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ORDER-DISORDER PHENOMENA IN COMPLEX ALLOYS: THE CASE OF A15-BASED SUBSTITUTIONAL ALLOYS

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ABSTRACT

We first discuss the applicability of the Generalized Perturbation Method to the study of ordering phenomena in complex alloys for which stability properties are electronically driven. In particular, according to previous work, it is recalled that a 3D-generalized Ising model is appropriate to address the problem of configurational order in A15-based substitutional alloys. A ground state analysis of this model, including 1st, 2nd and weak 3rd and 7th pair interactions, generates two new ordered states at the composition A_5B_3 and A_7B , apart from the well known A_3B configuration. The stability of these predicted configurations is examined as a function of temperature and concentration by means of standard statistical techniques. The results are discussed in relation with the experimental situation.

Many alloys and compounds with a tetrahedrally close packed (tcp) structure [1-3] display a high degree of atomic ordering. For this class of systems, there is a straight correspondence between the crystalline structure itself and a uniquely defined atomic configuration. The fact that their formation is realized in a very narrow range of concentration, as is the case for the Laves phases, is usually attributed to a dominant size factor or strain field effect[1]. In contrast, for a limited number of these tcp structures, including A15 and sigma, their formation is known to be mostly electronically driven. In that case, departure from a specific stoichiometric composition is observed and accounted for by the ability for the species to undergo sizable deformations. Because the concept of substitutional solid solution is applicable, it is interesting to study the peculiarities of atomic ordering processes, as a function of temperature and concentration, which are associated with the complexity and the non-symmetry of their crystalline structure. In addition, after the recent discovery of a quasiperiodic icosahedral phase in Al_6Mn [4], a connection with tcp phases was strongly supported[5], and, therefore, the question of how ordering mechanisms and local icosahedral frustration can assist the formation of quasiperiodic phases is of major interest. Although our study essentially deals with a perfect, undeformable tcp crystalline structure, here the A15 one, we will see that standard ideas regarding ordering mechanisms and order-disorder transitions are not applicable because of the existence of crystallographically non-equivalent lattice sites.

In a previous work[6], we have shown that an extension of the Generalized Perturbation Method[7] to transition metal alloys possessing an A15 crystalline structure could

describe order-disorder properties as accurately as for alloys based on simple lattices. In other words, for any particular configuration of an A15-based alloy A_2B_{1-c} , specified by a set of spinlike variables σ_n , where σ_n equals +1 or -1 depending on whether or not site n is occupied by an A species, the configuration-dependent part of the internal energy can be conveniently approximated by the following Hamiltonian:

$$H = \sum_{(nm)} J_{nm} \sigma_n \sigma_m - \sum_{\alpha} h_{\alpha} \sum_n \sigma_n$$

where J_{nm} is a pair interaction between sites n and m given by:
 $J_{nm} = 1/4 (J_{nm}^{AA} + J_{nm}^{BB} - 2J_{nm}^{AB})$.

Fig. 1 Primitive unit cell of the A15 crystalline structure. $\square$ and $\circ$ refer to sites of the bcc sublattice ($\alpha = I$) and the set of chains ($\alpha = II$) respectively.

In principle, because of the existence of two inequivalent sites in the A15 structure (see Figure 1), belonging either to the body centered cubic sublattice ($\alpha = I$) or the three orthogonal sets of linear chains ($\alpha = II$), distinct on-site energies h_{α} have to be taken into account. In the following, we will ignore this extra complication which, from electronic structure calculations, appears to be negligible[6]. Hence the last term of the RHS of the hamiltonian will be written as $-h \sum_n \sigma_n$, where h is the chemical potential. In addition, to keep the study simple, we will not consider the concentration dependence of the pair interactions as we should, from a proper electronic treatment based on the GPM. As for the case of alloys based on simple lattices, it should be pointed out that the GPM provides a clear connection between electronic structure calculations and statistical analysis via the formal introduction of an Ising model for a proper description of order-disorder phenomena. Formation energies as well as pair (and multi-site) interactions are uniquely defined quantities obtained from quantum mechanics. This Hamiltonian can also be referred to for subsequent treatments such as i) the search of the most probable ground states at zero temperature T , and ii) stability properties at $T \neq 0$ K, in conjunction with a variational method, within the Bragg-Williams or the Cluster Variation Method (CVM) - approximation[8], or with Monte-Carlo simulations[9].

Starting from the above introduced Ising model with only first and second neighbor pair interactions, J_1 and J_2 , standard analysis[10] leads (after the symmetry $A \leftrightarrow B$ is applied) to the existence of three probable ordered configurations: A_3B (the so-called A15 ordered state, of βW type) and A_5B_3 , named hereafter F, A15 and X respectively (see Figure 2). This new X phase is characterized by sublattice I fully occupied by A atoms whereas the three orthogonal sets of linear chains are alternatively occupied by A and B species. In order for the three states to exist (the most interesting case), the ratio J_2/J_1 should remain between $1/4$ and $1/2$, with a positive J_1 .

Fig. 2 Ground states based upon the A15 crystalline structure. For each configuration, the alloy composition is indicated in parenthesis.

