustrated, then the stacking sequence along [110] can be described by the code $\dots\uparrow\downarrow\uparrow\downarrow\dots$ (Horiuchi *et al.*, 1982). In addition to being interrelated by a glide operator, spinelloid sheets may also be related by a mirror or twin operation. This operation gives rise to adjacent structural units with the same orientation, and is found, for example, in the idealized β -phase polymorph of $(Mg,Fe)_2SiO_4$, wadsleyite (Fig. 1d). This structure can be represented by the stacking code $\dots\uparrow\uparrow\downarrow\downarrow\dots$, where the component sheets are alternately related by mirror and glide operations.

There are naturally an infinite number of possible stacking sequences which can be generated by combining mirror and glide operators. However, only six of the possible sequences have been reported as forming crystal structures. These six structures are the spinel and β -phase described above, the manganostibite structure ($\dots\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow\dots$) and three structures found only in the Ni_2SiO_4 - $NiAl_2O_4$ system (Ma, 1974; Akaogi, Akimoto, Horioka, Takahashi &

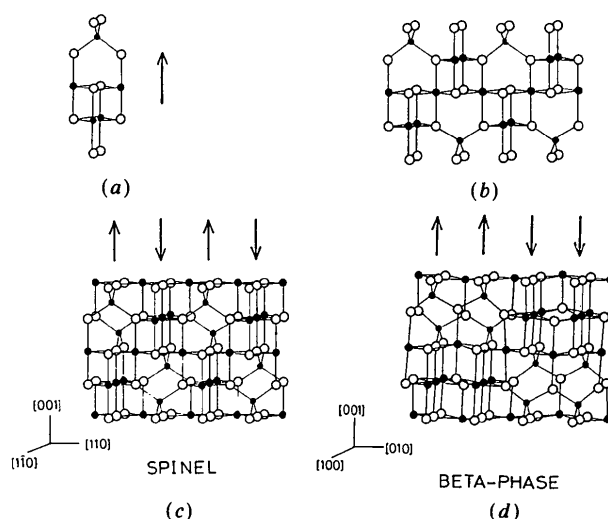


Fig. 1. Perspective views of (a) the 'basic structural unit' of spinelloids, after Horiuchi *et al.* (1982), (b) the constituent sheet from which spinelloid structures can be constructed, (c) the spinel structure, (d) the β -phase structure.

Horiuchi, 1982) with stacking formulae $\dots \uparrow \downarrow \dots$, $\dots \uparrow \uparrow \downarrow \dots$ and $\dots \uparrow \downarrow \downarrow \uparrow \downarrow \dots$. It should be noted, however, that recent high-resolution transmission electron microscopy studies (Davies & Akaogi, 1983) have shown that considerable stacking disorder can occur in these nickel aluminosilicate spinelloids. Previous workers (Hazen & Finger, 1981; Price, 1983) have attempted to explain why these six spinelloid structures should be more favoured than other possible spinelloid polytypes by considering the possible strain interaction between component spinelloid sheets or modules. In this paper, we present an analysis of both the observed spinelloid structures, and the development of polytypism in general, in terms of the ANNNI model, in which short-range competing interactions stabilize long-wavelength phases.

3. The ANNNI model

We have seen in § 2 that spinelloids may be built up from a basic structural unit which may be one of two states, conveniently labelled \uparrow and \downarrow . We now describe how to use this idea to map the spinelloid structures onto an effective magnetic system, which can be studied using standard techniques of statistical mechanics (Landau & Lifshitz, 1958).

(i) Each structural unit is associated with a lattice site. The resulting lattice is cubic.

(ii) The orientation of the unit on each site is then represented by an Ising spin variable, $s_i = +1$ or -1 , corresponding to \uparrow or \downarrow respectively.

(iii) The interactions between the structural units can be represented by a Hamiltonian which defines the interaction between the spins. First consider layers perpendicular to the [010] direction in the β -phase structure (Fig. 1d). The ground state of each of these layers is metamagnetic, that is ferromagnetic along [001] and antiferromagnetic along [100]. This can be described by a term in the Hamiltonian

$$H_0 = -J_0 \sum_{nn}^{[001]} s_i s_j + J'_0 \sum_{nn}^{[100]} s_i s_j, \quad (1)$$

where the interaction parameters $J_0, J'_0 > 0$, and \sum_{nn} denotes a sum over nearest-neighbour sites in the direction specified. As the temperature is raised the layers may deviate from their metamagnetic ground state by the flipping of the spins, s_i . The probability that a spin will flip is determined by $\exp(-2J_0/k_B T)$, where k_B is Boltzmann's constant and T is the temperature. In spinelloid polytypes we expect very few spins to deviate from the metamagnetic ground state of the layers, and we may therefore consider $J_0 \gg k_B T$.

