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ABSTRACT

The results of a recent low temperature analysis by Fisher and Selke of the Axial Next-Nearest Neighbor Ising (ANNNI) model appear to have some relevance to long period superstructures in certain binary alloys, in particular Ag_3Mg and Au_3Zn. This indicates that configurational entropy may be more important in such structures than had been previously thought.

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I. INTRODUCTION

Spatially modulated structures in condensed matter, in which some local property such as chemical composition, magnetization, or electric polarization varies in a periodic (or quasi-periodic) fashion, are known to occur in many materials. Various theoretical approaches have been suggested to explain such phenomena, including high temperature expansions [1], mean field theories [2-5], low temperature expansions [6], and soliton mechanisms [7]. One of the simpler theoretical models known to exhibit modulated behavior is the Axial Next-Nearest Neighbor Ising or ANNNI model. In d-dimensions, the model consists of ferromagnetic couplings within (d-1)-dimensional layers and competing ferromagnetic and antiferromagnetic interactions between nearest and next nearest neighbors respectively along the lattice direction orthogonal to the layers. This model was first introduced by Elliot [2] in 1961 who analyzed it within the framework of a molecular field approximation in an attempt to understand the magnetic behavior of rare earths. Other studies of the ANNNI model include high temperature expansion [1] and Monte Carlo Simulations [8,9].

Of particular interest, however, is a recent low temperature analysis of the ANNNI model by Fisher and Selke (FS) [6]. The results of these authors, for dimension $d > 2$, indicate the existence of an infinite sequence of distinct, commensurate, modulated phases. In the plane of temperature T versus competition parameter $\kappa = -J_2/J_1$ (the ratio of the coupling strengths of the axial next-nearest and axial nearest neighbors) an infinite number of phases springs from a multiphase point at ($T = 0$, $\kappa = \frac{1}{2}$), for which the ground state is infinitely degenerate (See Fig. 1a).

The purpose of this report is to illustrate the possible relevance of the ANNNI model to certain modulated structures that have been observed in binary alloys. Long period structures in alloy systems were originally explained by Sato and Toth [10,12] who contended that the formation of long periods lowers the electronic energy. This idea was extended by others [13,14] and a reasonable agreement with data on certain alloy systems was obtained. In the current version of this theory, the size of the long period is therefore determined solely by minimization of the electronic energy. In the ANNNI model, on the other hand, entropy effects play a central role in determining the periodicity of the modulation. Such entropy considerations may be important in some alloy systems that exhibit long periods as will be seen below.

II. MODEL AND NOTATION

The language used in this report will be that of magnetism. Specifically, we will be summarizing the analysis by FS of an Ising model, which is one of the simpler models for magnetism. An Ising model consists of uniaxial spins situated at each lattice site, the term "uniaxial" simply meaning that the spins can be oriented only "up" or "down" along a predetermined axis. The spin variable S_i at lattice site i can take the values ± 1. Pair-wise interactions depending on the relative spin orientation of the pair are assumed, usually between near neighbors.

The correspondence between such a model and a binary alloy system is made by treating $S_i = 1$ as an A atom at site i and $S_i = -1$ as a B atom at site i. Thus, one sees that the configurational entropy of an Ising model is equivalent to that of a binary alloy provided that

interaction energies are adequately described by pehnomenological pair interactions. Such a description of binary alloys purely in terms of pair interactions has been quite successful in describing various types of ordering. To complete the correspondence between the Ising model and the alloy one identifies the magnetic field H of the Ising model with the difference in chemical potential, $\mu = \mu_B - \mu_A$, of the A and B type atoms since H and μ enter the partition function in the same way.

The model analyzed by FS has the following Hamiltonian in the absence of a magnetic field:

$$H = -\tfrac{1}{2} \sum_{i,j,j'} (J_o S_{ij} S_{ij'} + J_1 S_{ij} S_{i\pm1,j} + J_2 S_{ij} S_{i\pm2,j}), \qquad (1)$$

where S_{ij} is the spin on the j^{th} site of layer i. The (2-dimensional) layers are stacked so that the directions from site S_{ij} to sites $S_{i\pm1,j}$ are perpendicular to the layers. If we define q' as the coordination number within a layer, then the full coordination number is q'+2. The full three dimensional lattice could be, for example, simple tetragonal or simple hexagonal. A spin S_{ij} interacts ferromagnetically ($J_o>0$) with its q' nearest neighbors, $S_{ij'}$, within the i^{th} layer. The interaction between spin S_{ij} and its two axial nearest neighbors, $S_{i\pm1,j}$, is also ferromagnetic ($J_1>0$). The coupling between S_{ij} and its two axial next-nearest neighbors is antiferromagnetic, with $J_2 = -\kappa J_1 < 0$. There is then a competition between the axial nearest and axial next-nearest neighbor couplings.

