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A model for polysomatism

GEOFFREY D. PRICE
Department of Geology, University College London, Gower Street, London WC1E 6BT

AND

JULIA YEOMANS
Department of Theoretical Physics, University of Oxford, 1 Keble Road, Oxford OX1 3NP

ABSTRACT. We show that the structures and phases developed in a variety of polysomatic series, including the biopyroboles, are similar to those predicted by a simple spin model—the Axial Next-Nearest-Neighbour Ising (ANNNI) model in a magnetic field. We argue that the different polysomatic structures can be considered as thermodynamically stable phases, composed of ordered sequences of chemically distinct structural modules. We suggest that the key factors which determine the stability of polysomatic phases are (*a*) the chemical potential, which controls the proportion of the different structural modules, and (*b*) the competing interactions between first and second neighbour modules within the structures.

KEYWORDS: polysomatism, biopyriboles, ANNNI model.

CRYSTAL structures can be analysed at many levels. At the most fundamental level, they are described in terms of the relative distribution of their constituent atoms, or of the coordination polyhedra of the component cations and anions. It is becoming increasingly apparent, however, that many families of structures can be usefully described in terms of larger basic structural units or modules. If such an approach to the description of crystal structures is adopted, many complex solids may be systematized in terms of series of stacking variants of the simple subunits. This approach was first popularized by Ito (1950) in his analysis of polytypism in minerals, and has been extended by many workers including Lima-de-Faria and Figueiredo (1976, 1978) and Thompson (1978) in their classification and analysis of mineralogical structures.

As discussed by Thompson (1981*a*) variations in the stacking of structurally compatible, isochemical modules give rise to polytypic families, epitomized by the classic polytypes such as SiC, ZnS, and CdI_2. A more general case exists, however, in which the constituent modules are structurally compatible yet chemically distinct. Under these circumstances, a series of structures with a range of chemical compositions can be produced by changes in the proportion of the two kinds of module. The resulting structures form what is known as a polysomatic series (Thompson, 1978). For example, if modules *A* and *B* are chemically distinct, the sequences ...*AAA*..., ...*ABAB*..., and ...*BBB*... constitute such a series, however it should be noted that the sequences ...*ABAB*... and ...*AABB*... are polytypes rather than polysomes since they are isochemical. Well known examples of polysomatic series include the biopyribole minerals (pyroxenes, amphiboles, and sheet silicates), the humite group, pyroxenoids and phases in the $CeFCO_3$-$CaCO_3$ system.

In principle there is an infinite number of structures that can be constructed from combinations of two modules. However, in practice it is found that certain stacking sequences occur much more frequently than others. A recent theory which has been very successful in explaining the observed variety of polytypes relates the stabilities of various stacking sequences to the interactions between component structural modules (e.g. Price and Yeomans, 1984). These interactions may be viewed as the result of the differences in free energy caused by the local, small scale distortions experienced by an idealized module when it forms part of a stacking sequence. It appears that the stability of a given stacking sequence is dependent upon the interaction, not only between adjacent modules, but also between pairs of modules separated by greater distances.

Based on these ideas, Smith *et al.* (1984) and Price and Yeomans (1984) provided an explanation for the observed equilibrium behaviour of many polytypic families in terms of the Axial Next-Nearest-Neighbour Ising or ANNNI model. This statistical mechanical model was originally developed to describe magnetic systems (Elliott, 1961; Fisher and Selke, 1981). To relate the polytypic compounds to the ANNNI model, Smith *et al.* (1984) and Price and Yeomans (1984) proposed that the basic polytypic structural units can be mapped on to a magnetic spin variable. The interactions between units were then represented by a Hamiltonian with competing first and second neighbour interactions. The resulting ANNNI model provides a simple equilibrium description of polytypism as the temperature and interaction parameters are varied. In particular short-range couplings can lead to the existence of polytypes with very long period stacking sequences. Other important features of polytypism are also explained by this model: notably that only a specific set of polytypes are stable for a given compound, that reversible phase transitions can occur, and that polytypes with short stacking sequences occur most frequently. A similar approach has recently been adopted by Angel *et al.* (1985) to model the more complex polytypic behaviour in the wollastonite system, and by de Fontaine and Kulik (1985) in their treatment of ordering in binary metal alloys.

