PHASE TRANSFORMATIONS IN HEXAGONAL-CLOSE-PACKED ALLOYS:
ANALYSIS WITH THE CLUSTER VARIATION METHOD

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ABSTRACT

We present a study of the hexagonal close-packed (hcp) Ising model for binary alloys
within the cluster variation approximation. Groundstates of order stabilized by nearest-neighbor
(NN) pair, triplet, and tetrahedron interactions were determined using the cluster configuration
polyhedron method; no previous hcp ground-state study has considered all of these interactions.
We predict physically realizable groundstates with stoichiometries A, AB (3 distinct structures),
A2B, A3B, and A4B3. The previously unreported A4B3 structure is stabilized by multiatom (i.e.
triplet, tetrahedron) interactions, while the others are stabilized by the two NN pair interactions.
The Cluster Variation Method (CVM) was used to calculate the finite-temperature phase-equilibria
for prototypical binary alloys. We present the first ordering phase diagrams computed with the
CVM which contain all relevant groundstates for both isotropic and anisotropic NN pair
interactions.

INTRODUCTION

In many problems concerning phase-equilibria of binary alloys A1−xB, the
thermodynamic behavior of (solid) alloys can be approximated by an Ising model. The
configurational energy associated with a given arrangement of atoms is then calculated using the
Ising model Hamiltonian with a specified set of effective interaction parameters. These interactions
can either be pairwise or multiatom, depending on the level of complexity required by the problem
at hand. In general, the problems associated with the configurational statistical mechanics become
more intractable as the range of the interactions increases. For either antiferromagnetic or
ferromagnetic interactions on the chosen lattice, there are two distinct, yet related, domains of
study: 1) Analysis of the structures with the lowest configurational energy (ground-states) as a
function of composition at T=0 K, and 2) Analysis of finite-temperature phase behavior.

Several approximate methods of computing groundstates of the Ising model on a given
lattice have been used, most of which revolve around constructing a set of constraints on some set
of configurational variables. The methods of Allen and Cahn1 and Kajinami2 are the most widely
used for ground-states of binary alloys. Ground-state analyses have been performed for numerous
Ising lattices (see Ref. [3] for a complete listing), but in the field of alloy theory, perhaps the most
widely studied of these are the fcc and bcc lattices. Groundstates of the hexagonal-close-packed
structure have not been analyzed as extensively as those of fcc and bcc.

The study of finite-temperature equilibrium can be carried out using any number of
statistical mechanical methods. The cluster variation method (CVM)4 is a simple and very useful
method for studying first-order phase transitions. The CVM has been formulated in several ways,
but the form that will be used here is based on the orthonormal cluster expansion of Sanchez et
al.5 This formulation of the CVM involves an expansion of the energy in terms of multiset
cluster functions; cluster probabilities used for computation of the entropy are also written as an
expansion in these variables. The ground-state problem can also be formulated in this framework,
where one uses the cluster expansion of the probabilities to obtain the necessary constraints in the
analysis. We will hereafter refer to this ground-state method as the cluster configuration
polyhedron method (CCPM). The interested reader is referred elsewhere for a detailed
discussions of the CCPM3,6 and the CVM3-6.

This paper presents an analysis of phase stability on the hcp Ising lattice using the
formalism of the CVM. The study of hcp groundstates has not been performed previously using
the CCPM. In this paper, we consider the hcp analog of the fcc tetrahedron approximation: the
tetrahedron–triangle (TT) approximation. The complete hcp ground-state search is performed in
this approximation, for which interactions corresponding to clusters up to the nearest-neighbor
I. HCP GROUNDSTATE ANALYSIS

The hexagonal-close-packed (hcp) structure is shown in Figures 1 (a) and (b); Fig. 1(b) is the (001) projection of Fig. 1(a). The NN pairs indicated in Fig. 1(a) as $V_1$ and $V_2$, are crystallographically distinct, but when the hcp $c/a$ is ideal, they span the same distance within the structure. In the remainder of this study, when $V_1 = V_2$, we will say that the structure is isotropic; if $V_1 \neq V_2$, the structure will be referred to as anisotropic. Even with an ideal $c/a$ ratio, the interactions $V_1$ and $V_2$ may be different because they are distinct by symmetry.

