First-principles study of multiple order-disorder transitions in Cd$_2$AgAu Heusler alloys

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The bcc-based Heusler alloys exhibit a series of order-disorder phase transitions as a function of temperature. The high-temperature phase is a disordered bcc solid solution, and the low-temperature phase is the Heusler structure. An intermediate ordered phase is also typically observed in real systems. A prototype cluster variation method (CVM) analysis is presented that shows that the relative stabilities of the Heusler and intermediate phases can vary continuously, depending on a fine balance between ordering tendencies in the constituent binary systems. Given these basic conclusions, a first-principles analysis of order-disorder transitions in Cd$_2$AgAu was performed. A cluster expansion Hamiltonian was constructed based on a series of linearized muffin-tin orbital calculations in the atomic sphere approximation. CVM calculations were then performed in the ternary bcc tetrahedron approximation. In addition to the transition temperatures, long-range order parameters, and sublattice occupations for Cd$_2$AgAu, an isoplethal section of the ternary phase diagram was also calculated. In general, agreement with experiment is excellent, given the first-principles nature of the calculation. This study clearly demonstrates the ability of first-principles statistical-mechanical calculations to treat complex ordering phenomena in *ternary* systems. [S0163-1829(96)04438-4]

I. INTRODUCTION

One ordered compound that has received a great deal of attention over the years is the Heusler alloy, a superstructure of the body-centered-cubic (bcc) lattice named after its original discoverer.[1] The first Heusler alloys discovered are of primary interest because of their exotic magnetic properties: Many are ferromagnetic despite the fact that the constituent elements are either paramagnetic or diamagnetic. The prototype Heusler alloy (Strükturbericht designation $L2_1$) with these interesting magnetic properties is Cu$_2$MnAl,[2] but a whole host of other Heusler alloys with similar properties exist, most possessing Mn as one of their minority elements [e.g., Cu$_2$MnX (X = Sn, Al, In, Ge), Cu$_2$CoSn, Au$_2$MnAl, and Co$_2$MnSn].[2–5] Nonmagnetic compounds with the $L2_1$ structure also commonly occur in transition-metal alloys [e.g., Zn$_2$AuX (X=Ag, Cu), Cd$_2$AgAu, and Ni$_2$TiAl]. Several Heusler compounds have been studied for potential applications in magneto-optical recording media,[6,7] although some show promise in other realms. For example, recent studies of the dual-phase alloy Ni$_2$TiAl/NiAl have shown that $L2_1$ Ni$_2$TiAl greatly improves the high-temperature creep resistance of $B2$ NiAl.[8–10] Aside from these important practical applications, Heusler alloys have also proved to be of interest for the series of order-disorder phase transformations that they undergo upon heating or cooling.

The Heusler structure is a bcc superstructure (space group $Fm3m$) of composition A_2BC with atoms A, B, and C split onto three distinct sublattices. The conventional bcc unit cell and sublattice labeling conventions are given in Fig. 1. Sublattice 1 contains the majority atom (A), while sublattices 2 and 3 contain the minority atoms (B and C). In the disordered state at high temperature, the alloy is a bcc solid solution, with atoms A, B, and C distributed randomly. If one begins in this disordered state and lowers the temperature,

there are two possibilities (see Fig. 2): (path 1) the alloy can undergo a direct transition to $L2_1$ at T_1 with ordering occurring simultaneously on all three sublattices, or (path 2) the alloy can order on two sublattices at (T_1) and then subsequently order into $L2_1$ at some lower temperature T_2. These two transition paths have been observed previously in some theoretical investigations based on a simplified Bragg-Williams approximation for the configurational entropy (see, for example, Refs. 11–13).

In most alloy systems that exhibit the Heusler structure (see, for example, Rothwarf and Muldawer[14]), the transition is indirect (path 2), with an intermediate phase possessing a structure analogous to CsCl (hereafter referred to as $B2'$, shown in Fig. 2). In this structure, the majority atoms partition onto sublattice 1, while the minority atoms remain disordered on sublattices 2 and 3. At some lower temperature T_2, the minority atoms partition onto sublattices 2 and 3,
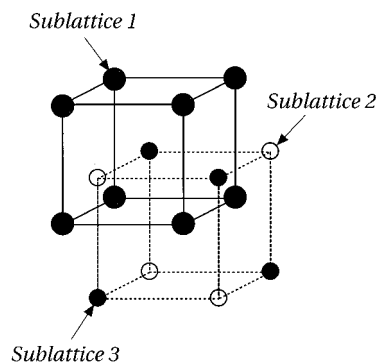