(iv) We now turn our attention to the interaction between layers, along the stacking direction. Consider first a nearest-neighbour interaction

$$H_1 = -J_1 \sum_{nn}^{[010]} s_i s_j, \quad (2)$$

Note that, at $T=0$, $2J_1$ is the difference in energy between a ferromagnetic ($\uparrow\uparrow$) and an antiferromagnetic ($\uparrow\downarrow$) alignment of two neighbouring spins. Both configurations occur frequently in the observed spinelloids, suggesting that J_1 is small. Therefore, a second-neighbour interaction in the stacking direction is likely to be relatively important, and should be included in the Hamiltonian:

$$H_2 = -J_2 \sum_{nnn}^{[010]} s_i s_j, \quad (3)$$

The arguments just presented suggest that the stacking sequences observed in the spinelloids can be modelled by a Hamiltonian

$$H = H_0 + H_1 + H_2 = -J_0 \sum_{nn}^{[001]} s_i s_j + J'_0 \sum_{nn}^{[100]} s_i s_j - J_1 \sum_{nn}^{[010]} s_i s_j - J_2 \sum_{nnn}^{[010]} s_i s_j, \quad (4)$$

This model, the so-called axial next-nearest-neighbour Ising or ANNNI model (Elliott, 1961), has recently received a lot of attention from statistical mechanicians (for a review see Bak, 1982). Its phase diagram, as a function of J_1, J_2 and T , is well established, and was obtained using sophisticated mean-field theory (Bak & von Boehm, 1980) and low-temperature series techniques (Fisher & Selke, 1980, 1981). The resulting phase diagram does indeed include many different, long-wavelength phases or, for our purposes, polytypes. Our next aim is to describe this phase diagram, and then to compare the stable phases to the stacking sequences observed in the spinelloids.

4. The ANNNI-model phase diagram

It is first convenient to introduce a notation which will facilitate the description of the states appearing in the ANNNI-model phase diagram (Fisher & Selke, 1980, 1981). As the ordering within the layers is invariant, we need only consider ordering in the stacking direction. In this direction a typical phase will comprise a repeating sequence of up and down spins, for example,

$$\dots \uparrow \downarrow \downarrow \uparrow \uparrow \downarrow \downarrow \downarrow \uparrow \downarrow \downarrow \uparrow \downarrow \downarrow \dots \quad (5)$$

Consecutive spins of the same sign will be termed bands. The repeating sequence in (5) comprises three bands of two spins or 2-bands, followed by one 3-band. This will be denoted $\langle 222 \rangle$ or $\langle 2^3 \rangle$. Other examples include the $\langle 12^2 \rangle$ sequence $\dots \uparrow \downarrow \uparrow \uparrow \downarrow \uparrow \downarrow \dots$, and the sequence $\dots \uparrow \downarrow \downarrow \uparrow \downarrow \downarrow \dots$ denoted by $\langle 13 \rangle$. More generally, $\langle n_1 n_2 \dots n_m \rangle$ will refer to a state where the repeating sequence is made up of m bands of length $n_1, n_2 \dots n_m$. This notation is analogous to the Zhdanov notation used in the description of polytypic materials.

Consider first the ground-state ($T=0$) phase diagram of the ANNNI model, which is shown in Fig. 2. For $J_2 > 0$ (ferromagnetic second-neighbour bonds) the ground state is ferromagnetic ($\dots \uparrow\uparrow\uparrow\uparrow \dots$ or $\langle \infty \rangle$) for $J_1 > 0$ and antiferromagnetic ($\dots \uparrow\downarrow\uparrow\downarrow \dots$ or $\langle 1 \rangle$) for $J_1 < 0$. Note that in both these cases first- and second-neighbour bonds are satisfied (that is in their lowest-energy configuration). However, for $J_2 < 0$ this is no longer the case, and there is competition between the ordering favoured by first- and second-neighbour bonds. For $|J_1|$ large, the first neighbours dominate and the $\langle \infty \rangle$ and $\langle 1 \rangle$ states are stable as before. However, for $|J_1|$ small, the ordering favoured by the second-neighbour bonds, namely $\dots \uparrow\uparrow\downarrow\downarrow\uparrow\uparrow \dots$ or $\langle 2 \rangle$, provides the ground state. On the boundary between $\langle 2 \rangle$ and $\langle \infty \rangle$, at $J_1 = -2J_2$, the ground state is highly degenerate, as all phases which contain no 1-bands have the same energy. The boundary between $\langle 1 \rangle$ and $\langle 2 \rangle$ at $J_1 = 2J_2$ is a similar, multiphase line, on which all phases containing only 1- and 2-bands have the same energy. Note, however, that the boundary between $\langle 1 \rangle$ and $\langle \infty \rangle$ is not a multiphase line, as here only the phases $\langle 1 \rangle$ and $\langle \infty \rangle$ coexist.

