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J. Kulik and D. de Fontaine

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by

J. Kulik and D. de Fontaine
Department of Materials Science
and Mineral Engineering
University of California
and
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

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J. KULIK AND D. de FONTAINE
Lawrence Berkeley Laboratory, Materials and Molecular Research Division,
University of California, Berkeley, California 94720, U.S.A.

ABSTRACT

The cause of the stability of long period superstructures is still something of a mystery. Typically, two very different models have been proposed: according to model I, the period of the superstructure (or modulation) is determined by lowering of the electronic energy resulting from the formation of a new Brillouin zone. According to model II, competing short-range interactions tend to produce long-period structures, the wavelength of which is determined by configurational entropy considerations. Model I is exemplified by the Sato and Toth theory, apparently applicable to long-period superstructures in Cu-Au, for example. Model II is exemplified by the Axial Next Nearest Neighbor Ising Model, for which a low-temperature free energy expansion has recently been given by Fisher and Selke. The latter model appears to apply to long-period superstructures in Ag_3Mg.

INTRODUCTION

Long period superlattices resulting from periodic antiphase boundaries are known to occur as stable structures in many binary alloy systems [1]. One of the best known of such structures is that of CuAu II, which is stable from about 380°C to about 410°C. Below this temperature range, the tetragonal CuAu I phase, consisting of planes of gold and copper atoms alternating along the c-axis, is stable. The orthorhombic CuAu II phase can be viewed as a regular long period modulation imposed on the CuAu I structure. This modulation occurs along one direction perpendicular to the c-axis and is a result of antiphase boundary planes at which the gold and copper layers are interchanged. Similar periodic antiphase structures have also been found in a wide range of CuAu alloys (Cu_3Au exactly at stoichiometry is a notable exception.) and in a large number of other binary systems.

A curious feature of these long period superlattices is the fact that the size M of the antiphase domains as measured by diffraction experiments is often not an integer. An explanation for this phenomenon was offered by Fujiwara [2] who showed that sharp superstructure reflections corresponding to non-integral M could result from appropriate mixing of domains of different sizes. An alternative model presented by Jehanno and Pério [3] allows for a certain amount of disorder at each antiphase boundary with the result that the boundaries become sinuous and the spacing fluctuates about the average M value.

Portier et al. [4] have recently pointed out that Fujiwara's model seems to apply to the alloy system Ag_3Mg. Studies on this alloy suggest that M varies discontinuously with concentration, taking only values which can be specified by well defined ratios. In contrast, the average domain size M of CuAu varies continuously with concentration, often taking on incommensurate values as indicated by the overlap without superposition of satellites from adjacent fundamental reflections in diffraction patterns [3,5]. The systems Cu_3Pd and Cu_3Pt seem to fall in the same category as CuAu while Au_3Zn may be classed with Ag_3Mg [4-7].

The current theory of the stability of long period superlattices, due to Sato and Toth [8-10], relies on electronic energy considerations. The formation of periodic antiphase domains introduces new Brillouin zones in reciprocal space. In particular, antiphase domains of the appropriate size will cause a new Brillouin zone boundary to come in contact with the Fermi surface, thus lowering the overall electronic energy. (This is similar to what happens in the Peierls instability of one-dimensional metals.) This idea was made more quantitative by Tachiki and Teramoto [11] and others [12,13] and reasonable agreement between calculations and real systems was obtained.

A significant feature of this theory is that the structure of the superlattice is determined solely by the energy of the conduction electrons; entropy plays no role in determining the periodicity. There are, however, a number of statistical mechanical models based on effective pair interactions, particularly Ising models with competing interactions, that have been theoretically examined and found to possess long period modulated structures as stable phases [14-20]. Entropy effects play an important role in the stabilization of these structures. The main point which we wish to emphasize in this article is that entropy effects may be essential in understanding the long period superlattices of some alloy systems.

THE ANNNI MODEL

Pair-wise interaction models applied to binary alloys are not always well justified from a band theoretical aspect. Nevertheless, Ising models have been very significant in predicting various ordered structures in binary systems [22,23]. It is in this light that we discuss the results of a recent low temperature analysis by Fisher and Selke (FS) of the Axial Next-Nearest Neighbor Ising (ANNNI) model [18]. These results appear to have some relevance to certain modulated structures observed in binary alloys [21]. The important point here is that unlike previous theoretical attempts to explain long period superlattices in alloys, descriptions of such systems in terms of Ising models with competing interactions (like the ANNNI model) incorporate entropy effects. These effects turn out to play a key role in determining the long periods in such models.

