
GROUND STATE DIAGRAMS FOR TERNARY FCC ALLOYS

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Abstract

We have investigated the possible ground states of a ternary FCC lattice model with nearest and next-nearest neighbor pair interactions by constructing an 8-dimensional configuration polytope and enumerating its vertices. Thirty one ternary ground states have been found, some of which correspond to structures that have been observed experimentally. In addition we present some prototype ground state diagrams for ternary systems.
1. Introduction

Binary alloy phase diagrams have been the subject of intense research, both theoretically (1, 2, 3, 4, 5, 6) and experimentally (7). Because most binary phase diagram compilations are relatively complete, theoretical computations on these systems have mainly been used to benchmark different first-principles approaches. The benefits of doing ab-initio phase diagram computations will be significantly larger in ternary systems. Since few ternary phase diagrams have been explored in detail with experimental techniques, first-principles models to compute phase stability in ternary alloys could be a valuable asset when studying these systems. An essential part of a first-principles phase diagram computation is the prediction of the ground states in the system. In this paper, we will present general ground state results for ternary systems.

2. Ternary Lattice Model and Energy Expansion

Ab-initio techniques for the computation of temperature-composition phase diagrams are invariably based on an underlying lattice model. Each substitutional configuration, \( \sigma \), is characterized in a lattice model by a set of spins \( \sigma_i \) which, in the binary case, take on the value +1(-1) when site \( i \) is occupied by an A (B) atom. This can easily be extended to a three-state spin model with \( \sigma_i = (-1, 0, 1) \) for ternary systems.

In binary alloys, lattice models have been remarkably successful in reproducing real phase diagrams, indicating the importance of configurational entropy for predicting the relative stability between phases. A more satisfying justification for the use of lattice models in alloy theory can be obtained by coarse-graining the partition function of an alloy down to the partition function of a lattice model (8). In this manner an effective lattice Hamiltonian, \( H(\{ \sigma \}) \) can be obtained which contains the effect of all excitations in the alloy, apart from substitutional excitations:

\[
H(\{ \sigma \}) = -\frac{1}{\beta} \ln \left[ \sum_{\text{all excitations}} \exp(-\beta E_{\text{state}}) \right] \quad (1)
\]

In general, this Hamiltonian is temperature-dependent. Since in most practical calculations electronic and vibrational excitation are neglected, \( H(\{ \sigma \}) \) only contains one term and is temperature-independent.

Similarly to what is used in computations on binary systems, we can expand the lattice Hamiltonian of a ternary system in a complete basis of cluster functions. Several bases have been proposed. Sanchez (9) suggested to use orthogonal Chebyshev polynomials in \( \sigma_i \) and \( \sigma_{-i} \). The orthogonality of the basis functions leads to a simple and powerful, definition of the ECI: they are the projection of \( H(\{ \sigma \}) \) onto cluster function \( \sigma_\alpha \). This definition has been judiciously followed in one of the methods to compute these effective interactions from first principles (1, 10) and its feasibility for ternary systems has recently been demonstrated as well (11). Wolverton (12) also introduced a basis of cluster occupation operators to describe ordering in a ternary system. Although this basis is not orthogonal, it has the advantage of being symmetric around the ternary equiatomic composition. In this ground state study, we will however, choose a set of basis functions suggested by Inden (13), and in a limited form by Taggart (14), as this basis is more apt for ground state models. In the \textit{S}-basis, as we will refer to it, the cluster functions are simple products of \( \sigma_i \) and \( \sigma^{-i}_j \). Consider two figures \( \beta \) and \( \gamma \) on the lattice, with \( \gamma \) completely in \( \beta \). The ternary cluster function \( \Phi_{\beta, \gamma} \) is defined as:
\[ \Phi_{\beta, \gamma} = \prod_{i \in \beta} \sigma_i \prod_{j \in \gamma} \sigma_j = \prod_{i \in \beta \gamma} \sigma_i \prod_{j \in \gamma} \sigma_j^3 \]

The set of all cluster functions for all combinations \((\beta, \gamma)\) forms a complete set in the space of all configurations. Although this basis is not orthonormal, it is desirable for ground state work as the values of the cluster functions are always integer in the S-basis.

