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The Energetics of Polytypic Structures: Further Applications of the ANNNI Model

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Abstract

The stability of long-period polytype stacking sequences can be shown to be dependent upon the energy contribution from interactions between the constituent modules (layers). Previous work has concentrated upon interactions between nearest and next-nearest (*i.e.* first and second) neighbour layers. It is shown that in some polytype systems, such as wollastonite, the equivalence of certain pairs of stacking sequences places constraints upon the allowed interactions between the modules. A mapping between these polytypic systems and a simple spin model, the Axial Next-Nearest-Neighbour Ising (ANNNI) model is developed in order to derive a theoretical phase diagram for these polytypes. The predictions of this phase diagram regarding the relative stability of polytype stacking sequences are shown to compare favourably with observations reported for natural mineral systems.

1. Introduction

Many crystal structures can be grouped into structural families based upon the stacking together of a number of structurally compatible modules. The classical polytypes are one type of such a family. As strictly defined, all modules (layers) are identical in chemical

composition and atomic positions, the various polytype structures differing only in the stacking sequence of the layers. However, Thompson (1981) has pointed out that, due to the stacking sequence itself, the layers in a particular polytype need not be crystallographically equivalent, so that the condition of strict structural and chemical equivalence might be relaxed in a practical definition of polytypism. Thompson therefore proposed that the term 'polytypism' should be used to describe the family of structural variants generated by changes in the stacking sequence of structurally compatible units, provided the overall chemistry remains unchanged. This definition of polytypism allows the internal structure of the modules to undergo small amounts of distortion so as to accommodate small stresses imposed on the module by the neighbouring modules in a stacking sequence.

The theories developed to explain the observed variety of stacking sequences in a given polytypic system may be grouped into two types. The kinetic theories suggest that growth mechanisms play a predominant role in generating polytypes, an early example being the spiral growth mechanism of Frank (1951). Although these may successfully explain the appearance of many polytype stacking sequences, they contribute nothing to our understanding of the relative stability of polytypically related structures, while the characterization of several reversible phase transformations between polytypes of SiC (Jepps & Page, 1983) suggests that polytypism is, at least partially, an equilibrium phenomenon. It was initially

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proposed that long-period stacking sequences are stabilized by vibrational entropy (Jagodzinski, 1954), but Weltner (1969) demonstrated that the contribution to the free energy from such effects alone was insufficient to stabilize polytypic structures. More recently it has been demonstrated (Smith, Yeomans & Heine, 1984; Price, 1983; Price & Yeomans, 1984; Price, Parker & Yeomans, 1985) that the relative stabilities of various polytype stacking sequences may be understood in terms of interactions between the component structure modules. These interactions may be equated with the energy differences brought about by the small distortions experienced by a module with the idealized structure when it is inserted into a given stacking sequence. It has been found that the stability of long-period polytypes is dependent upon the interactions not only between adjacent modules, but also between pairs of modules separated by greater distances. The competition between these interactions leads to entropic effects which then stabilize the longer periodicities.

Price (1983) attempted to explain the stability of the spinelloid polytypes in terms of the interactions between first, second, and third neighbour modules. He found that the majority of the phases observed experimentally appeared in the ground state of his model, that is at zero temperature, but he was unable to quantify the behaviour of such a model at elevated temperatures when entropic effects may stabilize further stacking sequences. A suitable interaction model had, however, already been developed by statistical mechanicians (e.g. Elliot, 1961; Bak, 1982) to describe ordering in magnetic systems. This 'Axial Next-Nearest-Neighbour Ising' (ANNNI) model involves only the interactions between first and second neighbour spins, but its phase diagram has been calculated for non-zero temperatures. Smith, Yeomans & Heine (1984) and Price & Yeomans (1984) showed that several polytypic systems could be modelled by the mapping of structure modules onto the magnetic spins of the ANNNI model. The resulting phase diagram successfully predicts the observed stabilities of polytypes in several mineral systems.

However, the model employed by Price & Yeomans (1984) turns out not to be directly applicable to polytypism in a certain class of structures. Their work was concerned primarily with predicting phase stability in the spinelloids. These are all derived by the stacking together of layers which have the spinel structure in one of two orientations. The resultant structures may then be described in terms of the orientations of the component layers, either up or down, which may then be mapped directly onto the magnetic spins of the ANNNI model. Price & Yeomans (1984) also attempted to explain the observed stable stacking sequences in other polytypic mineral systems with some success except in the case of wollastonite. The

reason for this is that polytype systems such as wollastonite differ in a fundamental way from such structures as the spinelloids. In the latter consecutive layers in either an up, \uparrow , or down, \downarrow , orientation are related by one of two stacking operators. Price (1983) called these T , which relates consecutive layers in the same orientation, $\uparrow\uparrow$ or $\downarrow\downarrow$, and S which relates two layers with opposite orientations, $\uparrow\downarrow$ or $\downarrow\uparrow$. The two structures generated by the stacking sequences $TTTT\dots$ ($=\uparrow\uparrow\uparrow\uparrow\uparrow$ or $\downarrow\downarrow\downarrow\downarrow\downarrow$) and $SSSSS$ ($=\uparrow\downarrow\uparrow\downarrow\uparrow$) are different. In many polytype systems there are also two stacking operators which, however, do not change the orientation of the layers, but do change their relative positions. These two operators are commonly referred to as T (=translate) and G (=glide). The T operator places the next layer in a position continuous with the preceding layer, while G introduces a glide or shear between two successive layers. Two classes of polytypic systems may then be distinguished upon the basis of their energetics.