In this paper we develop the ideas advanced by Price and Yeomans (1984) to study polysomatic sequences. As in the case of polytypes, there is in theory an infinite number of members of a given polysomatic family, but in fact, in any one series, only a limited number of phases are found. We attempt to model these systems by mapping the two chemically distinct units which are involved in a polysomatic sequence on to magnetic spins with orientations $\uparrow$ and $\downarrow$ respectively. A Hamiltonian is then constructed which includes the interactions between the modules, together with a chemical potential term which controls the relative abundance of the two species. The resulting model is shown to be equivalent to the ANNNI model in a magnetic field. In the following sections, we discuss some of the structural characteristics of polysomatic series and introduce the ANNNI model in a field. Finally, we discuss the application of the ANNNI model in a field to polysomatic behaviour.

Polysomatic series. The biopyriboles provide an excellent example of a polysomatic series (Thompson, 1978; Veblen and Buseck, 1979). This family includes a wide range of common minerals including pyroxenes, amphiboles, and trioctahedral micas (biotite, talc, etc.). The pyroxene structure is characterized by the development of infinite chains of corner-sharing SiO_4 tetrahedra, bound together by interstitial cations. In contrast, the micas contain infinite silicate sheets, while the amphiboles are double-chain silicates, and can be considered to be structurally intermediate between pyroxenes and micas. In fact, all biopyriboles can be regarded, in at least an idealized way, as being made up of modules, some of which are pyroxene-like and some of which are mica-like. Figs. 1*a* and *b* show examples of these modules. The pyroxene and mica modules are arranged in two dimensions to form component sheets or layers. Idealized biopyriboles can be viewed as being made of successive pyroxene and mica layers stacked parallel to (010). Biopyribole structures can consequently be described in terms of stacking formulae, which record the sequences of mica (*M*) and pyroxene (*P*) layers along [010]. Thus, the pyroxene structure, ...*PPP*..., can be denoted by the code (*P*), and the mica structure, ...*MMM*..., by the code (*M*), while the amphibole structure, which can be written ...*MPMP*..., can be described by the code (*MP*).

Despite the fact that there is an infinite number of potential stacking sequences only five have been found to form distinct phases (Thompson, 1981*b*). The principal series, containing the largest number of examples of biopyriboles conforms to the general formula $(M_{(n-1)}P)$, where n is a positive integer that

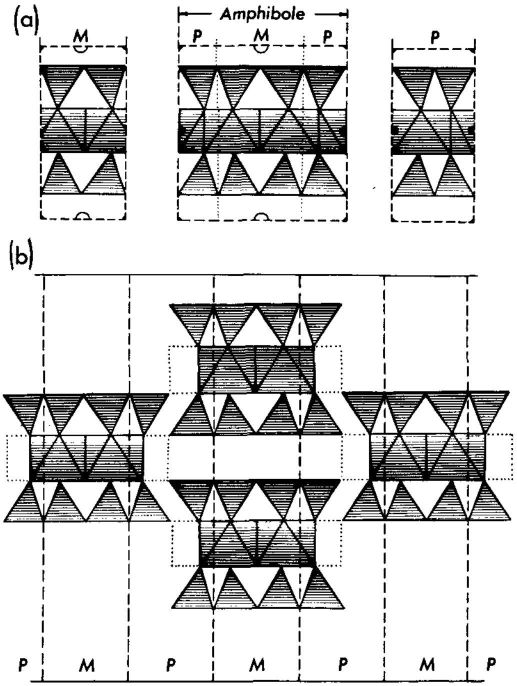

FIG. 1. (*a*) Idealized modules for biopyriboles as seen in cross section. The *A* and *K* sites of amphiboles and micas are shown as open half circles, and the *M*2 sites in pyroxene as solid half or quarter circles. All other *M* sites are shown as regular octahedra, and all Si sites as idealized tetrahedra. (*b*) Idealized section normal to *c* of an amphibole such as tremolite. Dashed vertical lines show (010) boundaries which divide the amphibole into mica (*M*) and pyroxene (*P*) modules. (After Thompson, 1978).

describes the characteristic width of the silicon-oxygen chains in the structure. Thus, $n = 1$ corresponds to the pyroxene structure, $n = 2$ to the amphibole structure, $n = 3$ to the triple chain jimthompsonite structure (*MMP*), and $n = \infty$ to the mica structure. No structures with other values of n have been observed. One other biopyribole has been observed, however, which does not conform to the above formula, namely the mineral chesterite, which has a stacking formula (*MMPMP*). Chesterite, therefore, is structurally intermediate between amphibole and jimthompsonite.

Both chesterite and jimthompsonite are naturally associated with structurally disordered biopyriboles. These two minerals seem only to form during the alteration of the amphibole anthophyllite to talc. It is therefore possible that they may be entirely metastable relative to anthophyllite and talc. Even if they are stable they certainly have only a narrow field of stability. Whether they are stable or not, the question still remains as to why the amphibole, chesterite and jimthompsonite sequences are adopted in preference to any of the other possible stacking arrangements such as (*MMMPP*), (*MMPP*) or (*MPP*) (Veblen and Buseck, 1979).