In its most general form, the Hamiltonian of the ternary system can be expanded in the S-basis as:

\[ H(\{\sigma\}) = \sum_{\beta} \sum_{\gamma \in \beta} V_{\beta, \gamma} \Phi_{\beta, \gamma} \]  

The expansion coefficients \(V_{\beta, \gamma}\) are Effective Cluster Interactions (ECI). When only substitutional disorder is allowed, the ECI are by definition temperature-independent. We recently indicated how the effect of high-temperature vibrations can be included in the ECI (15) to obtain better quantitative agreement with experiments. Because we are only concerned with prototype phase diagrams in this paper, we will limit ourselves to nearest (NN) and next-nearest neighbor (NNN) effective pair interactions. In that case, the ternary Hamiltonian can be written explicitly as:

\[ H(\{\sigma\}) = V_\phi + \sum_i \mu^\sigma \sigma_i + \sum_i \mu^\omega \sigma_i^2 + \sum_{i,j} V_{1,1}^\sigma \sigma_i \sigma_j + \sum_{i,j} V_{1,1}^\omega \sigma_i \sigma_j + \sum_{i,j} V_{1,1}^{\omega_1} \sigma_i \sigma_j^2 + \sum_{i,j} V_{1,1}^{\omega_2} \sigma_i^2 \sigma_j^2 + \sum_{i,j} V_{2,2}^\sigma \sigma_i \sigma_j + \sum_{i,j} V_{2,2}^\omega \sigma_i \sigma_j + \sum_{i,j} V_{2,2}^{\omega_1} \sigma_i \sigma_j^2 + \sum_{i,j} V_{2,2}^{\omega_2} \sigma_i^2 \sigma_j^2 \]

Eqn. (4) is the most general Hamiltonian for a three state spin model with NN and NNN interactions. In a more restricted form it is known as the Blume-Emery-Griffith model used for the study of superfluidity in helium, liquid crystal mixtures and electronic conduction models (16). The values of the ternary pair interactions can be related to the pair interactions in the three binary edge systems:

\[ V^\sigma = V^{AC} \]
\[ V^{\omega \omega} = V^{AB} - V^{BC} \]
\[ V^{\omega \omega_1} = 2V^{AB} + 2V^{BC} - V^{AC} \]

For multiplet interactions it is not possible to find the values of the ternary interactions from the binaries because there are more ternary multiplet terms than binary multiplet interactions.

As the effective interactions have the symmetry of the underlying lattice, eqn. (3) can be averaged over the whole lattice to get the energy per lattice site:

\[ h(\{\sigma\}) = \sum_{\beta} \sum_{\gamma \in \beta} V_{\beta, \gamma} m_{\beta, \gamma} \Phi_{\beta, \gamma} \] 

The primes indicate that the sums is only over the types of figures that are distinct, considering the symmetry of the lattice. The coefficient \(m_{\beta, \gamma}\) gives the number of \((\beta, \gamma)\) figures per lattice site and the correlation function, \(< \Phi_{\beta, \gamma} >\), is the average value of all the cluster functions defined on those clusters. Finding the ground states of eqn (6) for a given set of interactions is a non-trivial matter. Although the energy is linear in the correlation functions, the values of the correlations are restricted by the fact that they have to represent a physical probability distribution on the parent lattice. The difficulty in ground state studies lies in finding
the exact constraints the lattice imposes on the correlation functions. Once these constraints are found, eqn. (6) can be minimized with standard linear programming techniques (17).