Next let us consider the changes in the ground-state phase diagram as the temperature is increased from zero. We expect the picture to remain similar to that at $T=0$, except in the vicinity of the multiphase lines, where it is necessary to ask which of the degenerate, zero-temperature phases persist to finite temperatures. This question is answered in Fig. 3, which shows a schematic representation of the phase diagram of the ANNNI model for a fixed $0 < k_B T \ll J_0$ (Fisher & Selke, 1980, 1981). In the vicinity of the multiphase lines, infinite sequences of phases ($2^{n-1}3$) and $\langle 12^n \rangle$, $n = 1, 2, 3, \dots$, are stable. The way in which these phases spring from the multiphase line as the temperature is increased is illustrated in Fig. 4. All the phase boundaries are first order. The width of successive phases is proportional to $\exp(-8J_0 n / k_B T)$, and hence the phase sequences would very quickly become impossible to resolve experimentally. As the temperature is increased

further phases appear (Bak & von Boehm, 1980; Duxbury & Selke, 1983), but at these temperatures the layers are significantly disordered.

We have described how short-range competing interactions are sufficient to stabilize long-wavelength spin structures. For a given value of the interaction parameters and temperature, the stable phase corresponds to the phase of minimum free energy. Because of the competing interactions the energetic contribution to the free energy is very similar for an infinite number of different phases. Hence in the ANNNI model it is entropic factors that are important in determining the stability of a given phase.

5. A model for polytypic behaviour

It is now possible to interpret the behaviour of polytypic materials in terms of the ANNNI model. We can identify each phase in the ANNNI model with a polytypic structure, by equating the symbols introduced above to describe the sequence of spin bands to the sequence of structural units or operators in the polytype (*cf.* Zhdanov notation). For example, the spinel structure will be denoted by $\langle 1 \rangle$, the β -phase structure by $\langle 2 \rangle$, the manganostibite structure by $\langle 3 \rangle$, and so forth. The energy of interaction between basic structural units is then represented by the spin interactions, J_0 , J_1 and J_2 . For given J_1 , J_2 and $k_B T / J_0$, the stable polytype will correspond to the spin phase with minimum free energy, and can be determined from

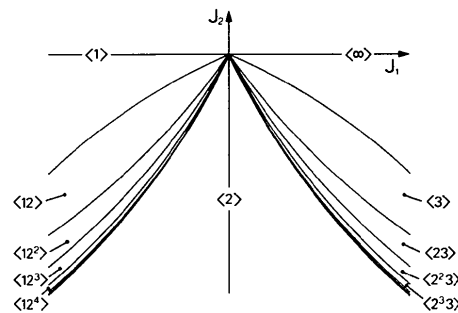


Fig. 3. Schematic phase diagram of the ANNNI model at a fixed temperature, $k_B T \ll J_0$.

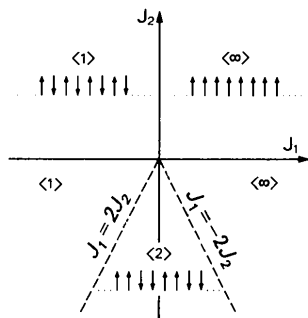


Fig. 2. The ground state of the ANNNI model. The dashed lines are multiphase lines.