The significance of this question is reinforced when other polysomatic series, such as that in the $CeFCO_3$-$CaCO_3$ system, are considered. Four minerals have been reported to occur in this system, all of which are composed of ordered layers consisting either of $CeFCO_3$ or of $CaCO_3$ (Donnay and Donnay, 1953; Van Landuyt and Amelinckx, 1975). If these layers are labelled A and B respectively, the structures of the four minerals can be described by the codes (A), (AB), (AAB), and ($ABAAB$). The fact that these sequences are exactly the same as those adopted by the biopyriboles suggests that they may represent particularly favourable configurations. In the following sections, we shall show that if we assume effective short-range competing interactions between the component modules, it is possible to explain why some polysomatic configurations appear to be more favoured than others.

The ANNNI model in a magnetic field. The ANNNI model was first developed to describe magnetic phases, and it is therefore convenient to discuss it using the terminology of magnetic systems. We consequently introduce the concept of an Ising spin variable, s_i, which can either take the value of $+1$ or -1. In the ANNNI model, a spin s_i is associated with each of the i sites of a cubic lattice. In an applied magnetic field (H), the spins interact in a way which is described by the Hamiltonian:

$$\mathscr{H} = -J_0\sum_{nn}{}^{\perp} s_is_j - J_1\sum_{nn}{}^{\parallel} s_is_j - J_2\sum_{nnn}{}^{\parallel} s_is_j - H\sum_{i} s_i. \quad (1)$$

The first term represents a strongly ferromagnetic interaction ($J_0 > 0$) between nearest neighbour (nn) spins which lie within planes perpendicular ($\perp$) to a unique axial direction ($\parallel$). This term requires that at zero temperature the spins in any one layer are aligned parallel to each other. The second and third terms describe interactions between first and second or next nearest neighbour (nnn) spins along the unique direction ($\parallel$). These interactions can either be ferromagnetic ($J > 0$) or antiferromagnetic ($J < 0$). The properties of the ANNNI model depend upon the relative signs and magnitudes of J_1 and J_2. The final term describes the effect of the applied magnetic field (H) on the interaction of the spins.

The low-temperature configurations of the model comprise sequences of bands or groups of consecutive layers with the same spin value terminated by layers of opposite spin. For example, the configuration:

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

is constructed from a basic unit of three two-bands followed by one three-band. We denote this $\langle 2\bar{2}2\bar{3}\rangle$ where, if necessary, bars are used to indicate that the spins lie antiparallel to the magnetic field ($s_i = -1$). In the absence of a magnetic field, the spins ↑ and ↓ are energetically equivalent and it is unnecessary to use the bar notation, and so a stacking sequence such as $\langle 2\bar{2}\rangle$ can be more simply written as $\langle 2\rangle$. Useful parameters which will be needed later are:

$$\kappa = \tfrac{1}{2}+\delta = -J_2/|J_1| \quad \text{and} \quad \eta = H/|J_1|. \quad (3)$$

The ground state (zero temperature state) of the ANNNI model in the absence of a magnetic field is shown in fig. 2*a*. For $J_1 > 0$ and $J_2 > 0$, the spins in the layers normal to the unique axial direction will be parallel, thus resulting in the ferromagnetic ground state $\langle\infty\rangle$. For $J_1 < 0$ and $J_2 > 0$, a ground state consisting only of 1-bands, $\langle 1\rangle$, will satisfy both interactions. However, for $J_2 < 0$ there is competition between first and second neighbour interactions. For $|J_1/J_2| > 2$ the first neighbour dominates the states $\langle\infty\rangle$ or $\langle 1\rangle$ persist. However, for $|J_1/J_2| < 2$ the second neighbour interaction results in a ground state comprised entirely of 2-bands, $\langle 2\rangle$. On the boundary between $\langle\infty\rangle$ and $\langle 2\rangle$ all states which contain no 1-bands have the same energy, because any such state can be constructed from lengths of $\langle 2\rangle$ and $\langle\infty\rangle$. Similarly, on the line between $\langle 1\rangle$ and $\langle 2\rangle$ all phases containing only 1- and 2-bands have the same energy. The boundaries along which the ground state is infinitely degenerate are known as multiphase lines. It should be noted that the $\langle\infty\rangle{:}\langle 1\rangle$ boundary is not a multiphase line.