In the first class of polytypes are those systems in which, like the magnetic spin systems, the structures generated by the stacking sequences $TTTT\dots$ and $GGGG\dots$ are different. The relationship between two of the polymorphs of $MgSiO_3$, clino- and protoenstatite falls into this category; clinoenstatite being the $TTTT\dots$ polytype, and protoenstatite the $GGGG\dots$ polytype. The energetics of such polytypic systems may be described by a direct mapping onto the ANNNI model as shown by Price & Yeomans (1984). In this paper we examine the energetics of the second class of polytypic systems, in which the internal symmetry of the layers forming the polytype is sufficient to make the two structures created by the stacking sequences $TTTT\dots$ and $GGGG\dots$ identical. Such systems include the polytypes of wollastonite, and the zoisite structures. In both cases the structure described by $TTTT\dots$ is the twin of the $GGGG\dots$ structure. These two sequences therefore represent structures which have the same energies, and as a consequence the interaction parameters between the 1st, 3rd, 5th \dots neighbour layers may be shown to be identically zero. The stability of such polytypes must therefore be modelled in terms of interactions between 2nd, 4th, 6th \dots neighbour layers. This requires a mapping of the polytype structures onto the ANNNI model which differs from that developed by Price & Yeomans (1984).

In this paper we shall develop an interaction model for this class of polytypes and deduce its relationship to the ANNNI model. For convenience this model will be termed the 'wollastonite model', although we shall show that it is applicable to many other polytypic systems. A phase diagram is then constructed for the wollastonite model in terms of the interactions between the polytype layers by mapping it onto the ANNNI model. The predictions of this phase diagram regarding the relative stabilities of polytype stacking

sequences are then compared with the sequences observed in natural mineral systems.

2. The wollastonite interaction model

The internal energy of a polytype is considered to comprise two components: the internal energy of the modules (layers) which is considered to remain constant and independent of the stacking sequence, and a contribution from the interactions between the modules. These long-range interactions arise from small adjustments to the internal structure of the modules imposed by the neighbouring modules in the stacking sequence. The contribution to the total internal energy of a stacking sequence of these interactions is therefore expected to be small. In their calculations of the energies of the spinelloids Price, Parker & Yeomans (1985) found that the interactions contributed of the order of 0.1% of the overall internal energy. Nevertheless these interactions do appear to play a major role in determining the differences in free energy between polytypes, and hence their relative stabilities.

The ANNNI model was developed in order to try to gain an insight into the factors which determine ordering in magnetic systems where long-period modulations develop based upon ordered layers of spins. In the ANNNI model a magnetic spin is associated with each point of a three-dimensional lattice, and interaction parameters are defined for neighbouring pairs of spins. These are chosen so as to keep the spins in two lattice directions ordered at low temperatures, while in a third direction orthogonal to these two a second parameter is introduced to describe the interaction between next-nearest-neighbour spins. Such a choice of coupling parameters results in a structure consisting of internally ordered layers of spins, but with the possibility of various spin sequences along the third axis. The analogy between the ANNNI model and polytypism based upon the stacking of a single type of layer is clear, and was formalized by Price & Yeomans (1984). In this and other papers (Price, 1983; Price, Parker & Yeomans, 1985) the ground-state energy per layer of a polytype is written as:

$$E = E_I - (1/N) \sum_i J_i \sum_{j=1}^N s_j s_{j+i} \quad (1)$$

where E_I is the internal energy of a layer, N is the number of layers in the repeat unit of a regular stacking sequence, and s_j, s_{j+i} are spin variables of the j th and $(j+i)$ th layers in the ANNNI model, which take the values +1 and -1 for 'up' and 'down' spins respectively. The J_i are the interaction parameters, equal to one half of the difference in energy between an i th-neighbour pair of layers with the same spins, and a pair with opposite spins. The assumptions made in the ANNNI model are that only J_1 and J_2

are significant in determining the stabilities of stacking sequences, and that the interaction between next-nearest neighbours is independent of the orientation of the intervening layer.

Price & Yeomans (1984) directly associated the up and down spins of the ANNNI model with the up and down orientations of the component layers in the spinelloids. In the case of wollastonite either the component (100) layers of a polytype stacking sequence are at a height $y=0$, or they are displaced to a position $y=1/2$. An up and a down spin may be associated with these two alternative positions (Fig. 1), the T stacking operator relating two consecutive layers with the same displacement along the b axis, and the G stacking operator giving rise to a relative displacement of $1/2[010]$ between consecutive layers. Although we shall use this relationship between the *layer position* in wollastonite and spin orientation in the ANNNI model to develop a phase diagram, the mapping between polytypes and spin systems may be generalized by considering a mapping between the spins of the ANNNI model, and the *stacking operators* of the polytypes. This line of derivation is pursued in the Appendix, and is useful because it shows that the wollastonite interaction model is applicable to other polytypic systems in which the stacking operator G is some fraction of a lattice vector other than one half.

We now need to introduce two forms of notation in order to describe the regular sequences of operators in polytypes, and the regular sequences of spins which appear in the ANNNI model. For the polytypes a regular stacking sequence may be described in terms of a repeating sequence of stacking operators.* For example the unobserved four-layer polytype of wollastonite would have the stacking sequence **TTGGTTGG** . . . , which is written as $\langle \text{TTGG} \rangle$, the angular brackets defining the infinitely repeated operator sequence. Because of the cyclic nature of this sequence the same structure may equally well be described as $\langle \text{TGGT} \rangle$, $\langle \text{GGTT} \rangle$, or $\langle \text{GTTG} \rangle$. Furthermore, because of the particular structures of the polytypes discussed here a sequence $\langle G \rangle$ generates the same structure, but in a twin orientation, as that produced by $\langle T \rangle$. It follows that a twin of a given stacking sequence may be generated by changing all of the operators to the other type. In the sequence used above as an example $\langle \text{TTGG} \rangle$ would become $\langle \text{GGTT} \rangle$ and is its own twin, while a sequence such as $\langle \text{TTG} \rangle$ is the twin of $\langle \text{GGT} \rangle$.