As a result of the in-layer interaction J_o being ferromagnetic, the low temperature states of this model will be comprised of layers each of which has all its spins oriented the same way. The phases predicted by FS have a periodic layered structure denoted $\langle 2^j 3 \rangle$, which means a sequence of 2j lattice layers alternately pointing two "up" and two "down"

followed by three layers having the opposite orientation of the previous pair. Figure 1a is a schematic drawing of the low temperatures phase diagram for the model in the κ-T plane. Also, shown in the figure is an example of a $<2^3 3>$ structure.

III. THE ANTIFERROMAGNETIC CASE

It is of interest to consider the ANNNI model for the case in which all three interactions, J_o, J_1, and J_2, are antiferromagnetic. This situation is most easily analyzed when the lattice is simple tetragonal, which results in the basal planes (layers) being simple square lattices. A simple square lattice with antiferromagnetic nearest neighbor interactions possesses a ground state in which each site has four nearest neighbors with the opposite orientation so that there are no "wrong bonds." Thus, we avoid the frustration that would occur, for example, in a hexagonal lattice. The results of FS can then be directly applied to this case in the following manner.

First, notice that each lattice site in a simple tetragonal structure can be labeled as "even" or "odd" such that each even (odd) site has four in-layer nearest neighbors and two axial nearest neighbors which are all odd (even). Now, changing the signs of J_o and J_1 is equivalent to a spin flip transformation in which all the spins on odd (or even) sites are reversed. To see this, recall the Hamiltonian from (1) above and write the partition function Z as

$$Z = \sum_{\{s\}} e^{-H/kT}$$

$$= \sum_{\{s\}} \exp\left\{\frac{1}{2kT}\left[\sum_{i,j,j'} (J_o S_{ij} S_{ij'} + J_1 S_{ij} S_{i\pm1,j}) + \sum_{i,j} (J_2 S_{ij} S_{i\pm2,j})\right]\right\},$$

where $\sum_{\{s\}}$ indicates a sum over all possible spin configurations and where we have separated the Hamiltonian H in the exponent into two summations, one involving the in-layer and axial nearest neighbors and the other involving the axial next-nearest neighbors. In the nearest neighbor summation the products of spin variables always appear in even-odd pairs. Thus, in a given configuration, a transformation that reverses all spins at the odd (or even) sites is equivalent to changing the signs of J_o and J_1. Since the axial next-nearest pairs always occur in an even-even or odd-odd combination, this transformation does not affect the term involving J_2. Now, the summation $\sum_{\{s\}}$ is over all possible configurations, so

$$Z(J_o,J_1,J_2) = Z(-J_o,-J_1,J_2).$$

The conclusion is that the equilibrium configurations for the case J_o,J_1, $J_2<0$ are obtained from those for the case $J_o,J_1>0$, $J_2<0$ simply by reversing the spins on all odd (or even) sites.

Figure 1b is a schematic drawing of the phase diagram in the κ-T plane for the case $J_o,J_1,J_2<0$, where now κ is defined by $J_2 = \kappa J_1$. This diagram is really the same as that in Figure 1a, being obtained by applying the aforementioned transformation to all the phases predicted by FS. An example of this transformation applied to a one-dimensional chain is illustrated in Figure 2 showing how a structure $<2^j3>$ is transformed to $<2^{j+1}1>$. An example of the $<2^41>$ phase on the full three-dimensional lattice is shown in Figure 3a.

What follows in the next section is a summary of the analysis of FS but, for illustrative purposes, modified to treat the case of antiferro-

magnetic nearest neighbor interactions. (As mentioned above, the analysis of this case is equivalent to the analysis of the case considered by FS). The reader may omit this next section without missing the purpose of this report.