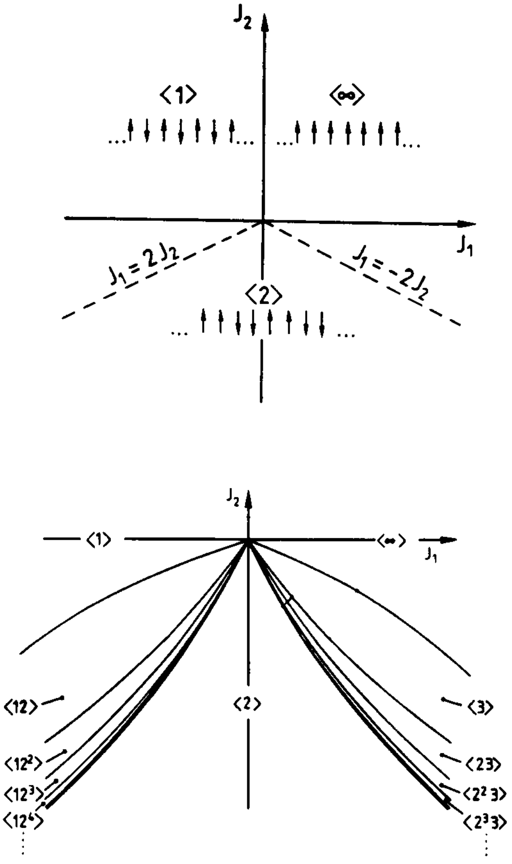

FIG. 2. (*a*) Ground state of the ANNNI model in the absence of a magnetic field, and (*b*) schematic low-temperature diagram of the ANNNI model.

As summarized by Price and Yeomans (1984), the effect of temperature on the ANNNI model in zero-field has been investigated by using a combination of low-temperature series and linear programming techniques (Fisher and Selke, 1981). An isothermal section of the ANNNI phase diagram at non-zero temperatures is given in fig. 2*b*. Near each multiphase line there is an infinite sequence of stable phases, $\langle 2^{m-1}3\rangle$, $m = 1,2,3\ldots$ between $\langle 2\rangle$ and $\langle\infty\rangle$, and $\langle 12^m\rangle$, $m = 1,2,3\ldots$, between $\langle 1\rangle$ and $\langle 2\rangle$. The phases are separated by first-order phase transformations. As m increases the phase fields become very narrow, with the width of the m^{th} field of the order $\exp(-8mJ_0/kT)$.

Several authors (e.g. Smith and Yeomans, 1983; Pokrovsky and Uimin, 1982) have analysed the phase diagram of the ANNNI model in an applied field. When a magnetic field is applied to the system, the spins ↑ (parallel to the applied field) and ↓ (antiparallel to the applied field) become energetically distinct. The application of a magnetic field favours the development of a ferromagnetically aligned state, $\langle\infty\rangle$; consequently the stabilization of antiferromagnetic states, such as $\langle 2\bar{2}\rangle$, requires larger values of $|J_2|$. This is reflected in the ground state of the ANNNI model in an applied magnetic field for $J_1 > 0$ (shown in fig. 3*a*), by the transformation of the multiphase point ($\kappa = \frac{1}{2}$, $\eta = 0$) into two multiphase lines, $\eta = 2\delta$, for $\eta > 0$, and $\eta = -2\delta$ for $\eta < 0$. At non-zero temperatures infinite sequences of commensurate phases appear near each multiphase line for $|\eta| < 1$. For sufficiently large fields, phases of the type $\langle(\bar{2}2)^{n-1}\bar{2}3\rangle$ are stable near $\eta = 2\delta$ and $\langle(2\bar{2})^{n-1}2\bar{3}\rangle$ near $\eta = -2\delta$ ($n = 1,2,3$). As expected on physical grounds, these phases form an infinite subset of those stable in zero field, which comprises all phases which have a finite magnetization in the direction of the field. The phase boundary between $\langle\infty\rangle$ and $\langle\bar{\infty}\rangle$ is not a multiphase line, and no new phases will appear as the temperature is raised.

The situation for $J_1 < 0$ is more complicated as shown in fig. 3*b*. Note that in a finite field $\langle\bar{1}2\rangle$ and $\langle 1\bar{2}\rangle$ are stable even at zero temperature. In the figure dotted lines represent multiphase boundaries which are unstable as the temperature is raised. As shown in fig. 4, at non-zero temperatures the sequence $\langle\bar{1}2(\bar{2}2)^n\rangle$ appears between $\langle\bar{1}2\rangle$ and $\langle 2\bar{2}\rangle$, and $\langle 1\bar{2}(2\bar{2})^n\rangle$ appears between $\langle 2\bar{2}\rangle$ and $\langle 1\bar{2}\rangle$ for all values of η ($n = 1,2,3$). On the boundary between $\langle\infty\rangle$ and $\langle\bar{1}2\rangle$, new phases which are made up of combinations of $\langle\bar{1}3\rangle$ and $\langle\bar{1}2\rangle$, for example $\langle\bar{1}3\rangle$, $\langle\bar{1}2\bar{1}3\rangle$ and $\langle(\bar{1}2)^2\bar{1}3\rangle$, appear as the temperature is raised for sufficiently large η. Similarly phases like $\langle 1\bar{3}\rangle$ and $\langle 1\bar{2}1\bar{3}\rangle$ appear between $\langle 1\bar{2}\rangle$ and $\langle\bar{\infty}\rangle$.