In describing regular sequences of spins it is convenient to use the band notation of Fisher & Selge (1980, 1981). A series of consecutive spins with the

* This stacking notation for polytypes is used in preference to that recommended by Guinier *et al.* (1984) in order to emphasize the relationships between polytype stacking and the quantum-mechanical spin models. In the approved notation the $\langle T \rangle$ and $\langle G \rangle$ polytypes are $Aabc$, $\langle TG \rangle$ is $M2abc$, $\langle TTG \rangle$ is $A3abc$, etc.

same sign is termed a band. Thus the repeating sequence in

$$\dots \uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow\dots \quad (2)$$

consists of two 2-bands followed by one 3-band. This is denoted $\langle 223 \rangle$ or $\langle 2^23 \rangle$. More generally, $\langle n_1, n_2, \dots, n_m \rangle$ denotes a regular sequence made up of m bands of lengths n_1, n_2, \dots, n_m .

The two stacking sequences $\langle T \rangle$ and $\langle G \rangle$ correspond to the spin sequences $\uparrow\uparrow\uparrow\uparrow\dots$ and $\uparrow\downarrow\uparrow\downarrow$, or $\langle \infty \rangle$ and $\langle 1 \rangle$ respectively. The ground-state energies per layer of these two sequences may be calculated from equation (1):

$$\begin{aligned} E\langle T \rangle &= E_I - J_1 - J_2 - J_3 - J_4 - \dots \\ E\langle G \rangle &= E_I + J_1 - J_2 + J_3 - J_4 + \dots \end{aligned} \quad (3)$$

As we are interested in polytypic systems where the structure generated by $\langle T \rangle$ is the twin of that generated by $\langle G \rangle$, these two stacking sequences must have the same internal energy:

$$\begin{aligned} E\langle G \rangle - E\langle T \rangle &= 2(J_1 + J_3 + J_5 + \dots) \\ &= 0. \end{aligned} \quad (4)$$

A similar exercise for pairs of twin-related stacking sequences with longer periodicities, *e.g.* $\langle TTG \rangle$ and $\langle TGG \rangle$, $\langle TGGG \rangle$ and $\langle TTTG \rangle$, leads to the conclusion that $J_i = 0$ for all odd i , and that the stability of a stacking sequence in a polytype of this sort is dependent only upon the interaction parameters J_i for which i is even.

In this study only the interactions between second- and fourth-neighbour layers, J_2 and J_4 , are considered so that the ground-state energy of a stacking sequence becomes from (1):

$$E = E_I - (J_2/N) \sum_{j=1}^N s_j s_{j+2} - (J_4/N) \sum_{j=1}^N s_j s_{j+4}. \quad (5)$$

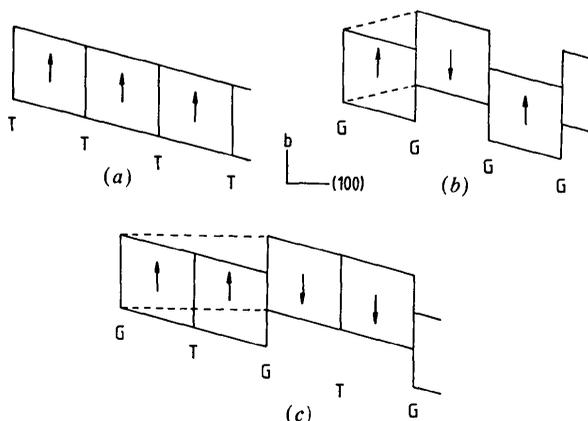


Fig. 1. The relationship between layer position and spin notation in wollastonite-like structures. Each (100) layer is represented by one unit cell and may be stacked in a position continuous with the previous layer as in the $\langle T \rangle$ polytype (a), or may be displaced by $1/2[010]$ as in the $\langle G \rangle$ polytype (b). (c) The stacking found in the $\langle TG \rangle$ polytype.

The assumption that $J_i = 0$ for all $i > 4$ allows us to employ the ANNNI model in developing a phase diagram for these polytype systems. In the next section the nature of the mapping of the polytypes onto the spin sequences of the ANNNI model is described, and a phase diagram is constructed.

3. Phase diagrams

Consider a sequence of layers in the type of polytype where $\langle T \rangle$ is the twin of $\langle G \rangle$, and $J_1 = J_3 = 0$ as a consequence. The 1st, 3rd, 5th \dots $(2n+1)$ th \dots layers in the sequence interact with one another *via* the parameters J_2 and J_4 , as do the 2nd, 4th, 6th, \dots $(2n)$ th layers. However, because $J_{2n+1} = 0$ there is no interaction between the odd-numbered layers in the sequence and the even-numbered layers. They thus form a pair of totally independent subsystems or lattices with no interaction possible between them. This means that any shift of the structure on one sublattice relative to the other has no effect on the energy of the system. And energetically each sublattice can be thought of as an independent spin system with the lattice parameter along the stacking direction double that of the true lattice. Each sublattice then has interactions between the nearest and next-nearest neighbours on that sublattice (being the J_2 and J_4 interactions of the true lattice) and therefore forms an ANNNI system.