In the CCP method, one needs to consider some set of clusters (referred to as the basis or maximal clusters) in order to obtain the constraints used in the ground-state (GS) problem. In a calculation which accurately treats correlation within the NN distance, it is necessary to consider all symmetry-distinct clusters which span this distance. The analysis of all symmetry-distinct clusters up to NNN has already been performed for the hcp structure. An accurate hcp CVM entropy must consider subclusters of both the NN tetrahedron ($1,2,3,4$) and the basal plane triangle ($1,6,7$) (see Figure 1(a)). These two basis clusters lead to 7 subclusters: one point, two NN pairs (sites $1,2$ and $1,6$ with corresponding interactions $V_1$ and $V_2$), three NN triangles ($1,2,3$, $1,2,4$, and $1,6,7$), and the NN tetrahedron. The cluster functions which correspond to these seven clusters of sites form the basis set for the tetrahedron–triangle (TT) CVM approximation in hcp. The ground-state analysis will thus be performed in the seven-dimensional configuration space spanned by these cluster functions.

The configurational energy of an alloy can be written using the cluster expansion of Sanchez et al., and with this expansion one can also express the probability of observing a certain configuration on a given cluster of sites (the cluster probability for that configuration). In the hcp TT approximation, there are 7 independent cluster functions with 16 distinct cluster probabilities. In order to obtain physically valid solutions, each of the cluster probabilities must be greater than or equal to zero. If each cluster probability is individually set equal to zero, the resulting equation defines a hyperplane in the seven-dimensional vector space spanned by the cluster functions. It can be shown that the set of all 16 hyperplanes forms a convex polytope of dimension 7 called the configuration polyhedron (CP). It is well-known in such problems that the minimum values of the energy will be obtained when the cluster functions correspond to one of the vertices of the CP. The enumeration of all vertices of a polytope defined by its hyperplanes is a (linear-programming) problem which occurs frequently in operations research, and the same methods can be used in the current analysis.

The vertices of the configurational polytope were enumerated using the algorithm proposed by Mattheiss. The full vertex search in the hcp TT approximation yielded a total of 29 vertices. All ground states with stoichiometries other than $AB$ are symmetric with respect to the exchange of $A$ and $B$ atoms (i.e. there is a 1/1 degeneracy). The number vertices with the degeneracy removed is 18: 7 $AB$ and 11 non-$AB$ ground states are predicted. The output of the vertex search is the set of cluster functions which correspond to that particular vertex. This information is not directly useful, so one must construct the physical structure(s) which correspond to the vertices. In many cases, more than one structure can give rise to a given set of cluster functions. This is the case, for example, when one has the possibility of structures related by anti-phase boundaries (APB's), e.g. the $L_12$ and $D_0{\bar{2}}$ superstructures of the fcc lattice. The structures which have the same cluster functions are energetically degenerate from the standpoint of the finite cluster expansion. If the range of the expansion is increased, i.e. a larger maximal cluster is chosen, then the degeneracy can be broken.

When the vertices from the GS search are analyzed, we find that only 7 of the 18 distinct vertices are constructible; the other 11 are inconstructible (i.e. they do not correspond to real structures). The ground states predicted are as follows: $AB$ (I), $AB$ (II), $AB$ (III), $A_2B$, $A_3B$, $A_3B$, and pure $A$. The $AB$ (I), $AB$ (II), and $A_3B$ phases give rise to an infinity of structures (degenerate at the level of TT) which are simply related by APB's. We will only consider the parent structures and not their related APB phases. The most common experimentally observed hcp-based superstructures are those with Strukturbericht designations $B_1$ (AB(I)), $B_9$ (AB(I)), and $B_9$ (AB(II)). In an attempt to obtain consistent nomenclature, we have given new designations for the $A_2B$, $A_3B$, and $AB$ (II) phases which
follow the Strukturbericht system as closely as possible: C49h, D7h, and B40, respectively.