In the next section, we shall show how polysomatic behaviour can be mapped on to the ANNNI model in a field.

Polysomatic behaviour and the ANNNI model in a field. We have seen that members of polysomatic series may be considered as various combinations of two types of structural unit, which we shall term A and B. As in the case of polytypic systems, we shall assume that the stability of polysomatic phases is determined by the interaction between these units. The energy of the interactions is described by the terms J_α^{AA}, J_α^{BB} and J_α^{AB} ($= J_\alpha^{BA}$), where, as in previous sections, $\alpha = 0,1,2$, for interactions between modules within the component polysomatic sheet, and between modules in adjacent layers (*nn*) and second neighbour modules (*nnn*) along the axial direction (∥) respectively.

To define the Hamiltonian of a polysomatic phase, we introduce a variable t_i, which is set equal to 1 if the module on site i is of type A and equal to 0

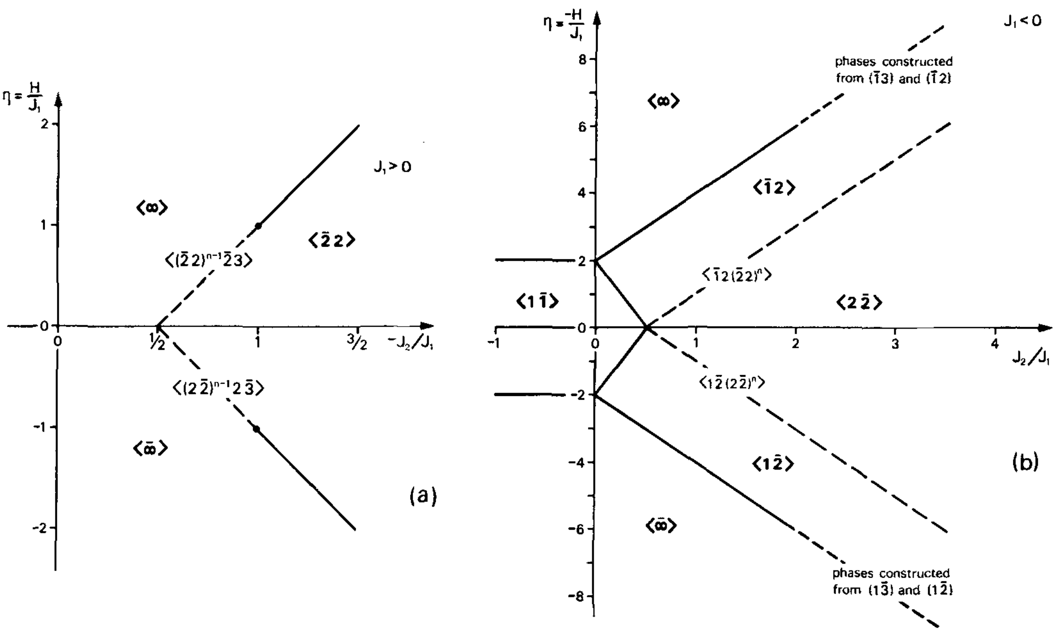

FIG. 3. Ground state of the ANNNI model in a magnetic field for (*a*) $J_1 > 0$ and (*b*) $J_1 < 0$. Ground state phases are indicated in bold type. At finite temperatures infinite sequences of phases appear in the vicinity of the multiphase boundaries, which are depicted by broken lines. The stable sequences are indicated in the figure; in each case n takes integer values 1,2,3....

if it is of type B. The Hamiltonian for a polysomatic compound can then be written as:

$$\mathscr{H} = \sum_{\alpha=0,1,2} [-J_\alpha^{AA}\sum t_i t_j - J_\alpha^{AB}\sum t_i(1-t_j) - J_\alpha^{BA}\sum(1-t_i)t_j - J_\alpha^{BB}\sum(1-t_i)(1-t_j)] - \mu^A\sum_i t_i - \mu^B\sum(1-t_i) \quad (4)$$

in which α takes the values 0, 1, and 2 for $\sum_{nn}^{\perp}$, $\sum_{nn}^{\|}$, and $\sum_{nnn}^{\|}$ respectively, and μ^A and μ^B are the chemical potentials which control the relative abundances of units A and B.