A significant aspect of the ANNNI model, especially when applied to alloys with an fcc structure, as will be done below, is the necessity of relatively long range pair interactions. A full explanation of such long range effective interactions in a real system will undoubtedly require consideration of electronic phenomena whose effective ranges are known to be relatively long [24].

The Hamiltonian for the ANNNI model on a simple tetragonal lattice in the absence of a magnetic field can be written

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

where the index i labels the (001) planes and j labels the sites within these planes. The spin variable S_{ij} can take values ±1. In the case analyzed by FS, a spin S_{ij} interacts ferromagnetically ($J_o>0$) with its four nearest neighbors, $S_{ij'}$, within the ith (001) plane. The interaction between S_{ij} and its two nearest neighbors, $S_{i\pm1,j}$, along the [001] direction (axial nearest neighbors) is also ferromagnetic ($J_1>0$). The coupling between S_{ij} and its two axial next-nearest neighbors, $S_{i\pm2,j}$ is antiferromagnetic, with $J_2 = -\kappa J_1 < 0$, so there is a competition between the axial nearest and axial next-nearest neighbor couplings. Figure 1 indicates the range of the three interactions on a simple tetragonal lattice.

Because J_o is ferromagnetic, the low temperature states of this model will be comprised of layers, i.e., (001)-type planes, each of which has all its spins oriented the same way. However, the analogy with an alloy system

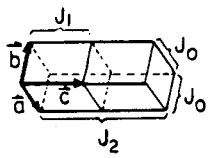

Figure 1.

Two unit cells of a tetragonal lattice showing the ranges of the interactions J_o, J_1 and J_2.

is better realized if $J_o<0$. Since the layers are square lattices with only nearest neighbor interactions, there are no frustration effects within these layers (as there would be, for example, in a plane hexagonal lattice), and one can easily make the transformation from positive to negative J_o. In the low temperature states, then, the (001) planes are antiferromagnetically ordered when $J_o<0$.

The results of the low temperature analysis of the ANNNI model by FS show the existence of an infinite sequence of distinct, commensurate, modulated phases. The antiphase structure of the predicted states is denoted $\langle 2^j 3\rangle$, j = 0, 1, 2,. . ., which means a sequence of 2j lattice planes antiphased every two planes along the [001] direction followed by three planes antiphased with respect to the preceding pair. Fig. 2 illustrates the $\langle 2^3 3\rangle$ antiphase structure on the tetragonal lattice defined in

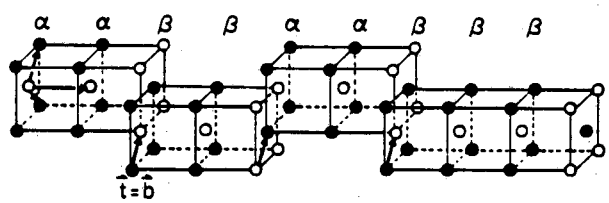

Figure 2. The $\langle 2^3 3\rangle$ structure predicted by the ANNNI model with $J_o<0$, $J_1>0$, and $J_2<0$. Planes labeled α and β are antiphased with respect to each other. $\vec{t}$ is the antiphase vector. The basis vectors are the same as those in Figure 1.

Fig. 1. Fig. 3, taken from FS is a schematic drawing of the full low temperature phase behavior of the ANNNI model in the κ-T plane.

It is also of interest to consider the case where J_1 is antiferromagnetic. This situation is, in fact, equivalent to the previous case and the results may be obtained directly from those of FS by performing a spin flip transformation on the $\langle 2^j 3\rangle$ states such that all spins on every second (001)-type plane are reversed. This results in $\langle 2^j 3\rangle$ being transformed into $\langle 2^{j+1} 1\rangle$. The (3,3) antiphase state, denoted $\langle 3\rangle$, is transformed to $\langle 21\rangle$ and the (2,2) antiphase state, or $\langle 2\rangle$ state remains the same to within a lattice translation of [001]c, where c is the lattice parameter along the [001] (axial) direction. The following one-dimensional example illustrates the transformation where the arrows indicate which spins are to be reversed:

$\langle 2^3 3\rangle$: ...++−++−−−++−−++−−−+...

↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓

$\langle 2^4 1\rangle$: ...−−++−−++−++−−++−−+−−...

This transformation is valid because the Hamiltonian (1) is invariant under a spin-flip in each second layer and simultaneous reversal of the sign of J_1.