In the TT approximation, it is possible to have multibody interactions, i.e., triangles and the tetrahedron. In order to ascertain which of the vertices in the groundstate analysis are stabilized by only effective pair interactions, we can write the energies of all vertices considering pair interactions \( V_1 \) and \( V_2 \) only. The lowest energy vertex is then computed as a function of interaction ratio \( (V_2/V_1) \) and normalized chemical field \( (\mu/V_1) \), thus yielding a ground-state map. A map can be constructed for \( V_1 \) either positive or negative (corresponding to ordering and clustering, respectively), although we will only present the case for \( V_1 > 0 \). The ground-state map for \( V_1 < 0 \) only contains two groundstates: A3 (disordered hcp, \( \alpha = V_2/V_1 < \mu/6V_1 \)), and B3 (AB(III), \( \alpha > \mu/6V_1 \)). The ground-state map for \( V_1 > 0 \) is given in Figure 1(c); in each region of the map, the stable phase is given along with its unit cell. This map agrees exactly with results of Kikuchi and Cahn\(^7\) for \( \alpha > 0 \), although these authors did not consider the possibility of multiatom interactions. All constructible ground states in Fig. 1(c) except the A4B3 phase \( (D7h) \) are stabilized by pair interactions. In addition, one inconstructible ground state with stoichiometry A3B2 is stabilized by NN pairs (shaded region, Fig. 1(c)). \( D7h \) is degenerate with both B40 and A3 along the double-bold line: triplet interactions are needed to break this degeneracy.

All but one of the vertices present in our analysis appear in several previous pair groundstate studies\(^10\)-14 which used only pair interactions. Structures which were not obtained in the present analysis were either next-nearest-neighbor groundstates, or were actually degenerate structures. The present approach predicts an A4B3 ground-state \( (D7h) \) which has not been seen in any of the previous studies\(^10\)-14. The absence of this phase from the other author's studies is a direct result of their use of only pair interactions. The \( D7h \) phase does not appear to have a prototype or previously existing Strukturbericht designation, so it is difficult to assess whether it actually occurs in nature.

One very interesting analysis was the study by Kanamori\(^11\) of the plane-hexagonal lattice up to NNN; he predicted an infinite series of groundstates (a devil's staircase) over a certain interaction range. Bichara, Crusius, and Inden mapped the two-dimensional results of Kanamori onto three dimensions, constructing a series of ground-state maps (coordinate axes identical to Figure 2) for various values of the NNN pair interaction \( (V_3) \).\(^15\) The map for \( V_3=0 \) corresponds to the situation in Figure 2, but the map of Bichara et al.\(^13\) predict a devil's staircase of phases in the stability region of the A3B2 inconstructible vertex. The correspondence on the GS map
between the inconstructible $A_3B_2$ vertex and the infinite series of ground-states is by no means coincidental. In fact, in order for the present results to be consistent with Kanamori's, this is the only possible result. The existence of an infinite series of ground-states implies the following: an hcp ground-state analysis using any configurational polyhedron method must have at least one inconstructible vertex at any level of approximation which includes at least the NN pairs. Assume a CP analysis produces a finite number of vertices, all of which are constructible. This implies that, at the level of approximation used, the analysis is exact; there are no more ground-states for that set of interactions. This contradicts the existence of the devil's staircase predicted by Kanamori, and hence there must be at least one inconstructible vertex.

II. HCP CVM PHASE DIAGRAMS

In the cluster variation method (CVM), one sets up a variational free energy which is a function of the multisite correlation functions. For a given entropy approximation (set of cluster functions), one then minimizes the free energy with respect to the correlations. Once the free energy has been computed for all relevant phases, binary concentration-temperature (c-T) phase-diagrams are synthesized using standard common-tangent constructions. In this section, we will be considering CVM calculations of prototypical ordering systems ($V_2/V_1$) for different values of $V_2/V_1$. Ordering will be considered for both isotropic and anisotropic NN pair interactions only; no triplet or tetrahedron interactions will be considered. Calculations are performed in the tetrahedron-triangle (TT) and tetrahedron-octahedron (TO) entropy approximations. The independent clusters in the TT approximation have already been given. The tetrahedron and octahedron maximal clusters are given by sites $(1, 2, 3, 4)$ and $(1, 2, 3, 6, 7, 8)$ in Fig. 1(a); the disordered phase has 14 independent cluster functions with these basis clusters (see Ref. [8]). The phase diagram calculations presented here necessitated computing the free energy for the B19, DO19, and C49h phases. Hence, the independent cluster functions and entropy expressions were derived for all of these structures in both the TT and TO approximations. A complete presentation of the entropy expressions and cluster information for these structures will not be given here.