IV. LOW TEMPERATURE ANALYSIS

Because the in-layer exchange integral J_o is negative, in the ground state a given spin in one of the layers will have the opposite orientation of its four nearest neighbors in the layer. Clearly, there are two ways to obtain this condition for a given layer and one can then label each layer as type α or type β. The relation between these two types of layers can be seen in Figure 3. The ground state and low temperature states of the system can be described by specifying the type of each layer, e.g. α or β. FS make such a description in terms of k-bands, which are sequences of k adjacent layers of the same type terminated at both ends by layers of the opposite type. For the ANNNI Hamiltonian with all interactions antiferromagnetic, it turns out that in the ground state there will be only 1-bands and 2-bands because, for $\kappa < 1$, (with κ defined by $\kappa = J_2/J_1$) any bands larger than these will tend to increase the energy. Minimization of the ground state energy indicates that for $\kappa > \frac{1}{2}$ a (2,2) antiphase state, or $\langle 2^{\infty} \rangle \equiv \langle 2 \rangle$ state in the notation described above, is stable. In other words, the ordering of the layers is $\alpha\alpha\beta\beta\ldots$ For $\kappa < \frac{1}{2}$, the ordering of the layers is antiferromagnetic, i.e., $\alpha\beta\alpha\beta\ldots$, which is denoted as $\langle 1 \rangle$. Exactly at the point $\kappa = \frac{1}{2}$, the ground state (T = 0) turns out to be infinitely degenerate. Any sequence of 2-bands and 1-bands has the same energy at this multiphase point. The systematic low temperature expansion of FS determines which of the

ground states at the multiphase point remain as stable phases at finite temperature. The expansion parameter for this low temperature analysis is $w \equiv e^{-2|J_o|/k_BT}$, the Boltzmann factor for a wrong in-layer bond. Convergence of the free energy expansion requires that w be sufficiently small.

Now one extends the concept of a k-band to the more general concept of band sequences, denoted by μ or ν, which are binary sequences of 1's and 2's representing a particular sequence of 1-bands and 2-bands in the system. Corresponding to these band sequences are the structural variables ℓ_μ which, for a system of L layers, are defined by

$$L_\mu = \ell_\mu L,$$

where L_μ is the number of band sequences of type μ in a particular configuration of the system. An important point here is that the free energy expansion turns out to be linear in these structural variables [6, 15]. Structural relations among the ℓ_μ (they are not all independent) and the constraint $\ell_\mu \geq 0$ for all μ restrict the allowed states to a convex polytope p in a structural space L spanned by a set $\{\ell_\mu\}$ of standard (independent) structural variables. In general, the reduced free energy f can be written

$$f = -\frac{F}{Nk_BT} = a_o(w,x;\kappa) + \sum_\nu a_\nu(v,x;\kappa)\ell_\nu \qquad (2)$$

where the dependence of the coefficients a_ν on $x \equiv e^{-2|J_1|/k_BT}$ is indicated. The quantity a_o is independent of the structural variables.

The problem is now reduced to one of linear programming; the free energy is minimized on a vertex of p [16]. All vertices found up to second order in the low temperature expansion represent periodic structures. Predictions for higher order also indicate that minimiza-

tion of the free energy occurs at vertices which represent periodic structures.

To proceed with the low temperature expansion, one begins by examining the first excited states, i.e., states with one spin flip which introduces a factor $w^{q'}$ into the expansion of the free energy as a result of q' "wrong" bonds within a layer. One finds that only three structural variables (ℓ_2, ℓ_{21}, and ℓ_{211}) are necessary to describe the states in this first order approximation. It turns out that one new periodic structure, namely <21>, has a region of stability in the κ-T plane. That is, for a certain range of values of κ and T the free energy is minimal on the vertex of p which represents the <21> structure. Of course, at this stage of the analysis, the polytope p is in a space of only three dimensions (spanned by ℓ_2, ℓ_{21}, and ℓ_{211}). The dimension of the structural space increases rapidly with the order of the expansion. Fortunately, a general argument (proved by FS) restricts the search for new external vertices (stable phases) to a small region of the polytope. In the κ-T plane, the region of stability for the <21> structure appears in between the regions where <1> and <2> are stable. (See Figure 1b.)

On the <21>:<2> "boundary", that is, on the locus in the κ-T plane on which the free energies of the <21> and <2> phases are equal, one finds that in fact all phases comprising only the sequences μ=2 and μ=21 have the same free energy to first order. Phrased differently, all phases with only 2-bands and 1-bands such that there are no adjacent 1-bands have the same free energy to first order. It is possible, then, that some new phase is stable in the vicinity of this boundary. Indeed, in second order, one finds that the <221> phase has a region of

stability. However, the <1>:<21> boundary turns out to be stable to all orders and a true first order phase transition occurs there.