To relate (4) to the Hamiltonian of the ANNNI model in a magnetic field, we make the substitution $s_i = 2t_i - 1$. Hence an A module is represented by $s_i = 1$ or ↑ and a B module by $s_i = -1$ or ↓. The resulting Hamiltonian is, to within a constant term,

$$\mathscr{H} = \sum_{\alpha=0,1,2} [\tfrac{1}{4}(-J_\alpha^{AA} - J_\alpha^{BB} + 2J_\alpha^{AB})\sum s_i s_j + \tfrac{1}{2}(-\mu^A + \mu^B - 2J_0^{AA} + 2J_0^{BB} - J_1^{AA} + J_1^{BB} - J_2^{AA} + J_2^{BB})\sum_i s_i]. \quad (5)$$

This is directly comparable to the Hamiltonian (1) with the choice of variables:

$$J_\alpha = \tfrac{1}{4}(J_\alpha^{AA} + J_\alpha^{BB} - 2J_\alpha^{AB}),\ \alpha = 0,1,2 \quad (6)$$

$$H = \tfrac{1}{2}(\mu^A - \mu^B + 2J_0^{AA} - 2J_0^{BB} + J_1^{AA} - J_1^{BB} + J_2^{AA} - J_2^{BB}). \quad (7)$$

Having established the mapping between the Hamiltonians for the polysomatic series and the ANNNI model in a field, we can re-express the ANNNI phase diagrams (figs. 3 and 4) as chemical potential diagrams. For the special case $J_\alpha^{AA} = J_\alpha^{BB} = 0$, the mapping is simply:

$$J_\alpha = -J_\alpha^{AB}/2 \quad (8)$$

$$H = (\mu^A - \mu^B)/2 \quad (9)$$

in which case the ground state diagram is the same as fig. 3, except for a change of length scales. Other values of J_α^{AA}, J_α^{BB}, etc. have no effect on the nature of the phase boundaries, but do in general change the relative shapes of the phase fields by altering the position and slopes of the phase boundaries. For example, if $J_\alpha^{BB} = J_\alpha^{AB} = 0$ we have the mapping:

$$J_\alpha = J_\alpha^{AA}/4 \quad (10)$$

$$H = \tfrac{1}{2}(\mu^A - \mu^B + 2J_0^{AA} + J_1^{AA} + J_2^{AA}) \quad (11)$$

which results in the ground state diagrams shown in fig. 5. These diagrams have the same relative disposition of phase fields as those in fig. 3; however the positions of the fields and the slopes

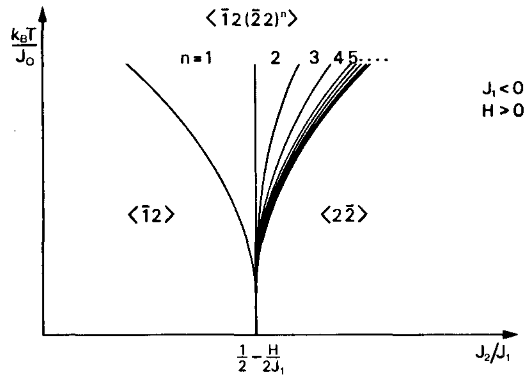

FIG. 4. Schematic low-temperature diagram of the ANNNI model in a field in the vicinity of the multiphase line $\frac{1}{2}$-$H/2J_1$, $J_1 < 0$, $H > 0$, showing how an infinite sequence of commensurate phases spring from a multiphase point.

between the boundaries have been altered as a result of the mapping.

It is now possible to interpret the behaviour of polysomatic materials in terms of the ANNNI model. We can identify each phase of the ANNNI model in a field with a polysomatic structure, by equating the sequence of spin bands with the stacking sequence of the polysome. For example, if in considering the biopyriboles we take M to correspond to $s_i = +1$ or ↑ and P to correspond to $s_i = -1$ or ↓, the codes $\langle \bar{\infty} \rangle$ and $\langle \infty \rangle$ correspond to those of the pyroxene (P) and mica (M) structures, $\langle 1\bar{1} \rangle$ to the amphibole structure (MP), $\langle 2\bar{1} \rangle$ to jimthompsonite (MMP), and $\langle 2\bar{1}1\bar{1} \rangle$ to chesterite ($MMPMP$). We can then use the phase diagrams determined for the ANNNI model in a field to establish which polysomatic stacking sequence would be expected to be stable for given values of μ^A, μ^B, J_α^{AA}, etc. Transformations between polysomes will occur because of changes in chemical potential or in the interaction energies as a function of pressure and temperature. Thus, as the conditions to which a polysome is subjected vary, the point defined by the corresponding interactions and the temperature will describe a trajectory, which may pass through many different polysomatic phases. The exact form and extent of this path, and hence the sequence of stable polysomes, will critically depend upon the relationship of J_α^{AA}, etc., with the external conditions. It is expected, however, that changes in the interaction parameters will be small compared to changes in chemical potential, and that trajectories will generally be approximately parallel to the chemical potential axis.