It is now possible to derive a phase diagram for the wollastonite model in terms of the interaction parameters J_2 and J_4 from that calculated for the ANNNI model. For each region of the ANNNI phase diagram in which a given spin sequence is the most stable phase the equivalent polytype stacking sequences can be deduced. To do this the ANNNI spin sequence is transferred to both sublattices to generate one stacking sequence. But because the two sublattices are independent the spins on one may be reversed so as to produce a second stacking sequence. For example, one of the ground-state sequences in the ANNNI model is $\langle \infty \rangle$ with the spin sequence $\uparrow\uparrow\uparrow\uparrow\uparrow\dots$ (or $\downarrow\downarrow\downarrow\downarrow\downarrow\dots$). If this is transferred to both sublattices with the same orientation on both:

$$\begin{aligned} & \uparrow \cdot \uparrow \cdot \uparrow \cdot \uparrow \cdot \uparrow \cdot \uparrow \\ + & \uparrow \cdot \uparrow \cdot \uparrow \cdot \uparrow \cdot \uparrow \cdot \uparrow \\ \hline & = \uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow \end{aligned}$$

then the $\langle T \rangle$ polytype is produced. If, however, the spins on one sublattice are reversed:

$$\begin{aligned} & \uparrow \cdot \uparrow \cdot \uparrow \cdot \uparrow \cdot \uparrow \cdot \uparrow \\ + & \downarrow \cdot \downarrow \cdot \downarrow \cdot \downarrow \cdot \downarrow \cdot \downarrow \\ \hline & = \uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow \end{aligned}$$

the $\langle G \rangle$ polytype, the twin of $\langle T \rangle$ is generated. Further structures may be generated from one ANNNI spin sequence by translating the spins on one sublattice

relative to the other along the stacking direction. In this way two or more polytypes can be mapped onto a single ANNNI phase. A simple example is the spin sequence $\langle 3 \rangle$ which appears at non-zero temperatures in the phase diagram of the ANNNI model. If the series of 3-bands of spins are transferred to the two sublattices of the polytype without relative displacement the sequence $\langle \text{TTTTG} \rangle$ is generated:

$$\begin{array}{r} \uparrow \cdot \uparrow \cdot \uparrow \cdot \downarrow \cdot \downarrow \cdot \downarrow \\ + \\ \cdot \uparrow \cdot \uparrow \cdot \uparrow \cdot \downarrow \cdot \downarrow \cdot \downarrow \\ \hline = \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \end{array}$$

But if the spins on the second sublattice are translated by one position the $\langle \text{TTTGGG} \rangle$ polytype results:

$$\begin{array}{r} \uparrow \cdot \uparrow \cdot \uparrow \cdot \downarrow \cdot \downarrow \cdot \downarrow \\ + \\ \cdot \downarrow \cdot \uparrow \cdot \uparrow \cdot \uparrow \cdot \downarrow \cdot \downarrow \\ \hline = \uparrow \downarrow \uparrow \uparrow \uparrow \downarrow \downarrow \downarrow \downarrow \downarrow \end{array}$$

These two sequences have the same free energy if only the J_2 and J_4 interactions are considered, and are thus said to be degenerate. As a result of this degeneracy the area in the polytype phase diagram corresponding to the stability field of the $\langle 3 \rangle$ phase in the ANNNI model will contain both $\langle \text{TTTTG} \rangle$ and $\langle \text{TTTGGG} \rangle$. Longer spin sequences in the ANNNI phase diagram tend to map onto more polytype stacking sequences, because there exist more possible relative translations of the spin sequences on the two sublattices. As a consequence the phase fields of the wollastonite model contain several polytype stacking sequences and are thus multiply degenerate.

The ground states of the ANNNI model as a function of J_1 and J_2 are shown in Fig. 2(a). For values of $J_2 > 0$ equation (1) shows that sequences in which second-neighbour spins have the same sign have lower energies, and are thus stabilized relative to spin sequences in which second-neighbour spins have opposite signs. With $J_1 > 0$ sequences in which nearest-neighbour spins also have the same sign are favoured, while for $J_1 < 0$ nearest-neighbour spins of

opposite sign stabilize the spin sequence. For $J_2 > 0$ both first- and second-neighbour couplings are satisfied by the spin sequences $\langle 1 \rangle$ for $J_1 < 0$, and by $\langle \infty \rangle$ for $J_1 > 0$.

However, for $J_2 < 0$ there is competition between the configuration of second-neighbour spins whose low-energy state would be of opposite sign, and the configuration preferred by the J_1 interaction. For large values of $|J_1|$ this interaction predominates, and the two phases $\langle 1 \rangle$ and $\langle \infty \rangle$ remain stable, while for small values of $|J_1|$ a third phase, $\langle 2 \rangle$, is stabilized by the competition between J_1 and J_2 . On the boundary between $\langle 2 \rangle$ and $\langle \infty \rangle$, $J_1 = -2J_2$, the ground state is highly degenerate, as all phases which do not contain any 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 spin sequences comprising entirely 1- and 2-bands alone have the same energy. Note, however, that the boundary between $\langle 1 \rangle$ and $\langle \infty \rangle$ is not a multiphase line, and only the spin sequences $\langle 1 \rangle$ and $\langle \infty \rangle$ co-exist here.

The ground-state phase diagram of the wollastonite model is given in Fig. 2(b). This has been derived from that of the ANNNI model by mapping each of the ground-state ANNNI phases onto the two sublattices of the polytype model as described above. The $\langle \infty \rangle$ ANNNI phase maps onto the $\langle \text{T} \rangle$ polytype, and its twin $\langle \text{G} \rangle$, and the $\langle 2 \rangle$ ANNNI phase similarly maps onto the twin-related pair $\langle \text{TTTGG} \rangle$ and $\langle \text{TGGG} \rangle$. The remaining ground-state ANNNI phase, $\langle 1 \rangle$, generates only the $\langle \text{TG} \rangle$ polytype which is its own twin.

At finite temperatures the ANNNI model phase diagram remains essentially the same for most values of J_1 and J_2 . However, in the regions near the multiphase lines $J_1 = 2J_2$ and $J_1 = -2J_2$ (J_2 negative) entropic effects cause the breakdown of the degeneracies between various spin sequences which exist on these multiphase lines in the ground state. Fig. 3(a) shows the way in which the phase fields develop in the ANNNI model at low temperatures (Fisher & Selke, 1980, 1981); J_0 is the interaction parameter between neighbouring spins within a layer and serves to normalize the temperature scale.