Examination of the GS map in Fig. 1(c) shows that there are three groundstates at the interaction ratio $V_2/V_1=1$: B19, DO19, and A3. The $A_3B_2$ and C49h phases share a single degenerate point in the GS map with the B19 and DO19 phases when $V_2/V_1=1$, but these phases will not be considered. This is in fact an approximation, since it may be possible for the entropy to stabilize the degenerate phase(s) when $T > 0$ K. A low-temperature expansion could possibly prove rigorously whether one of the degenerate phases would exist at finite temperature. CVM calculations were performed for the first time in the TT and TO approximations for $V_2/V_1=1$ for the three phases in question. The results of the calculations are shown in Fig. 2(a); since no triplet

![Figure 2: hcp CVM phase diagrams. In each diagram, the TT and TO approximations are given by bold and thin lines, respectively. Monte-Carlo results of Crusius and Inden (dashed lines) are superimposed. (a) Isotropic interactions, $\alpha = 1$. (b) Anisotropic interactions, $\alpha = 0.8$. (c) $\alpha = 0$, TT and TO give the same result. It can be seen that as $\alpha$ goes from one to zero, the C49h phase becomes more stable and the B19 and DO19 phases become less stable.](image-url)
interactions are considered, the phase diagram is symmetric around c=0.5, hence only half of it will be shown. The results of the Monte-Carlo calculations of Crusius and Inden\textsuperscript{16} are given with dashed lines. Both the B19 and DO\textsubscript{19} phases are seen to have a large stability range, and both congruently disorder at or near their respective stoichiometries. In addition, there is a eutectoid reaction in which the disordered phase decomposes into the B19 and DO\textsubscript{19} phases. This phase diagram is completely analogous to the prototype fcc phase diagram\textsuperscript{17}. Three things change when the level of approximation is increased from TT to TO: 1) both the DO\textsubscript{19} and B19 order-disorder transition temperatures decrease, 2) the width of the two-phase regions decreases, and 3) the temperature at which the eutectoid reaction occurs decreases relative to the B19 and DO\textsubscript{19} transition temperatures.

In the region of the GS map where 0 < \( \alpha = V_2 / V_1 < 1 \), there are four ground-states: B19, DO\textsubscript{19}, A\textsubscript{3}, and C4\textsubscript{9}h. The phase diagram for \( \alpha=0.8 \) (TT only) is shown in Figure 2(b), while that for \( \alpha=0 \) (TT and TO) is shown in Figure 2(c). Monte-Carlo results of Crusius and Inden\textsuperscript{16} are superimposed for comparison. When \( \alpha=0.8 \) (Figure 2(b)) the C4\textsubscript{9}h phase exhibits a very narrow range of stability and has a transition temperature which is much less than those of the B19 and DO\textsubscript{19} phases. The B19 and DO\textsubscript{19} transition temperatures have also decreased compared to the case of isotropic interactions. When the interaction ratio is zero, there is no coupling between the close-packed planes, and the B19 and DO\textsubscript{19} phases are no longer observed, as seen in Figure 2(c). The TT and TO results for this calculation were almost identical. The absence of the B19 and DO\textsubscript{19} phases when \( \alpha=0 \) is consistent with the GS map: these two phases only exist at degenerate points. As the value of \( \alpha \) is decreased from one to zero, the transition temperatures of the B19 and DO\textsubscript{19} phases continuously decrease while that of C4\textsubscript{9}h continuously increases.

The CVM results agree almost exactly with previous studies of hcp performed by Kikuchi\textsuperscript{7}, although this author did not consider equilibria with the B19 phase. The agreement between the present results and Monte-Carlo depends on the CVM approximation: as the level of the CVM approximation is increased from TT to TO, there is better agreement with the results of Crusius and Inden\textsuperscript{16}. In general, all of the transition temperatures (hcp \( \rightarrow \) B19, hcp \( \rightarrow \) DO\textsubscript{19}, and hcp \( \rightarrow \) DO\textsubscript{19} + B19) are lower in the Monte-Carlo analysis. The TO results agree fairly well near the B19 and DO\textsubscript{19} transitions, but there is still quite a large discrepancy at the triple point. The same type of behavior is observed in CVM and MC calculations on the fcc lattice\textsuperscript{17}.