In this paper, we are not in a position to calculate the relative or absolute magnitudes of the interaction parameters for any given polysomatic series. However, we can use the form of the ANNNI model phase diagrams described above in a qualitative fashion to interpret the behaviour of a variety of polysomatic families. If we consider the biopyriboles, there is no doubt that mica, $\langle \infty \rangle$, pyroxene, $\langle \bar{\infty} \rangle$ and amphibole, $\langle 1\bar{1} \rangle$, are stable phases. By inspection of fig. 3*b*, we can readily see that these structures correspond to ground states of a system in which $J_1 < 0$. It follows from figs. 3*b* and 5*b* that jimthompsonite, $\langle 2\bar{1} \rangle$, could occur as a stable phase in this system if $J_2 < 0$. In such circumstances, the observed sequence of phase changes on the dehydration of talc to the pyroxene enstatite are compatible with a simple trajectory on a phase diagram such as that in fig. 5*b*. If the trajectory has its origin in the $\langle \infty \rangle$ field and follows a path closely parallel to the chemical potential axis, then changes in the chemical potential successively stabilize the $\langle 2\bar{1} \rangle$, $\langle 1\bar{1} \rangle$ and $\langle \bar{\infty} \rangle$ phases. As discussed above, it is possible that chesterite, $\langle 2\bar{1}1\bar{1} \rangle$, only occurs as a metastable phase in nature. This inference is supported by our ANNNI model analysis, in which the $\langle 2\bar{1}1\bar{1} \rangle$ phase is always metastable at finite temperature with respect to the $\langle 2\bar{1} \rangle$ or $\langle 1\bar{1} \rangle$ phases. However, calculations show that the degree of metastability is small near the $\langle 1\bar{1} \rangle$:$\langle 1\bar{2} \rangle$ boundary, and that once formed this phase would be expected to be long lived. We are not in a position however, to state that J_2 in this system is negative. It is quite possible that J_2 is positive for the biopyribole systems and that both jimthompsonite and chesterite only occur as metastable phases. All that we can obtain from the ANNNI approach is the indication that it is possible under suitable conditions for phases of the type $\langle 2\bar{1} \rangle$ to be stable.

Other mineralogical examples of polysomatic behaviour (Thompson, 1978) which can be explained in a comparable manner include the $CeFCO_3$-$CaCO_3$ system discussed previously, the humite series of minerals, chlorites and septachlorites, and the pyroxenoids. The humite minerals can be considered to be made from two units, one which has the olivine (Mg_2SiO_4) structure (O) and the other which has the norbergite ($Mg_2SiO_4 \cdot Mg(OH,F)_2$) structure ($N$). Olivine ($O$) and nobergite ($N$) represent end members of the humite series, which also contains the intermediate phases chondrodite (ON), humite (OON), and clinohumite ($OOON$). By mapping the series (O), ($OOON$), (OON), (ON), and (N) on to the ANNNI phases $\langle \infty \rangle$, $\langle 3\bar{1} \rangle$, $\langle 2\bar{1} \rangle$, $\langle 1\bar{1} \rangle$, and $\langle \bar{\infty} \rangle$, the stability of the humite phases can again be interpreted by reference to fig. 5*b*. Similarly, pyr-