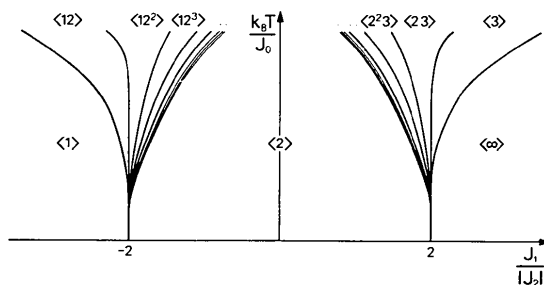


Fig. 4. Schematic phase diagram of the ANNNI model as a function of temperature ($k_B T / J_0 \ll 1$) and $J_1 / |J_2|$.

the ANNNI-model phase diagrams shown in Figs. 3 and 4. Transformations between polytypes occur because the effective interaction energies J_1 and J_2 vary as a function of pressure, temperature and chemical environment. As the conditions to which the polytype is subjected vary, the point defined by the coordinates J_1 , J_2 and $k_B T/J_0$ may describe a trajectory which passes through many different phases. The exact form and extent of this path, and hence the sequence of stable phases, will critically depend on the exact relationship between J_1 , J_2 and the external conditions. By using this approach many complex aspects of polytypic behaviour can be explained.

The phase relationships between spinelloid polytypes in the Ni_2SiO_4 – NiAl_2O_4 system have been studied in detail by Akaogi *et al.* (1982). They found that compositions close to $\text{Ni}_3\text{Al}_2\text{SiO}_8$ can adopt one of three spinelloid structures. At pressures, P , less than 5 GPa a spinelloid with the β -phase, $\langle 2 \rangle$, structure is encountered. However, with $5 < P < 7$ GPa, a spinelloid with the $\langle 122 \rangle$ structure is stable, while with $P > 7$ GPa the $\langle 12 \rangle$ structure is adopted. These transformations are virtually independent of temperature, and are reported to be first order in nature. This sequence of transformations can be accounted for by considering that variations in J_1 and J_2 , as a function of increasing pressure, define a trajectory on the phase diagram shown in Fig. 3, which starts in the $\langle 2 \rangle$ phase and moves to the $\langle 12 \rangle$ phase, passing through the $\langle 122 \rangle$ phase. The failure to observe any longer-period structures (e.g. $\langle 12^3 \rangle$) in this series of transformations may be accounted for by the very small region of stability predicted for these long-period phases.

As well as the pressure dependence exhibited by the $\text{Ni}_3\text{Al}_2\text{SiO}_8$ spinelloid polytypes, it is also found that the structures adopted by spinelloids in the Ni_2SiO_4 – NiAl_2O_4 system as a whole are highly composition dependent. At pressures greater than about 4 GPa, the spinel structure, $\langle 1 \rangle$, is adopted by the two end members, while the manganostibite structure, $\langle 3 \rangle$, is developed by $2\text{Ni}_2\text{SiO}_4:3\text{NiAl}_2\text{O}_4$, and the $\langle 13 \rangle$ structure is formed by $\text{Ni}_2\text{SiO}_4:3\text{NiAl}_2\text{O}_4$. This variation in spinelloid stability reflects the dependence of J_1 and J_2 upon the bulk composition of the phase (Price, 1983), and results in spinelloids with differing compositions corresponding to different stable phases of the ANNNI model (Fig. 3). It should be noted, however, that a $\langle 13 \rangle$ polytypic structure does not occur in the ANNNI phase diagram. Previous attempts to rationalize the stability of spinelloid polytypes (Hazen & Finger, 1981; Price, 1983) have also failed satisfactorily to explain why the $\langle 13 \rangle$ structure should be adopted. If the $\langle 13 \rangle$ phase is indeed thermodynamically stable, we must conclude that the approximations inherent in the ANNNI model do not take full account of all the factors which determine polytype stability. The limitations of the ANNNI model will

be discussed in § 6. However, we first illustrate how it can be successfully applied to a variety of other polytypic materials.

The pyroxene MgSiO_3 occurs as one of three polymorphic structures, known as the minerals clinoenstatite, orthoenstatite and protoenstatite. These three phases can be considered as polytypes (Iijima & Buseck, 1975), with packing sequences $\langle \infty \rangle$, $\langle 2 \rangle$ and $\langle 1 \rangle$ respectively. In this system, the role of temperature appears to be most important in determining the relative magnitudes of J_1 and J_2 . At temperatures above 1253 K, protoenstatite is the stable phase, but on cooling it is thought to convert first to orthoenstatite, $\langle 2 \rangle$, and then below 923 K to clinoenstatite (Deer, Howie & Zussman, 1978). The mechanism and kinetics of this inversion, however, make it difficult to define transformation temperatures exactly. The inferred sequence of polytypic phase transformations, $\langle 1 \rangle$ – $\langle 2 \rangle$ – $\langle \infty \rangle$, is compatible with a simple trajectory in the J_1 , J_2 space of Figs. 3 and 4 for $J_2 < 0$. No intermediate phases (e.g. $\langle 12 \rangle$ or $\langle 3 \rangle$) have been found in this system although high-resolution transmission electron microscopy (see, for example, Iijima & Buseck, 1975) has revealed that considerable stacking disorder is developed in some partially inverted enstatites.