One approach to finding these constraints, that has worked successfully for most binary problems, has been to approximate the crystal's probability distribution by probabilities generated for small clusters. Since the probability for a given atomic configuration on a cluster can be written as a linear function of all the correlation functions on that cluster, the requirement that probabilities be between zero and one imposes linear inequalities between the correlation functions. In the space of basis functions, these inequalities define a convex polytope that bounds the allowed values of the correlation functions. The vertices of this configuration polytope are the possible ground states of our model. This can easily be understood by noting that the energy is a linear function of the correlations, hence, it will only reach an extremum at the boundary of the existence domain. This procedure does not always yield acceptable results. As the inequality constraints are derived from configurations on a small cluster they might not be restrictive enough compared to inequalities resulting from the infinite system. In this method, the exact configuration polytope is thus always approached from the outside, and formulating constraints on a larger cluster may cut off some of the vertices that are obtained from probability distributions on smaller clusters. These vertices can not correspond to a physical state of ordering and are referred to as inconstructable vertices.

In the following section we attempt to enumerate all possible ground states for a ternary lattice model with NN and NNN interactions by finding all the vertices of the configuration polytope in the 8-dimensional space.

3. Configuration Polytope for NN and NNN Pair Interactions

The Hamiltonian in eqn. (4) is defined in an 8-dimensional space (6 pair correlations and 2 point correlations). The configuration polytope in this space was determined (6, 18) by formulating constraints on the regular octahedron and tetrahedron clusters. Combined, these two clusters define 71 constraints in 60 variables. The constraints between the 8 correlations functions of interest can be obtained by eliminating the other 60-8 = 52 correlation functions. This procedure resulted in 729 constraints which define a polytope with 4862 vertices. To enumerate the vertices of this polytope, both the Double Description Algorithm (19) and the Reverse Search Method (20) were used. Considering structures that are related by permutations of A, B and C atoms as identical, 980 distinct structures remain. Nine of these correspond to the ground states of the binary lattice model with NN and NNN interactions. Of the 971 vertices with ternary compositions, 31 could be constructed with unit cells smaller than 32. The remaining 940 vertices are either inconstructable or have a unit cell with more than 32 atoms. The two-dimensional projections of the 31 structures are shown in fig. 1.

For some of the structures with small unit cells we have found experimental evidence in real ternary systems. Structure 4a, which is the only ternary ground state possible if the interactions are limited to the nearest neighbor distance, has been observed in Cu2NiZn (21). The structure is similar to the binary Li10, but with the minority atoms ordered in one of the (001) planes. A different secondary ordering occurs in structure 4c which corresponds to the CdPt2Zn phase. In this structure, Cd and Zn segregate each to their own (001) plane, alternating with pure Pt (001) planes. Structure 4b is the Rh2SnX phase, where X can be Co, Cr, Fe or V. This ordered phase can be considered as the antiphased variant of the Cu2NiZn structure. Table 1 lists the space group, size of the primitive unit cell and prototype for these three structures.
Fig. 1. \{001\} projections of the ternary ground state superstructures of fcc with first and second nearest neighbor interactions. White, grey and black circles correspond to A, B and C atoms respectively. Large circles are in \{00n\} planes, and small ones in \{00n+1/2\} planes. Half-shaded circles correspond to atoms alternating in the [001] direction, while circles with a shaded quadrant correspond to particles occupying every fourth sites in the [001] direction. Rotations of the shaded parts indicate different \{00z\} planes. The structures are labeled with the number of atoms in their primitive unit cells and letters to distinguish between structures with the same number of atoms. Structures 8c1, 8c2 and 8c3 correspond to the same vertex in the configurational polytope and have the same energy for the range of interactions used.
Table I: Experimental prototypes have been found for three of the structures shown in fig. 1.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Prototype</th>
<th>Space Group</th>
<th>Pearson Symbol</th>
<th>atoms in unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>Cu₂NiZn</td>
<td>P4/mmm</td>
<td>tP4</td>
<td>4</td>
</tr>
<tr>
<td>4c</td>
<td>CdPt₂Zn</td>
<td>P4/mmm</td>
<td>tP4</td>
<td>4</td>
</tr>
<tr>
<td>4b</td>
<td>Rh₂SnCo</td>
<td>P4/ncm</td>
<td>tP16</td>
<td>4</td>
</tr>
</tbody>
</table>