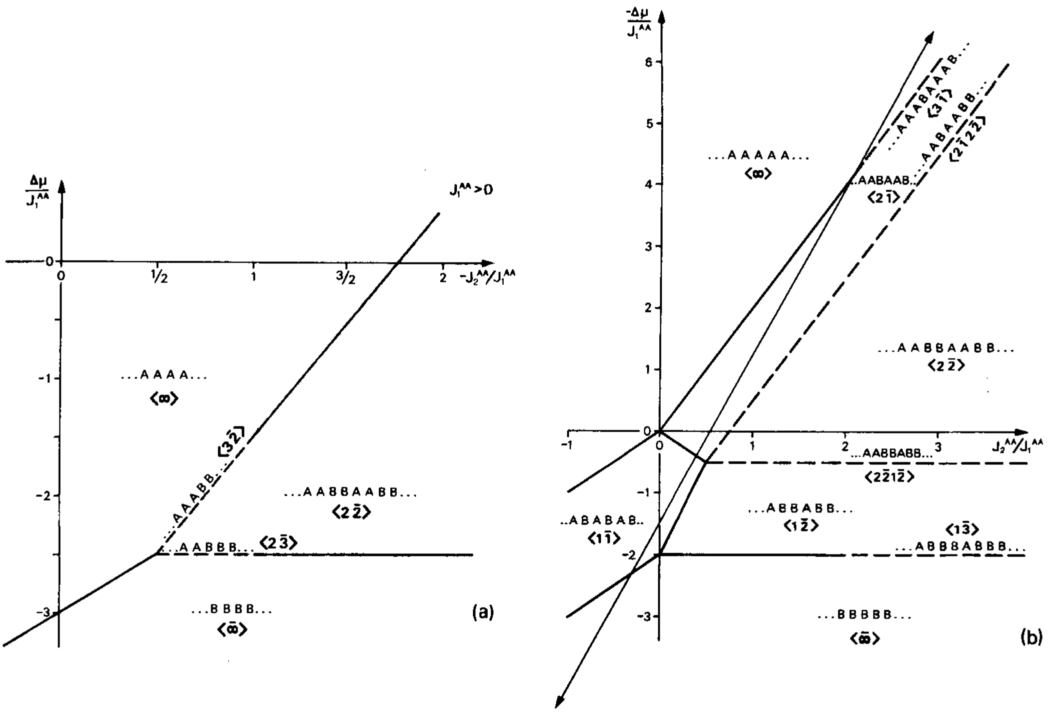

FIG. 5. Ground-state phase diagram of the ANNNI model in a field written in terms of the chemical potential $\Delta\mu = \mu_A - \mu_B$ for the case $J_\alpha^{AB} = J_\alpha^{BB} = 0$, $\alpha = 0,1,2$: (*a*) $J_1^{AA} > 0$; (*b*) $J_1^{AA} < 0$. The ground states and most important finite temperature phases are indicated. In (*b*), a possible trajectory describing the behaviour of biopyriboles is shown.

oxenoids have been described (e.g. Thompson, 1978) as being composed of wollastonite (*W*) and pyroxene-like slabs (*P*), with known forms having structures described by the codes (*W*), (*WP*), (*WPP*), and (*WPPP*). The explanation for the development of these structures is the same as that proposed for the humite group of minerals. Finally, in contrast, the septachlorite and chlorite phases are composed of brucite (*B*) and talc (*T*) layers. Their structures can be described by the stacking codes (*TB*) and (*TTBB*) respectively. These two phases are polytypic modifications within the larger polysomatic series, but nevertheless correspond to adjacent ground state structures $\langle 1\bar{1}\rangle$ and $\langle 2\bar{2}\rangle$ in the ANNNI phase diagram shown in figs. 3*b* and 5*b*.

Conclusion. We have presented an analysis of the ANNNI model in a magnetic field, and have shown how the model can be applied to describe the energetics of polysomatic phases. The ANNNI picture provides a mechanism involving short-range competing interactions through which such phases can exist as stable equilibrium states. Moreover, it indicates, as is indeed observed, that specific configurations of structural units will be favoured. We conclude that the key factors controlling the stability of polysomatic phases are, (*a*) chemical potential, which controls the proportion of the component modules, and (*b*) nature of the competing interactions between first neighbour and second neighbour layers in the structure.

It should be noted, however, that the finite temperature phases of the ANNNI model are stabilized by spins flipping ($\uparrow \rightleftharpoons \downarrow$). This must, of course, be a gross over-simplification of the excitations that lead to structural changes in the real crystal. Nevertheless, the known equilibrium behaviour of several mineralogical polysomatic series, including the biopyribole, pyroxenoid and humite families of minerals appear to be described by our model. In addition, it appears that the polysomatic behaviour of other systems, such as the hexagonal barium ferrites (Van Landuyt *et al.*, 1973, 1974) and the recently described hydro-serpentines (Mellini *et al.*, 1985), may also be broadly described by the ANNNI model. However, these systems are insufficiently characterized to enable thermodynamically stable and metastable phases and behaviour to be distinguished. Further work on such complex polysomatic series will enable the limitations of our application of the ANNNI picture to be determined. From our present understanding of mineral behaviour, however, we conclude that the ANNNI model provides a powerful way of describing the factors which determine the crystal structures of a large range of materials, that can be described in terms of constituent structural units or modules. We believe that our approach will prove to be increasingly useful, not only in understanding mineral systems such as those described here, but also in describing inorganic and metallurgical structural families.

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