The analysis was extended to the third neighbor pair interaction J_3 (see Figure 1) without introducing any additional ordered states, provided J_3 is small compared with J_1 and J_2 , a hierarchy in agreement with electronic structure results[6]. The study of the low energy excitation spectrum for the X phase shows that longer range interactions need to be introduced in order to stabilize the X phase at finite temperature and prevent the disordering of the chains (i.e. to lift the degeneracy of the X phase). The first interaction which fulfills this requirement is a weak seventh pair interaction, J_7 which connects two parallel chains (see Figure 1). For positive J_7 , a new ground state at the composition A_7B , called Y in Figure 2, is obtained. This state corresponds to sublattice II fully occupied by A atoms whereas an "antiferromagnetic order" characterises sublattice II.

In agreement with previous electronic structure studies, we will consider the following hierarchy:

$J_1, J_2 \gg J_3, J_7$ with $1/4 < J_2/J_1 < 1/2$, $J_3 > 0$ and $J_7 < 0$. With this selection, the three states F, A15 and X can be stable at finite temperature. Low temperature expansions can be performed for the various phase equilibria[11] and analytic expressions for the low temperature part of the phase diagram can be obtained. Surprisingly, the Bragg-Williams approximation gives an exact description of the low temperature A15 (A_3B) - X (A_5B_3) phase equilibrium. In the whole range of temperature and concentration, equilibrium thermodynamical properties

were derived from CVM calculations and compared with those obtained from a Bragg-Williams treatment as well as with Monte-Carlo simulations. The results are very similar and detailed analysis will be given elsewhere[11]. In Figure 3 we present a typical A15-based order-disorder phase diagram for $J_2/J_1 = 0.4$, $J_3/J_1 = 0.0$ and $J_7/J_1 = -0.01$ in the canonical representation (i.e. T versus c), as computed with an appropriate CVM approximation.

Fig. 3 Theoretical A15-based order-disorder phase diagram for $J_2/J_1 = 0.40$, $J_3/J_1 = 0.0$ and $J_7/J_1 = -0.01$. The diagram is symmetric about $c = 1/2$.

Some comments are in order. First, at the stoichiometric composition A_3B , there is no real order-disorder transition as T increases, as illustrated in Figure 4 where the long range

order (LRO) parameter η , given by $\eta = \frac{\langle \sigma_{II} \rangle - \langle \sigma_I \rangle}{2}$ is plotted as a function of temperature.

($\langle \sigma_{\alpha} \rangle$ refers to an ensemble average value of the point correlation function on sublattice α).

Below the composition A_5B_3 , a two phase field exists at low temperature between X (A_5B_3) and $\bar{X}$ (A_3B_5), the two phases differing only by the occupancy of sublattice I. Similar to the liquid-gas transition, here applied to sublattice I, X transforms continuously into $\bar{X}$ and vice-versa, hence the notation X' in Figure 3. A similar remark applies to the phase equilibrium between A15 (A_3B) and F (A). Finally the second order line which delimits the domain of stability of X' in temperature refers to the disordering of the "antiferromagnetic order" along the linear chains. This behavior is illustrated in Figure 4 where the LRO parameter η , defined as

$\eta = -\frac{\langle \sigma_{II}^1 \rangle - \langle \sigma_{II}^2 \rangle}{2}$ is given as a function of temperature. ($\langle \sigma_{II}^1 \rangle$ and $\langle \sigma_{II}^2 \rangle$ correspond to the ensemble average values of the point correlation functions of two consecutive sites along a chain).

Although A15 is the only phase persisting at high temperature, the short range order should be different above A15 (A_3B) and at lower concentration. Above A15 (A_3B), as T increases, the Bragg peaks associated with the A15 structure broaden due to short range order (SRO) diffuse scattering, whereas at lower concentration, in addition to the Bragg peaks of the

A15 structure, additional SRO diffuse peaks at typical positions (100), (001), (111), (221), (212), ... (in units of $2\pi/a$, where a is the lattice parameter of the A15 structure) should be observed.

Fig. 4 LRO parameter η as a function of temperature: a) for $c = 3/4$ and

$$\eta = \frac{\langle \sigma_{II} \rangle - \langle \sigma_I \rangle}{2}, \text{ (solid line),}$$

b) for $c = 1/2$ and

$$\eta = \frac{\langle \sigma_{II}^1 \rangle - \langle \sigma_{II}^2 \rangle}{2} \text{ (dashed line)}$$

corresponding to the parameters given in Figure 3.

We have investigated order-disorder phenomena in A15-based alloys and predicted new ordered phases which might exist. For those alloys which display an A15 structure in a broad range of concentration such as V-Rh, V-Ir and V-Ga, it would be interesting to study carefully SRO diffuse scattering intensities as obtained by x-rays or neutrons in an attempt to reveal the X phase which may exist at low temperature. In the meantime we have shown that the existence of crystallographically inequivalent sites in a lattice produces a number of peculiarities, a remark which should apply to other cases as well, as for example non-equivalent interstices in interstitial alloys.

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