The appearance of the new <221> phase in second order necessitates consideration of the new boundaries <21>:<221> and <221>:<2>. The inductive argument of FS, appropriately modified to the present case, indicates that the general $<2^{k-1}\ 1>$:$<2^{k}\ 1>$ boundary, which appears in k^{th} order, is stable in all subsequent orders. However, the general $<2^{k}\ 1>$:<2> boundary, also appearing in k^{th} order, is not a true boundary. In the vicinity of this boundary a new phase $<2^{k+1}\ 1>$ has a region of stability.

One can show that $<2^{k+1}\ 1>$ is in fact the only possibility for a new structure in the vicinity of the $<2^{k}\ 1>$:<2> pseudoboundary; no others need be considered. The stability of this phase is a consequence of the fact that the coefficient

$$a_{2^{k}1} \approx w^{kq'}\,(k+1)(1-x^{2})(1-x^{2\kappa})^{k}$$

of the structural variable $\ell_{2^{k}1}$ in the expansion (2) of the reduced free energy is positive thus allowing f to become maximal when $\ell_{2^{k}1}$ takes on its maximum allowed value.

Similarly, at the $<2^{k-1}\ 1>$:$<2^{k}\ 1>$ boundary one needs to consider only one possible interpolating structure, namely $<2^{k-1}\ 1\ 2^{k}\ 1>$. The corresponding coefficient

$$a_{2^{k-1}\ 1\ 2^{k}\ 1} \approx -w^{(2k-1)q'}\,x^{2-2\kappa}(1-x^{2\kappa})^{k}$$

is negative in leading order indicating that this phase is not stable within the range of validity of the low temperature expansion.

Figure 1b shows a schematic phase diagram of the system in the κ-T plane. Notice that as the temperature is varied at some fixed $\kappa \gtrsim \frac{1}{2}$ the

system goes through a series of discrete transitions. These transitions are all of first order as can be seen by the fact that the interfacial tension $\sigma_k(T)$ between the phases $\langle 2^{k-1}\ 1\rangle$ and $\langle 2^k\ 1\rangle$ is positive:

$$\sigma_k(T) = \tfrac{1}{2}\, k_B\, T\, x(1-x)^{2k}\, w^{(2k-1)q'}$$

By carrying out the calculations to third order, that is counting all possible configurations for three spin flips, one can determine the boundary $\kappa_2(T)$ between the phases <21> and <221> correct to third order in $w^{q'}$ (See FS). Subsequent boundaries are found using the recursion relation

$$\kappa_{k+1}-\kappa_k = \tfrac{1}{2}\frac{k_B T}{|J_1|}(1-x^2)[1-x+6xuw^{q'}(1-\tfrac{1}{3}x^2)]$$
$$(k+\tfrac{1}{2})[k+1-(k+2)w^{q'}u]w^{q'k}u^{k-1} \qquad (3)$$

where $u = 1-x\exp[-2w^{q'}(2-3x+x^3)]$. This recursion formula was used to generate the plot in Figure 4 which shows the phase widths in the κ-T plane with the positions of the boundaries referenced to $\kappa_2(T)$. Each phase is characterized by a mean wavevector

$$q_j = \pi j/(2j+1)\ a,\ (j = 0,1,2,\ldots),$$

where a is the lattice parameter. For large k, equation (3) indicates that the widths of the phase regions decrease exponentially rapidly. The mean wave vector ultimately varies quasicontinuously as

$$\bar{q}(T,\kappa) - q_{\langle 2\rangle}(T) \sim 1/\ln\{[\kappa_{\langle 2\rangle}(T) - \kappa]^{-1}\},$$

where $\kappa_{\langle 2\rangle}(T) \geq \kappa$ is the locus in the κ-T plane which defines the extent of the <2> phase, and $q_{\langle 2\rangle} = \pi/2a$ is the wavevector of this phase.

V. RELEVANCE TO ALLOY SYSTEMS

We are currently aware of two alloy systems which form modulated structures suggestive of the configurational entropy effects manifested in the low temperature phases of the ANNNI model. Figure 3a illustrates a possible phase of the ANNNI model for the cases J_o, J_1, $J_2 < 0$, while Figure 3b is for the case J_o, $J_2 < 0$ and $J_1 > 0$. Comparing these structures with those of Ag_{3+x} Mg and Au_{3+x} Zn shown in Figures 3c and 3d [17,18], one sees a remarkable similarity.