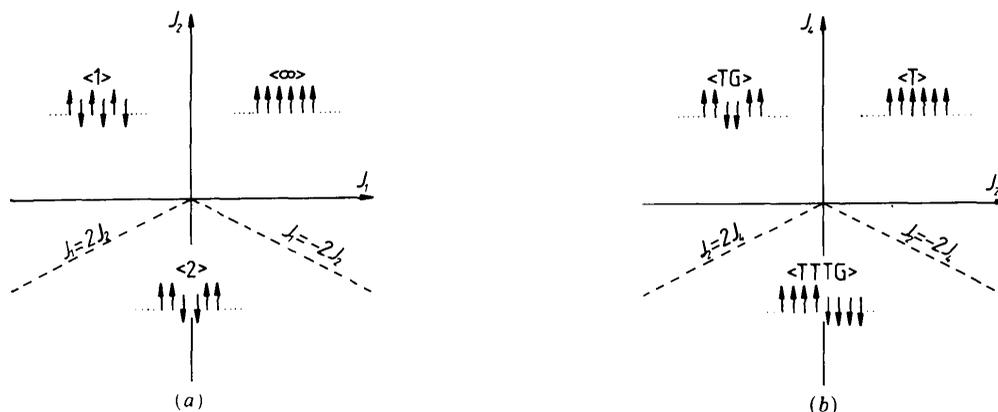


Fig. 2. The ground states of (a) the ANNNI model, and (b) the wollastonite model.

The phase diagram of the wollastonite model for $J_2 < 0$ is shown in Fig. 3(b). As for the ground states, each ANNNI spin sequence is transferred to both sublattices of the polytype model to generate the stable stacking sequences for the corresponding values of J_2 , J_4 , and temperature. However, as we have already illustrated for the $\langle 3 \rangle$ ANNNI spin sequence, each ANNNI phase maps onto more than one polytype stacking sequence, all of which have the same free energy. In the ANNNI phase diagram there is a regular series of stable spin sequences between $\langle 1 \rangle$ and $\langle 2 \rangle$ which may be described as $\langle 12^N \rangle$, and the sequences $\langle 2^N 3 \rangle$ form a similar stable series between $\langle 2 \rangle$ and $\langle 3 \rangle$. Two analogous series do exist in the polytype phase diagram. The $\langle 12^N \rangle$ ANNNI phases map onto a series of polytypes $\langle \text{TG}(\text{TTTG})^N \rangle$, and the $\langle 2^N 3 \rangle$ ANNNI phases map onto the $\langle (\text{TTTG})^N \text{TTTTG} \rangle$ polytypes. However, the degeneracies between the polytypes tend to obscure this pattern, and also give rise to other series of stable polytypes. For example, $\langle 122 \rangle$ also maps onto $\langle (\text{T TG})^2 \text{TTTG} \rangle$, which is a combination of the second polytype mapped from $\langle 12 \rangle$, $\langle \text{T TG} \rangle$, with the $\langle \text{TTTG} \rangle$ sequence.

An alternative presentation of the phase diagram for the wollastonite model is made in Fig. 4, which is an isothermal section at non-zero temperature. Note that this section is drawn for a temperature at which $K_B T \ll J_0$; at higher temperatures the layers become increasingly disordered in the ANNNI model (Duxbury & Selke, 1983). Our attention is restricted to lower temperatures because this in-layer disorder

is absent from most of the silicate structures to which the model is applied. In wollastonite itself such disorder gives rise to bustamite-like stacking sequences along the c axis which are only observed very rarely as growth features (Angel, 1985). In the next section the predictions of the wollastonite model regarding phase stability will be compared with observations made on naturally occurring polytype systems.

4. Discussion

The widths of the phase fields in the ANNNI model and, by implication, the wollastonite model, decrease exponentially with increasing length of the repeat unit of the stacking sequence. So, in addition to the entropy-stabilized stacking sequences occupying multiply degenerate phase fields in the wollastonite model, the decreasing widths of the fields will make the experimental resolution of longer-period polytypes difficult. Furthermore, the phase diagram is drawn in terms of two interaction parameters which are functions of the structure of the layer modules forming the polytype, and they may thus be expected to vary with temperature and pressure, as well as with the chemical composition of the layers. Nevertheless, it is informative to compare the predictions of the model with actual polytype systems, as this allows us to deduce whether such a model gives a consistent description of the phases which occur in a polytypic system, and to suggest possible relationships between the interaction parameters and the intensive variables imposed upon the polytypic system.

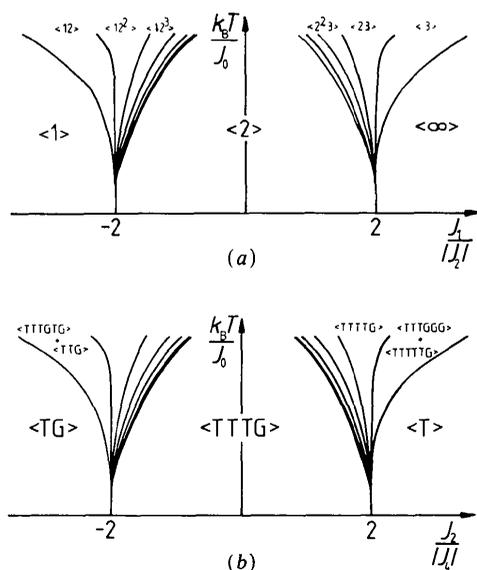


Fig. 3. Schematic phase diagrams, as a function of temperature ($K_B T/J_0 \ll 1$) and ratios of interaction parameters, for (a) the ANNNI model (with $J_2 < 0$), and (b) the wollastonite model (with $J_4 < 0$). The phase field labelled $\langle \text{TTTTG} \rangle$ also contains $\langle \text{T}^5 \text{GT}^3 \text{G} \rangle$ and $\langle \text{T}^3 \text{G}^3 \text{TG}^3 \rangle$.