When the interactions are anisotropic, the C4\textsubscript{9}h phase appears between the DO\textsubscript{19} and B19 phases in the phase diagram, and the hcp \( \rightarrow \) C4\textsubscript{9}h transition temperature depends on the value of the interaction ratio. The same behavior is observed in the MC analysis of Ref. [16], although the MC transition temperatures are again lower. In the case when \( \alpha=0.8 \) (Figure 2(b)), the CVM predicts C4\textsubscript{9}h to transform into the DO\textsubscript{19} phase with a eutectoid reaction still occurring between hcp, B19 and DO\textsubscript{19}. The Monte-Carlo predicts the A\textsubscript{2}B to disorder into the hcp solid solution, with two eutectoid reactions hcp \( \rightarrow \) C4\textsubscript{9}h + B19, C4\textsubscript{9}h + DO\textsubscript{19}. As the level of CVM approximation is successively increased (for \( \alpha=0 \)), the transitions would most likely change to the point that the hcp \( \rightarrow \) C4\textsubscript{9}h + B19, C4\textsubscript{9}h + B19 reactions would be observed, in agreement with the Monte-Carlo results.

For \( \alpha=0 \), the only stable ordered phase is C4\textsubscript{9}h (Figure 2(c)), where we predict a finite transition temperature for long-range order (LRO) at c=0.5, and first-order transitions all the way across the concentration range except at c=0.5, where the transition is second order. There is almost exact agreement between the phase diagram of Fig. 2(c) and the CVM phase diagram of the 2-D triangular lattice calculated by Burley\textsuperscript{19}. The hcp Monte-Carlo results of Crusius and Inden\textsuperscript{16} predict a lower hcp \( \rightarrow \) C4\textsubscript{9}h transition temperature (as expected), and they predict only second-order transitions (dashed line, Figure 2(c)). Metcalfe\textsuperscript{20} performed Monte-Carlo simulation on the 2-D triangular antiferromagnet (equivalent to ordering interactions with \( \alpha=0 \)), finding results quite similar to those of Crusius and Inden. Wannier\textsuperscript{21} proved analytically that there is no LRO at T=0 and c=0.5 for the 2-D triangular antiferromagnet. Thus, the CVM result presented in Figure 2(c) is incorrect regarding the finite transition temperature at c=0.5 and the order of the transitions between hcp and C4\textsubscript{9}h. This is perhaps not surprising since C4\textsubscript{9}h is essentially two-dimensional, and mean-field theories are known to give poor results as the dimensionality of the system decreases. The two-dimensional character of this phase is further illustrated by the identity of the TT and TO results for \( \alpha=0 \). The equality of these results reflects the fact that the partition function can be factorized by planes when \( V_2 = 0 \).
IV. CONCLUSION

Ising models are a powerful tool which can be used to study ordering phenomena for substitutional alloys on various lattices, but very little attention has been given to ordering in hexagonal-close-packed (hcp) alloys. Previous ground-state analyses in hcp have not allowed for the possibility of many-body interactions between atoms. We have performed a study of the hcp Ising model in the cluster variation approximation. Ground-states of order stabilized by interactions within the range of the nearest-neighbor (NN) tetrahedron were computed using constraints based on the tetrahedron and triangle clusters in hcp. The ground-state search yields results consistent with previous NN pair ground-state analyses, although we predict a new structure with stoichiometry $A_4B_3 (D_{7h})$ which is stabilized by triplet interactions. In addition, it has been shown that any hcp groundstate search which uses a configuration polyhedron method must have at least one inconstructible vertex in order to be consistent with the infinite series of groundstates predicted by Kanamori. Prototypical ordering phase diagrams for binary hcp alloys were computed for several different values of the two NN pair interactions. The analysis presented in this study considered equilibria between all groundstates for the chosen interactions, which has not been done previously with the CVM. The observed phase equilibria for isotropic pair interactions are roughly analogous to ordering in fcc, but anisotropic pair interactions yield much more interesting behavior. Discrepancies between the CVM and Monte-Carlo are due to the mean-field treatment in the CVM of correlations beyond the maximal cluster(s).

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