Direct comparison of the structures in Figure 3 is of course not valid because the lattices are not equivalent and the stoichiometry of the alloy systems is of the type A_3B. However, we propose the following model. Divide the fcc lattice of Ag_3Mg into 2 tetragonal sublattices as illustrated in Figure 5 and do the same for Au_3Zn. One sublattice will consist purely of Ag (or Au). The second sublattice will be an equal mixture of the two atomic species in the alloy. If one assumes at the outset that there is some mechanism which accounts for a DO_{23} type ordering (Figure 6) and then one adds to the model a set of effective pair interactions J_o, J_1 and J_2 which act appropriately within the second sublattice, then one can explain the structures shown in Figures 3c and d.

Clearly, this is a rather qualitative explanation and much work, both theoretical and experimental, is needed to gain an understanding of the mechanism responsible for the structures of Ag_3 Mg and Au_3 Zn.

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FIGURE CAPTIONS

Figure 1a. Schematic phase diagram of the axial next-nearest neighbor Ising or ANNNI model in the plane of temperature T and competition parameter $\kappa = -J_2/J_1$ with $J_1 > 0$ and $J_2 < 0$. This diagram shows the infinite sequence of commensurate, layered antiphase states, $\langle 2^j 3\rangle$, at low T. This figure was taken from Fisher and Selke.

Figure 1b. Schematic phase diagram of the ANNNI model for the case $J_1 < 0$ and $J_2 < 0$. The shape of the diagram is the same as in Figure 1a, but here the phases are of the type $\langle 2^{j+1}1\rangle$.

Figure 2. Linear chains of Ising spins with long period structures $\langle 2^3 3\rangle$ and $\langle 2^4 1\rangle$ with periods 9a and 18a respectively, where a is the lattice constant. The $\langle 2^4 1\rangle$ structure can be obtained from the $\langle 2^3 3\rangle$ structure by reversing all spins on odd (or even) sites as indicated by the arrows. Notice that a structure $\langle 2^j 3\rangle$ with j odd has period (2j+3)a and transforms to $\langle 2^{j+1}1\rangle$ with period (4j+6)a, while a structure $\langle 2^j 3\rangle$ with j even has period (4j+6)a and transforms to $\langle 2^{j+1}1\rangle$ with period (2j+3)a.

Figure 3a. The $\langle 2^3 1\rangle$ structure on a tetragonal lattice with $J_0, J_1, J_2 < 0$. Notice the two types of layers labeled α and β (See text) which are related by an antiphase vector $\vec{t} = \frac{\vec{b}}{2}$ as shown. Also pictured are two tetragonal unit cells illustrating the ranges of the three interactions J_0, J_1, and J_2.

Figure 3b. The $\langle 2^3 3\rangle$ structure on a tetragonal lattice with $J_0, J_2 < 0$, and $J_1 > 0$.

Figure 3c. Structure observed in Ag_3Mg (Ag = ●, Mg = ○). The antiphase vector is

$$\vec{t} = \frac{\vec{a}_o + \vec{b}_o}{2}$$

expressed in terms of the standard basis vectors for an fcc structure. Notice the similarity to Figure 3a.

Figure 3d. Structure observed in Au_3Zn (Au = ●, Zn = ○). Notice the similarity to Fig. 3b.

Figure 4. Variation of the mean wave vector $\bar{q}(T,K)$ with κ at fixed, low temperature. The scale $\Delta_o(T) \sim \exp(2q'|J_o|/k_BT)$ is defined precisely in FS. In this plot, $\exp(-2q'|J_o|/k_BT) \cong 0.5$.

Figure 5. Subdivision of the Ag_3Mg structure (or Au_3Zn) into two tetragonal sublattices, one consisting entirely of Ag (or Au), the other consisting of half Ag and half Mg (or half Au and half Zn).

Figure 6. The DO_{23} structure.