Wollastonite

The two most common polytypes found in nature are $\langle \text{T} \rangle$ and $\langle \text{TG} \rangle$, these being the only two to occur as sufficiently large unfaulted single crystals to allow complete X-ray structure determinations to be carried out. These two common polytypes occur as the two major ground-state structures in the interaction model, as well as remaining stable for a large range of the interaction parameters at non-zero temperatures (Fig. 4). The third ground-state polytype, $\langle \text{TTTG} \rangle$, was reported by Henmi, Kawahara, Henmi, Kusachi & Takeuchi (1983), and is now generally agreed to be the only four-layer polytype of wollastonite which occurs naturally. Wenk (1969) did report the occurrence of what he believed to be the other possible four-layer polytype $\langle \text{TTGG} \rangle$, but Jefferson & Bown (1973) showed that the diffraction data obtained by Wenk from this sample were more consistent with it being a mixture of $\langle \text{TG} \rangle$ and $\langle \text{T} \rangle$ polytypes. This was confirmed by a subsequent investigation of Wenk's original sample by transmission electron microscopy (W. F. Muller, personal communication). No further occurrences of $\langle \text{TTGG} \rangle$

have been reported, even as short stacking sequences in disordered material.

Only three other polytypes have been found in sufficiently ordered states to allow even their cell dimensions and stacking sequence to be derived from X-ray diffraction data. These are $\langle \text{TG} \rangle$ and $\langle \text{TTTTG} \rangle$ (Henmi *et al.*, 1983), both of which appear in the phase diagram at elevated temperatures with stability fields of significant size, and $\langle \text{TTGTGTG} \rangle$ (Henmi, Kusachi, Kawahara & Henmi, 1978) which maps onto the ANNNI spin sequence $\langle 1^2 \rangle$. This seven-layer polytype is thus one of the structures which is stable on the multiphase boundary between $\langle \text{TG} \rangle$ and $\langle \text{TTTTG} \rangle$ in the ground state, but does not appear in the low-temperature region of the phase diagram shown in Figs. 3(b) and 4. However, in the ANNNI model $\langle 1^2 \rangle$ does have a restricted stability field at higher temperatures where significant disorder is present within the layers, so $\langle \text{TTGTGTG} \rangle$ will have a similar stability field in the phase diagram of the wollastonite model. Whether its occurrence in the material examined by Henmi *et al.* (1978) is due to growth within this restricted stability field, or to metastable growth under other conditions cannot be determined. Metastability is always a consideration in these systems because the free-energy differences between polytypes are so small.

Possible relationships between the interaction parameters and the intensive variables may also be deduced for wollastonites. Henmi *et al.* (1983) studied skarns containing wollastonites and showed that the $\langle \text{TG} \rangle$ polytype is stabilized relative to the $\langle \text{T} \rangle$ polytype by increasing temperature. A microprobe analysis of one of the samples which shows this structural variation was carried out by the present authors. There was no detectable variation in chemical composition between the polytypes, so the variation in the relative stabilities of the polytypes within the skarn may be attributed to temperature alone. We may thus conclude that as temperature increases the J_2 interaction parameter changes from positive to negative values, while the predominance of the $\langle \text{T} \rangle$ and $\langle \text{TG} \rangle$ polytypes

in nature suggests that J_4 is positive (see Fig. 4) for most conditions under which wollastonite is formed. Experimental deformation of ordered wollastonite is known to induce stacking disorder (Wenk, 1969; Guggenheim, 1978) which could suggest that increasing pressure causes J_4 to become negative, thereby placing the system within the area of closely spaced multiply degenerate phase fields. In such an area where many stacking sequences have very similar energies disordered stacking would be expected to occur. Alternatively this observed increase in stacking disorder may be a kinetic effect not related to the thermodynamic model developed here.

The interaction parameters for wollastonite may also be related to the adjustments made by the structure due to the stacking sequence. Wollastonite is a single-chain silicate with three tetrahedra in the repeat unit along the chain. The silicate chains run parallel to the b axis and are linked together by parallel bands of large cation sites. Angel (1985) has shown that the introduction of a $1/2[010]$ shear on (100) of the $\langle \text{T} \rangle$ polytype, which is the effect of a G stacking operator, changes the configuration of the tetrahedral chains around the cation sites. It is therefore to be expected that the J_2 and J_4 parameters are mainly dependent upon the relaxation of the tetrahedral chains around the cation sites adjacent to the shear planes.

Zoisite and clinozoisite

The relationship between these two structures was first noted by Ito (1950). Both contain aluminium octahedra which share edges to form chains running parallel to the b axis which are cross-linked by calcium ions, SiO_4 tetrahedra, and Si_2O_7 groups. Ito proposed that the orthorhombic zoisite structure was a unit-cell twin of clinozoisite derived by introducing an n -glide twin operator parallel to (100) between every unit cell of the monoclinic polymorph. Careful refinement of the two structures by Dollase (1968) showed that although this relationship is qualitatively correct, many of the structural parameters of a zoisite structure generated in this way differ significantly from those of the refined structure. More recently Ray, Putnis & Gillet (1985) have shown that the zoisite structure may be generated by the introduction of $1/4[001]$ shears on (100) into every alternate layer of clinozoisite cells, and that the introduction of this same $1/4[001]$ shear into every clinozoisite cell regenerates the same monoclinic structure, but in a twin orientation. The structures based upon the stacking of (100) layers of clinozoisite structure are therefore polytypes of the same class as wollastonite, in that a structure described by the stacking sequence $\langle \text{G} \rangle$ (G in this case being a $1/4[001]$ shear) is the twin of $\langle \text{T} \rangle$, where T generates a succeeding layer in an unsheared position. Clinozoisite and zoisite are therefore represented by the stacking sequences $\langle \text{T} \rangle$ and $\langle \text{TG} \rangle$