Wollastonite (CaSiO_3) is another well known mineral, which exhibits two major polytypic variations, with stacking sequences describable by $\langle \infty \rangle$ and $\langle 2 \rangle$. Recent observations by Henmi, Kawahara, Henmi, Kusachi & Takeuchi (1983) indicate that at high temperatures the $\langle 2 \rangle$ polytype may be stabilized relative to the $\langle \infty \rangle$ structure. In a temperature range intermediate between those dominated by the $\langle 2 \rangle$ and the $\langle \infty \rangle$ phases, they reported the occurrence of minor amounts of polytypes with $\langle 3 \rangle$, $\langle 4 \rangle$ and $\langle 5 \rangle$ structures. Within the ANNNI picture, the $\langle 3 \rangle$ phase is stable, while the $\langle 4 \rangle$ and $\langle 5 \rangle$ phases can be expected to appear as metastable phases. This point is discussed further in § 6.

In addition to the mineral polytypic behaviour described above, the ANNNI model can successfully explain the wurtzite, $\langle 1 \rangle$, to zinc-blende, $\langle \infty \rangle$, transformations which occur in the classic ZnS and AgI polytypes, transformations between hexagonal perovskite polytypes, and all the recently observed reversible transformations in the SiC system (Smith *et al.*, 1984). Jepps & Page (1983) have reported three sets of reversible SiC transformations (all determined under slightly different physical or chemical conditions) which correspond to $\langle 1 \rangle$ – $\langle \infty \rangle$, $\langle \infty \rangle$ – $\langle 3 \rangle$ and $\langle 3 \rangle$ – $\langle 2 \rangle$. The occurrence of these SiC polytypic inversions is particularly striking given the topological distribution of these phases on the ANNNI phase diagram (Fig. 3). It is also interesting to note that the large majority of stable polytypes observed in SiC are comprised of 2- and 3-bands (Trigunayat & Chadha, 1971), suggesting a ferromagnetic first-neighbour

interaction in SiC. For CdI₂, however, 1- and 2-bands predominate, indicating that the effective J_1 is antiferromagnetic. An exact correspondence between the phases of the ANNNI model and the classical polytypes is not, however, observed. Indeed it can hardly be expected, both because of problems of metastability and because the ANNNI model is unlikely to reproduce correctly all of the symmetries or elementary excitations of close-packed and other polytypic compounds.

6. Discussion

In this paper we propose a model of polytypism, in which the basic polytypic structural units are mapped onto magnetic spin variables. The interactions between the units are then written in terms of a Hamiltonian with competing interactions. This provides a simple equilibrium mechanism by which short-range couplings can lead to the existence of polytypes with very long stacking sequences. Many of the other important features of polytypism are also explained by this model; notably that only a specific set of polytypes are stable for any given compound, that reversible phase transitions are observed and that polytypes with short stacking sequences occur most frequently.

Many phases, for example $\langle 4 \rangle$, $\langle 5 \rangle$, $\langle 233 \rangle$, which are observed in polytypic compounds do not appear in the phase diagram of the ANNNI model shown in Figs. 3 and 4. The ANNNI model does lock in to many more phases at higher temperatures (Bak & von Boehm, 1980), but at such temperatures the layers are significantly thermally disordered, a state unlikely to be found in real compounds. However, within the ANNNI picture we should expect many complicated phases to appear in nature as metastable states. To see this consider Fig. 5, where the free energies of the phases $\langle 2 \rangle$, $\langle 23 \rangle$, $\langle 3 \rangle$, $\langle 4 \rangle$, $\langle 5 \rangle$ and $\langle \infty \rangle$ are plotted

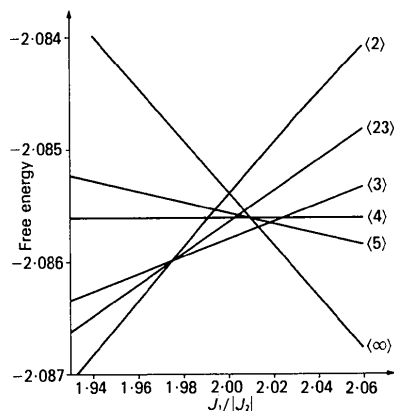


Fig. 5. Free energy (in units of J_0) of the shorter-wavelength phases near the multiphase point $J_1/|J_2| = 2.0$. The results were obtained for $k_B T/J_0 = 2.0$, $J_1/J_0 = 0.1$, using a mean-field approximation.