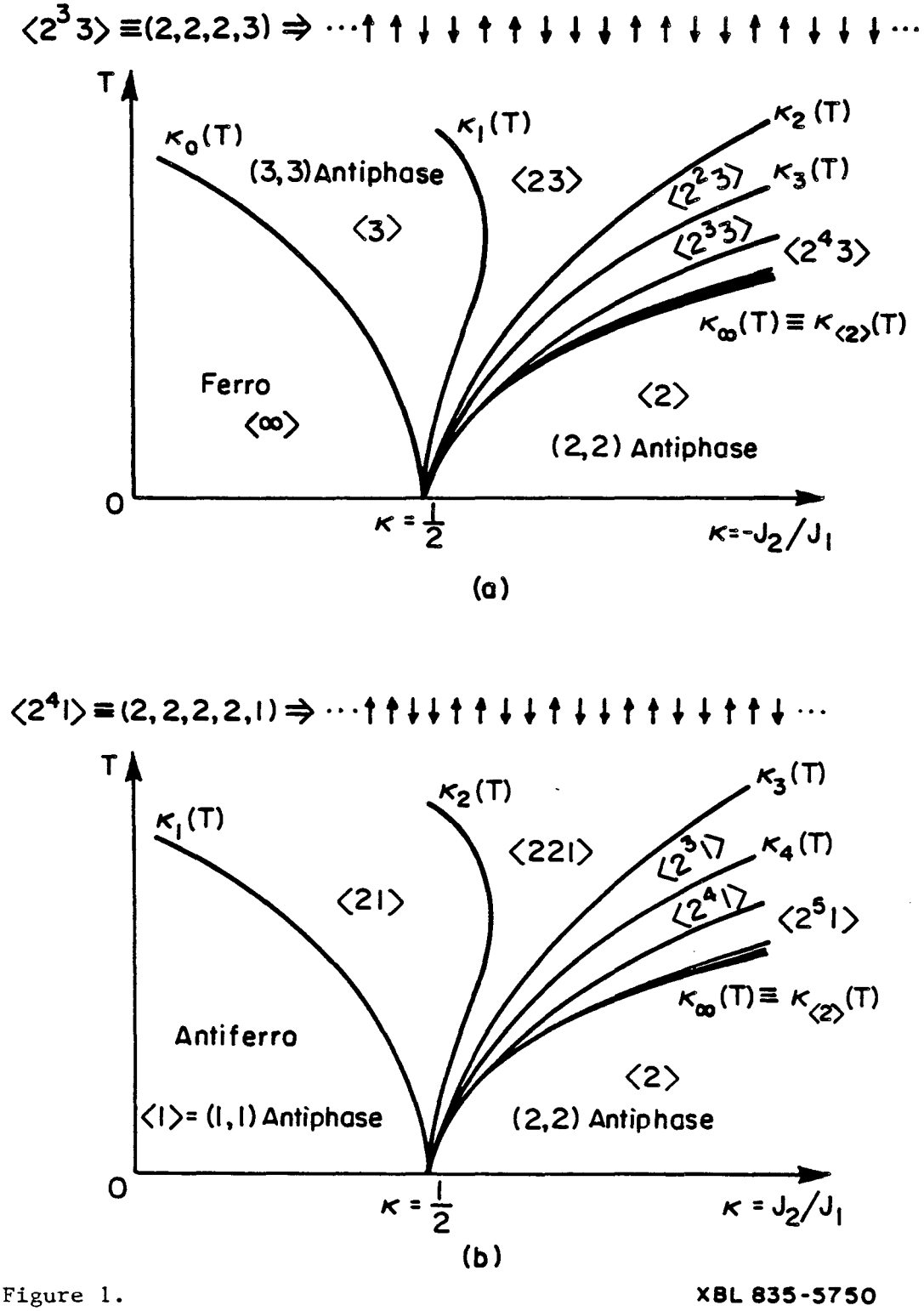

Figure 1.

XBL 835-5750

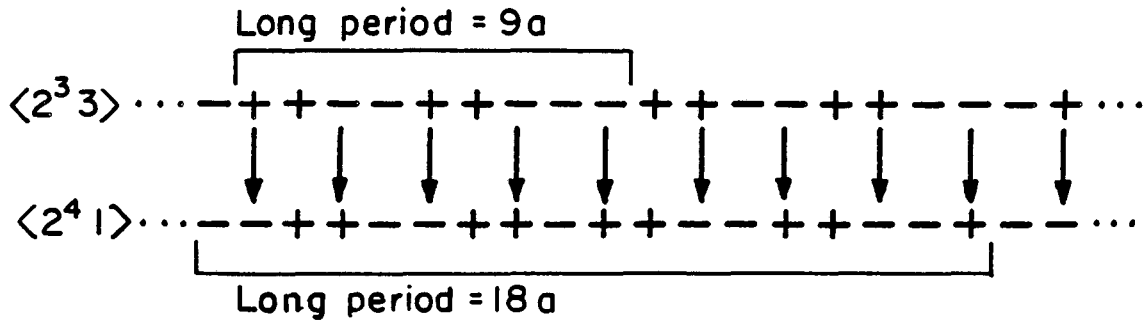

Figure 2.