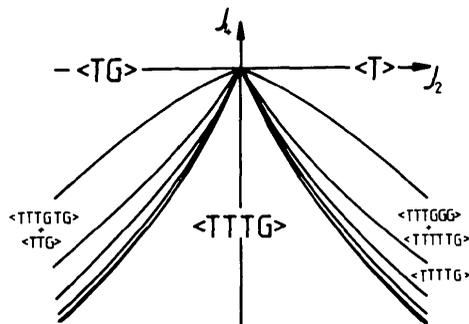


Fig. 4. An isothermal section taken at $0 < K_B T / J_0 \ll 1$ of the phase diagram of the wollastonite model. As for Fig. 3(b) the phase field labelled $\langle \text{TTTTG} \rangle$ also contains $\langle \text{T}^5 \text{G}^3 \text{T}^3 \text{G} \rangle$ and $\langle \text{T}^3 \text{G}^3 \text{TG}^3 \rangle$.

respectively. Faulting and disordered sequences are rare in these minerals and longer-period polytypes are unknown, which suggests that the interaction parameter J_4 is positive for this polytype system. The orthorhombic form, $\langle\text{TG}\rangle$, is believed to be the high-temperature polymorph at the end-member composition of $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}\text{OH}$ (Jenkins, Newton & Goldsmith, 1983); the monoclinic form being stabilized, however, by the substitution of Fe for Al in the octahedral sites. The parameter J_2 thus has a trajectory in the model phase diagram (Fig. 4) which passes from negative to positive values on decreasing temperature and increasing iron content. The change in J_2 with Fe substitution is due to the relaxation of the octahedral chains and the adjoining Si_2O_7 group by rotation on increased Fe content of the Al(3) site (Dollase, 1968).

Hydrated calcium chain silicates

Two hydrated structures which are closely related to wollastonite have been reported to show polytypism very similar to that observed in wollastonite. The structure of foshagite was refined by Gard & Taylor (1960) and consists of wollastonite-like silicate chains joined together by parallel bands of cations. In wollastonite the cation bands are three sites wide, but in foshagite there are four sites across each band, and the extra calcium in the formula is balanced by the addition of hydroxyl groups to the structure to give a composition $\text{Ca}_4\text{Si}_3\text{O}_9(\text{OH})_2$. Xonotlite is a double-chain analogue of foshagite with cation bands three sites wide and pairs of wollastonite chains cross-linked by shared oxygens between the offset tetrahedra (Kudoh & Takeuchi, 1979). Both of these mineral structures exhibit polytypic stacking variation of (100) layers in addition to stacking variation along the [001] axis which is analogous to the relationship between the structures of wollastonite and bustamite (Angel, 1985). In this paper we will only discuss the variation in the stacking sequences of (100) layers, as the variation along [001] should be described by the ANNNI model itself, or the two types of structural variation described together in a combined model for stacking variation along two axes.

Two polytypes of xonotlite have been refined by X-ray structure determination, these being an analogue of $\langle\text{TG}\rangle$ wollastonite (Mamedov & Belov, 1956), and a structure with a doubled c axis and a $\langle\text{T}\rangle$ stacking sequence of (100) layers (Kudoh & Takeuchi, 1979). Surveys of stacking sequences in this mineral by selected-area electron diffraction (Gard, 1966; Chisholm, 1979) indicate that the $\langle\text{T}\rangle$ stacking sequence is the most common, together with disordered sequences. In foshagite stacking variation along the c axis is far less common than along the a axis, and nearly all observed samples have a c -axis stacking arrangement analogous to that of bustamite.

In the stacking along [100] of (100) layers the $\langle\text{T}\rangle$ polytype is dominant in natural samples, while $\langle\text{TG}\rangle$ is commonly found in synthetic material (Gard & Taylor, 1960). This difference must reflect the effect on the J_2 parameter of the differences in the conditions under which synthetic and natural foshagite samples are formed.

The observed dominant stacking sequences, $\langle\text{T}\rangle$ and $\langle\text{TG}\rangle$, along [100] in both xonotlite and foshagite suggest that, as in wollastonite, J_4 is positive while J_2 is a function of temperature and possibly other variables. Structurally these two parameters are related to the relaxation of the tetrahedral chains around the cation sites, as in wollastonite, but there will also be a contribution from the hydroxyl groups. Gard (1966) showed that in xonotlite stacking sequences in which all the cation sites are coordinated by an equal number of hydroxyl groups are stabilized relative to those structures in which this distribution is unequal. Kudoh & Takeuchi (1979) also noted that the more equal distributions were also those in which the $\text{OH}\cdots\text{OH}$ distances were largest. These factors are also present in foshagite, where the introduction of a single $1/2[010]$ shear into a $\langle\text{T}\rangle$ stacking sequence moves the silicate chains which lie adjacent to the shear plane relative to the adjoining cation band. This will promote the redistribution of the H atoms associated with this band, as they are allocated to those oxygens not coordinated to silicon. The distribution of hydroxyl groups in foshagite is thus also a function of the stacking sequence along [100] and will make a contribution to the J_2 and J_4 interaction parameters.

Pectolite-serandite

The relationship between the structure of the pectolite-serandite solid-solution series, $(\text{Ca}, \text{Mn})_2\text{NaHSi}_3\text{O}_9$, and that of wollastonite was discussed by Prewitt & Buerger (1963). They showed that the pectolite structure possesses the same pseudosymmetry as wollastonite, so that a $\langle\text{T}\rangle$ and a $\langle\text{G}\rangle$ ($\text{G} = 1/2[010]$) stacking sequence are twin-related. Muller (1976) carried out a survey of the stacking sequences in samples of these two minerals and found that pectolite frequently exhibits stacking disorder of (100) layers, as well as existing as both $\langle\text{T}\rangle$ and $\langle\text{TG}\rangle$ polytypes. By contrast serandite, the manganese end-member, only appears to exist as the $\langle\text{T}\rangle$ polytype with infrequent stacking faults. As with wollastonite we expect the J_2 and J_4 interaction parameters to be related to the degree of distortion around the cation sites. The observations made by Muller suggest that these are sufficient in serandite to keep J_2 and J_4 positive, and thereby prevent polytypic stacking variation. In pectolite the larger calcium ion is more easily coordinated by the silicate chains, and less distortion is therefore introduced by sequences of stacking vectors other than $\langle\text{T}\rangle$ or $\langle\text{G}\rangle$.