as a function of $J_1/|J_2|$, near the $\langle 2 \rangle : \langle \infty \rangle$ boundary. These results were obtained using a mean-field approximation (Bak & von Boehm, 1980) for $J_0 = J'_0$, $k_B T/J_0 = 2.0$ and $J_1/J_0 = 0.1$. Note that the free energies of the different phases differ only by the order of 1 part in 10^4 , for $J_1/|J_2| = 2.0$. A similar result holds, near the $\langle 2 \rangle : \langle \infty \rangle$ boundary, for all phases which contain no 1-bands, and near the $\langle 1 \rangle : \langle 2 \rangle$ boundary for all phases which comprise only 1- and 2-bands. Hence once such phases are formed, perhaps during rapid growth at high temperatures, decay to the stable phase in this vicinity will be extremely slow.

We should note, however, that the development of the $\langle 13 \rangle$ phase of the spinelloids remains a mystery, as its free energy is not close to any of the ANNNI phases. However, we should hardly expect the ANNNI model to predict all equilibrium structures, since absolute accuracy cannot be expected from such an idealized model, which ignores longer-range forces and the effect of detailed structural features, such as cation disorder (Akaogi & Navrotsky, 1984), upon polytype stability. In particular, in the close-packed compounds a more realistic picture is expected if the three atomic positions, A , B and C , are mapped onto a three-state model, the Potts model with competing interactions. This model has more realistic spin flips, and preserves more of the symmetries of the original system. Its phase diagram is currently under investigation. The Potts-model approach is also likely to be applicable in analysing polytypism in micas, where successive sheets can be related by more than two possible stacking vectors (Thompson, 1981).

It should also be noted that although we have limited our application of the ANNNI model to polytypic systems, preliminary studies indicate that it can be used satisfactorily to explain the structures exhibited by polysomatic materials (Thompson, 1978). These materials correspond to families of structures which can be obtained by stacking in varying proportions two or more chemically distinct units, and thus represent a more general form of the problem addressed in this paper. Examples of such polysomatic phases include the biopyroboles (Thompson, 1978), the $\text{CeFeCO}_3\text{-CaCO}_3$ minerals (Zen, 1967), and the leucophoenicite-humite family of minerals (White & Hyde, 1983) which adopt $\langle 1 \rangle$, $\langle 12^n \rangle$, $\langle 2 \rangle$, $\langle 2^n 3 \rangle$ and $\langle 3 \rangle$ structures.

In this paper we have not attempted to calculate the magnitude of the interaction parameters which appear in the magnetic Hamiltonian. It is clear that they correspond to the small differences in phonon, strain and electronic free energies of different stacking sequences. A first-principles calculation would be extremely difficult. It may, however, be possible to understand the way in which these parameters vary with temperature and pressure hence driving the compound through its different stable phases, by using lattice simulation techniques (Catlow, Thomas,

Parker & Jefferson, 1982; Price & Parker, 1984). Such an investigation is in progress.

We should like to encourage experimentalists to test the ideas presented in this paper by obtaining more experimental results on the phase diagrams of polytypic compounds as a function of temperature and pressure. Data are at present scarce due to the difficulties imposed by the inevitable presence of defects which are known to affect strongly the stability of polytypic phases.

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Use of Dynamical Scattering in the Structure Determination of a Minute Fluorocarbonate Mineral Cebaite $\text{Ba}_3\text{Ce}_2(\text{CO}_3)_5\text{F}_2$ by High-Resolution Electron Microscopy

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Abstract

A method for determining the crystal structure using the dynamical extinction effect in the electron diffraction appearing in high-resolution electron micrographs is proposed for the mineral cebaite $\text{Ba}_3\text{Ce}_2(\text{CO}_3)_5\text{F}_2$ whose heavy-atom positions have not previously been determined but only estimated. The specimen is thicker than the maximum thickness

for which the weak-phase-object approximation is applicable, so that the extinction effect becomes predominant and the image contrast of light atoms is enhanced. Using electron micrographs of huanghoite $\text{BaCe}(\text{CO}_3)_2\text{F}$, whose atomic structure is known and related to that of cebaite, the optimum thickness and imaging condition, which can reveal the image of light atoms as well as heavy atoms, are investigated. The optimum thickness is found to be 45 to 50 Å