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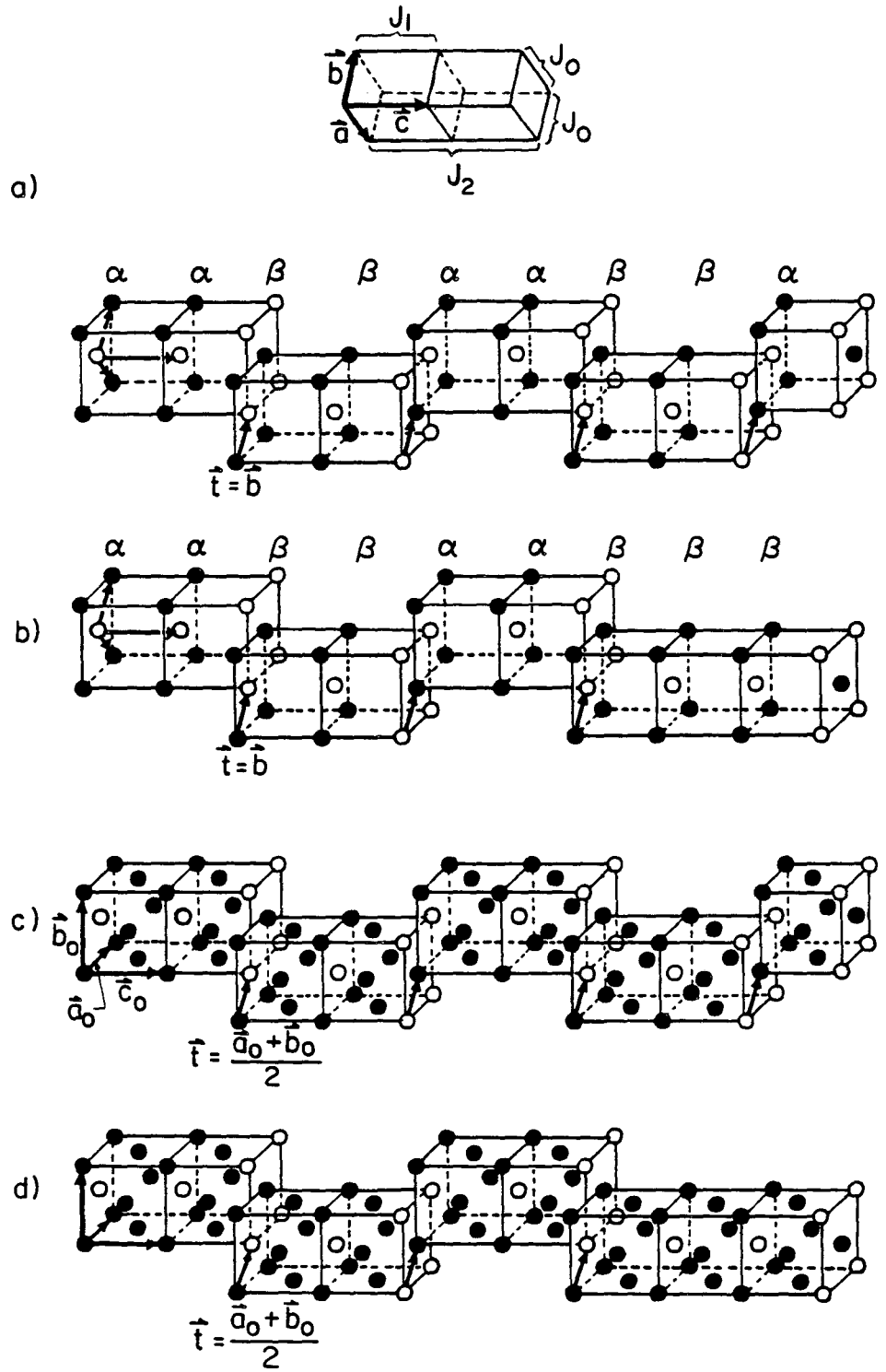
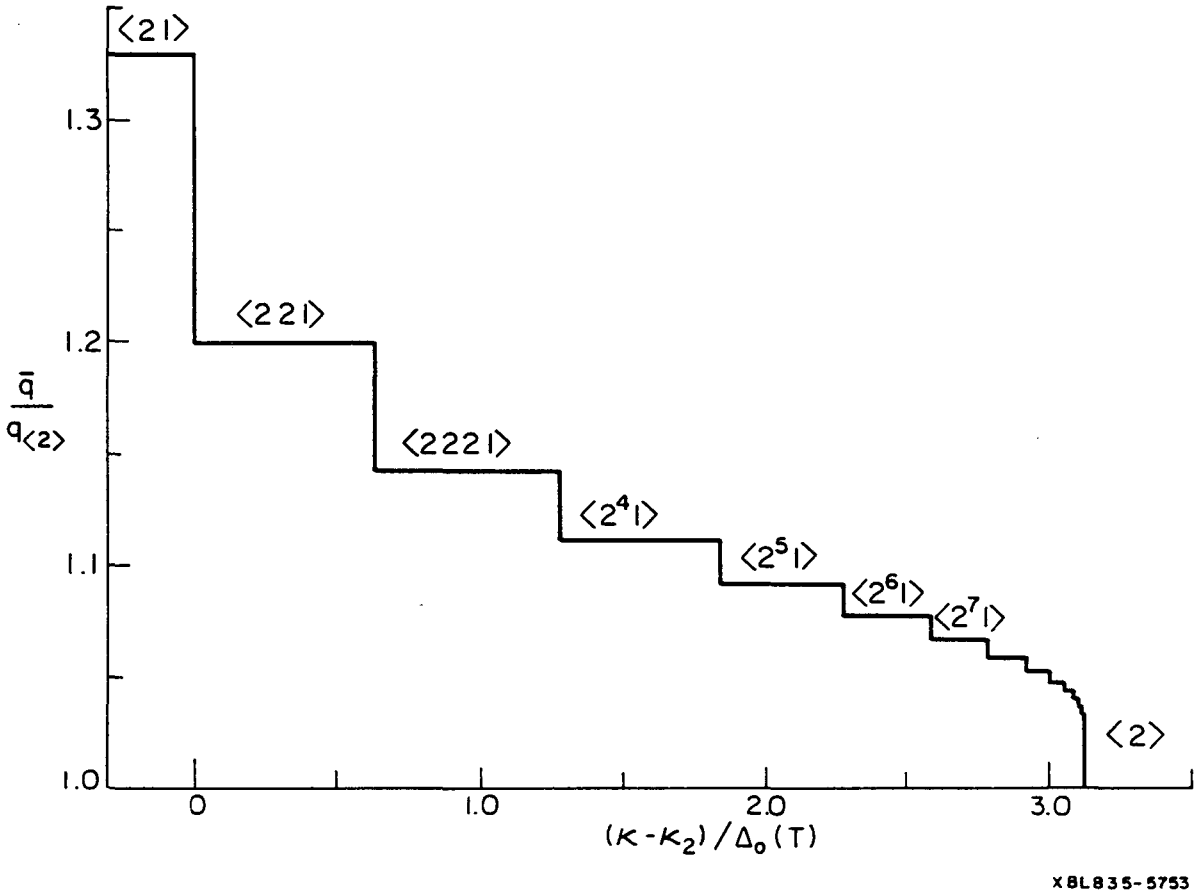