The (TG) polytype appears to be the most common stacking sequence in pectolite after (T), in line with the prediction of our model. This could be explained by J_2 becoming more positive with increasing manganese content.

5. Conclusions

We have demonstrated that, energetically speaking, there are two classes of polytypes based upon the stacking of nominally identical layers by two stacking vectors. The class of polytypes treated in this paper differs from the more common class (*e.g.* spinelloids, pyroxenes) in that an exchange of all the stacking operators in a repeat sequence produces the same structure in a twin orientation. Since twin-related structures have the same energy, an interaction model applied to such a polytypic system has constraints imposed upon some interaction parameters which differ from those used in previous models used to explain polytype stability. By applying these constraints we have developed an interaction model for this second class of polytypes in which the relative stabilities of polytype stacking sequences are dependent upon the interactions between second- and fourth-neighbour pairs of layers. The assumptions made in this model of polytypism should be stated explicitly:

(1). Interactions between pairs of layers more distant than fourth neighbours are assumed not to contribute to the free energy of a stacking sequence.

(2). The pair-wise interactions used in this type of model [equation (1)] are assumed to be independent of the configuration of the intervening layers.

If, however, these configurations do contribute to the energy of a polytype stacking sequence we should add extra terms to the Hamiltonian which depend upon the product of consecutive layer spins, such as

$$-(K/N) \sum_{j=1}^N s_j s_{j+1} s_{j+2} s_{j+3}. \quad (6)$$

Although some of these possible extra terms must be zero in the class of polytypes considered here because of the equivalence of twin-related stacking sequences, others such as (6) are still permitted, and may contribute to the free energy of a polytype. The reason we have chosen to neglect these terms is that the phase diagram for the wollastonite interaction model may easily be derived from that calculated for the ANNNI model. The introduction of further terms such as (6) into the Hamiltonian results in models for which the ground states may still be calculated, but which are currently unsolved at non-zero temperatures. The success with which the wollastonite interaction model predicts the stabilities of the observed stacking sequences of wollastonite poly-

types suggests that these other possible interaction terms are less important than those considered in our model.

By consideration of the structures of this class of polytypes we have also indicated how the interaction parameters might be related to various structural features. The use of axial Ising spin models such as the ANNNI and the wollastonite models to describe the energetics of polytype systems has been shown to be a potentially powerful tool for the prediction of the relative stabilities of polytype stacking sequences.

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APPENDIX

Within the main part of the paper we have equated the two possible positions of the layers in wollastonite with two spin-like variables which may have the values +1 or -1. It is the purpose of this Appendix to show that a more general description of the energetics of such polytypic systems is obtained if we write the energy, or strictly speaking the Hamiltonian of the system, directly in terms of the sequence of stacking operators.

Let us associate a variable t_j with each stacking operator in the stacking sequence, which has a value +1 for the T operator and -1 for the G operator. Since each operator relates two consecutive layers in the polytype with spin variables s_j and s_{j+1} we note that there is a mapping between the layer spins and the operator spins:

$$s_j s_{j+1} \rightarrow t_j. \quad (A1)$$

This follows because a T operator ($t_j = +1$) relates two layers with the same spin variables, the product of which is always +1, while the G operator relates two layers with different spin variables, and hence a product of -1.

The energy of a stacking sequence may now be written in terms of the interactions arising from a sequence of operators. Using the transformation (A1) equation (5) becomes

$$E = E_I - (J_2/N) \sum_{j=1}^N t_j t_{j+1} - (J_4/N) \sum_{j=1}^N t_j t_{j+1} t_{j+2} t_{j+3} \quad (A2)$$

where the first term is a nearest-neighbour interaction, and the second describes a four-spin interaction which depends on the configuration of four consecutive layers.

By considering the energetics of the wollastonite model in terms of the interactions between stacking operators we have been able to show that the model possesses two important features:

(1). The interaction represented by J_4 does include a contribution from the configuration of the layers between the j th and $(j+3)$ rd neighbour layers.

(2). The association of spins with layer position used in the body of the paper suggests that $|G|$ must be one half of a lattice vector, but the derivation in terms of operators places no such constraint upon the magnitude of the displacement associated with the glide operator G . This justifies the use of the wollastonite model in systems such as zoisite where $G = 1/4[001]$.

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A Structure Classification of Symmetry-Related Perovskite-Like ABX_4 Phases*

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Abstract

An exhaustive count is performed of all possible perovskite-like ABX_4 phases, with the assumption that the only occurring symmetry-reducing operation is the tilting of regular BX_6 octahedra. Each structure is schematically represented and is fully determined by its structure symbol, the space group and the diffraction features, which are condensed in a powerful shorthand notation: the 'diffraction typology'. Attention is paid to the displacement of the A cation and the resulting antiferroelectricity. The interrelations between the structures are presented in the

'family tree' formalism in order to provide insight concerning the group-to-subgroup relations as a helpful tool in the prediction of phase transitions.

1. Introduction

Perovskites with general structure formula ABX_3 such as $SrTiO_3$ and $NaNbO_3$ undergo phase transitions featuring the condensation of soft phonon modes upon lowering the temperature (Ahtee, Glazer & Megaw, 1972; Kay & Bailey, 1957). The perovskite-like ABX_4 compounds such as $RbVF_4$ and $RbFeF_4$ have a basic structure that is very similar to the basic ABX_3 structure as can be seen by comparison of Figs. 1(a) and 1(b): in the ABX_4 case the BX_6 octahedra are only two-dimensionally corner linked, thus form-

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