Diffraction experiments on structures like $\langle 2^j x\rangle$, where x = 1 or 3, will produce satellite reflections indicative of a long period equal to (2j+x)c for j odd or (2j+x)2c for j even. It is likely, however, that only

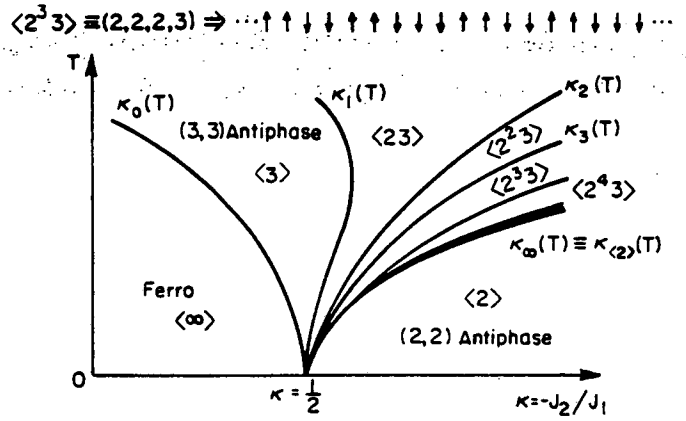

Figure 3. Schematic phase diagram for the low temperature phases of the ANNNI model (taken from FS).

the strongest satellites would be observable, particularly for large j. These would be the ones corresponding to the average domain size $\bar{M} = (2j+x)/(j+1)$.

RELEVANCE TO BINARY ALLOYS

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 4a shows the structure of

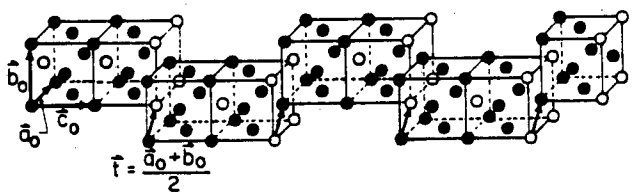

Figure 4a. Antiphase structure observed in Ag_3Mg (from Portier et al.). $\vec{t}$ is the antiphase vector.

Ag_3Mg deduced by Portier et al. [4]. Figure 4b shows the structure of $Au_{3+}Zn$ reported by Van Tendeloo and Amelinckx [25]. Comparing Figure 4b with Figure 2 one sees a remarkable similarity. In particular, one should compare the tetragonal ANNNI model with the tetragonal sublattice which contains half Au and half Zn atoms. This phase of Au_3Zn can be designated $\langle 2^3 3\rangle$ in analogy with Figure 2. Likewise, Figure 4a is analogous to the ANNNI model with $J_1<0$. The $\langle 2^j 1\rangle$ structure in Ag_3Mg has been observed for j = 2, 3, 4 and 6, depending on the concentration of Mg. The $\langle 2\rangle$ phase (DO_{23} structure) has, of course, also been seen [4].

Investigations of the temperature dependence of the average domain size in Ag_3Mg [26] and $Au_{3+}Zn$ [27] have indicated behavior opposite to that expected from the phase diagram of Figure 3. However, an alloy system is a complex one and the analogy with the ANNNI model may very well neglect other

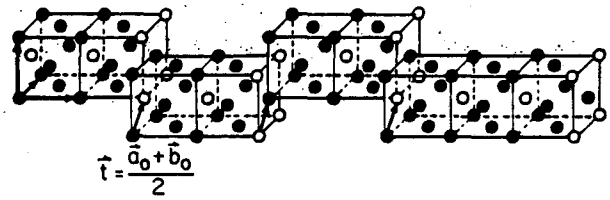

Figure 4b. Antiphase structure in Au_3Zn reported by Van Tendeloo and Amelinckx.

processes that affect the superlattice. The dependence of M on concentration may turn out to be the more interesting aspect.

The point which we wish to emphasize is that in the alloy systems Ag_3Mg and Au_3Zn competition between effective pair interactions may be essential in understanding the formation of long periods in these alloys. As a final remark, we call attention to experimental results on the alloy system Cu_3Al. This system has been observed to have antiphase domains of size 4 and 5. Periodic structures which can be denoted <4>, <45>, <445>, and <5> have been reported [28]. We conjecture that there is an analogy between this system and an anisotropic Ising model on a tetragonal lattice with competing interactions along the c-axis between nearest neighbors and up to fourth nearest neighbors. A one spin-flip analysis has indicated the existence of a <4> state and a <5> state. We conjecture that a higher order analysis performed in the manner of FS will reveal the existence of states with the structure <4j5>. The system Cu_3Al, like Ag_3Mg, may be one in which effective interactions compete with each other, and the configurational entropy determines the stable structure. Clearly, much work, both theoretical and experimental, is needed in the study of long period superlattices in binary alloys. We currently plan to begin an experimental study on such systems.

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