Figure 3.

XBL 835-5752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⟨2⁶1⟩
⟨2⁷1⟩
⟨2⟩
1.3
1.2
1.1
1.0
q̄ / q⟨2⟩
0
1.0
2.0
3.0
(κ-κ₂)/Δ₀(T)
X8L835-5753

Figure 4.

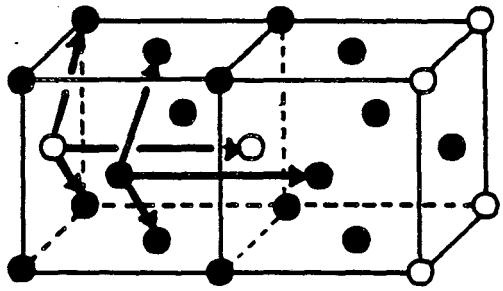

Figure 5.

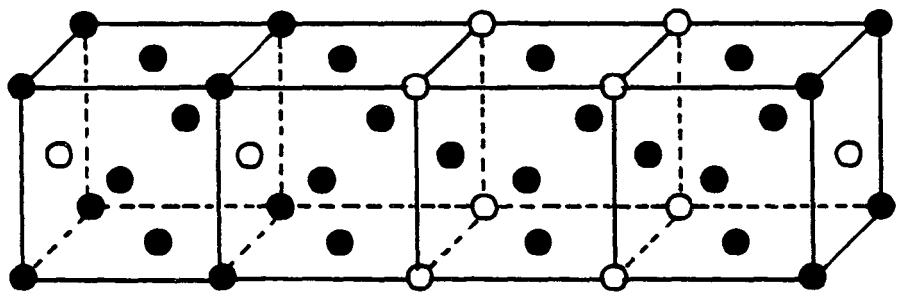

Figure 6.

XBL 835-5754

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