4. Prototype Ground State Diagrams

In fig. 2 we show the ground state diagrams for a number of ternary prototype systems. Because the polytope method with tetrahedron and octahedron as maximal clusters produces a large number of inconstructable vertices, we have used the constraints from a double tetrahedron and octahedron to compute these diagrams. Since we only use pair interactions, the interactions in the ternary system are uniquely defined by the three binary systems. Ternary systems will therefore be cataloged according to the types of binary edge systems. Figure 2a shows the ternary ground state map for three identical binary systems with ordering (positive) nearest neighbor and clustering (negative) next-nearest neighbor interactions. The only ternary structure is the Cu₂NiZn - type compound (4a on fig. 1). Keeping all second neighbor interactions negative, but mixing two ordering systems with a phase separating system results in no ternary compounds being stable as shown in fig. 2b. Surprisingly this last result depends sensitively on the value of the second neighbor interaction in the phase separating system: In fig. 2 we show the ground states for a system with the same binary edges as in fig. 2b, except for the sign of V₂ in the phase separating system. The positive V₂ in the phase separating system induces ordering in the opposite corner. A recent ab-initio evaluation of the effective interactions in the Ti-Rh-V system indicate that this system behaves as predicted in fig. 2c. Fig. 2d shows the ground state map for a fully frustrated ternary system with all binary pair interactions of the ordering type. Although there are 43 ternary vertices in this diagram most of them are inconstructable, indicating that the double tetrahedron and octahedron can not capture the frustration between ordering second nearest neighbor interactions.

5. Discussion

In contrast to the success of the binary ground state analysis with the tetrahedron and octahedron clusters, the ternary ground state search resulted in a large number of inconstructable vertices, indicating that frustration effects on figures larger than the tetrahedron and octahedron need to be accounted for. Whenever a constructable vertex is obtained however, the result is exact, which gives the polytope method definite advantages over other methods to determine ground states, like simulated annealing and Monte Carlo procedures. The diagrams of fig. 2a-2c are therefore accurate for the given set of interactions.

Comparing the ground state triangles in fig. 2b and 2c illustrates how systems with similar binary edges can have different ternary compounds stable. This possibility may make it difficult to guess at ternary phase diagrams by interpolating between the binaries. When going from binary to ternary systems, the complexity of the computations increases significantly. In binary systems only 9 distinct structures can be stabilized with first and second neighbor interactions \(^\text{5}\). Although we do no have a complete result for the corresponding ternary
analysis, it is clear that there will be many more possible ground states in ternaries. A second neighbor interaction distance may, in general, not be enough to study real systems. Systematic \textit{ab initio} studies on binary systems have shown that in many systems pair interactions up to the fourth nearest neighbor distance need to be included to obtain a converged expansion for the energy. There is no reason to believe that this will be different for a ternary energy expansion. It is not clear whether the polytope method, as used here, will be tractable to predict ground states with fourth nearest neighbor interactions.

![Diagram](image)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Ground state diagrams for some prototype ternary systems. A compound is stable at the intersection of all lines.}
\end{figure}

a) \(V^{AC}_1 = V^{BC}_1 = V^{AB}_1 = 1\)

b) \(V^{AC}_1 = V^{BC}_1 = 1; V^{AB}_1 = -0.5; V^{AC}_2 = V^{BC}_2 = V^{AB}_2 = -0.1\)

c) \(V^{AC}_1 = V^{BC}_1 = 1; V^{AB}_1 = -0.5; V^{AC}_2 = 0.3; V^{BC}_2 = V^{AB}_2 = -0.1\)

d) \(V^{AC}_1 = 1.2; V^{BC}_1 = 1.1; V^{AB}_1 = 1.0; V^{AC}_2 = 0.12; V^{BC}_2 = 0.11; V^{AB}_2 = 0.1\)

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References