FIG. 1. The Heusler ($L2_1$) structure with the three distinct sublattices indicated. Sublattice 1 (occupied by majority species A) comprises one simple cubic sublattice, whereas sublattices 2 and 3 (occupied by species B and C) make up another simple cubic lattice.
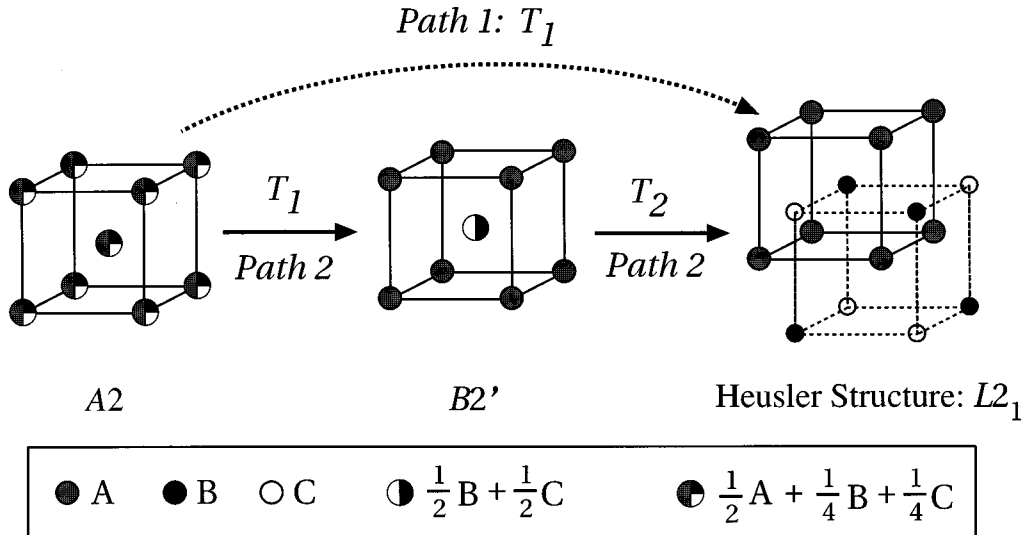
Path 1: T_1

FIG. 2. Two possible transition paths between the disordered state (indicated on the far left) and the Heusler structure (far right). In path 1, the transition between the disordered phase and $L2_1$ is direct, whereas in path 2, there is an intermediate phase with CsCl symmetry. "Atoms" containing more than one pattern designate a disordered mixture of the species with the indicated shadings.

yielding the $L2_1$ structure. In several systems,[14] the high-temperature $A2 \rightarrow B2'$ transition does not occur at stoichiometry A_2BC because the alloy melts before it disorders, although the transition is observed off stoichiometry. Previous prototype,[11–13,15–19] phenomenological,[9,20] and *ab initio*[21–23] studies have been made of these phase transitions. The present work extends these results by eliminating most of the approximations made in the past concerning interaction parameters, sublattice occupations, and relative transition temperatures. An analysis of the complete *ternary* order-disorder problem is done using phenomenological interaction parameters, followed by an *ab initio* analysis of the phase transitions in the nonmagnetic Heusler alloy Cd_2AgAu.

II. FORMALISM

The technique most widely used to model the configurational thermodynamics of alloys is based on a generalized Ising model.[24–26] A periodic Ising lattice is constructed and different configurations of the alloy on this lattice are then assigned using pseudospin variables (occupation operators) σ_i, where $\sigma_i = 1$, 0, or -1 if site i is occupied by an A, B, or C atom, respectively. The configuration on the lattice is then specified with the vector $\boldsymbol{\sigma} = (\sigma_1, \ldots, \sigma_N)$. In a classic paper by Sanchez, Ducastelle, and Gratias,[27] it was shown that any function that depends on the configuration $\boldsymbol{\sigma}$ can be written as a linear, orthonormal cluster expansion using a complete set of *cluster functions*:

$$f(\boldsymbol{\sigma}) = \sum_{\alpha} m_{\alpha} f_{\alpha} \langle \phi_{\alpha}(\boldsymbol{\sigma}) \rangle, \qquad (1)$$

where f_{α} are the so-called *cluster expansion coefficients*, $\langle \phi_{\alpha}(\boldsymbol{\sigma}) \rangle$ are lattice-averaged values of the *cluster functions*, and m_{α} are the number of clusters of type α per lattice site. The sum in Eq. (1) runs over all symmetry-distinct clusters α of sites in the lattice. With all 3^N terms, the expansion is *exact*; in practice, the expansion is truncated at a level that is acceptable for the problem at hand. A more complete discus-

sion of the form of the functions in the ternary cluster expansion and of its properties can be found in Refs. 27–29.

When the function of configuration being cluster expanded is the configurational energy, the expansion coefficients f_{α} are usually referred to as *effective cluster interactions* (ECI's, V_{α}). These ECI's provide the interface between quantum and statistical mechanics and are thus the essential component in any *ab initio* thermodynamic calculation. Numerous methods[30–34] exist for the calculation of ECI's; in the present approach, a structure inversion method[30] (SIM) is used. In this method, one simply computes the energy for several configurations and then expresses the energy of each configuration using the cluster expansion with values of the lattice-averaged cluster function (LACF) for that configuration. This generates a set of linear equations in the unknown ECI's that can then be solved by a variety of techniques. In order to determine N ECI's, we need M different equations, where $M \geqslant N$. When $M = N$, the system can be solved immediately by matrix inversion, assuming the matrix of the LACF for the structures is not singular. In the case where $M > N$, the system is solved by performing a least-squares fit to the input energies. The ECI's are determined by minimizing the objective function

$$\mathcal{O} = \sum_{i=1}^{M} \omega_i \left[E_i - \sum_{\alpha=1}^{N} m_{\alpha} V_{\alpha} \langle \phi_{\alpha} \rangle_i \right]^2, \qquad (2)$$

where ω_i are weights for each structure. It has been found that the results obtained using the SIM can be sensitive to the choice of input structures.[35] Hence, care must be taken to ensure that the set of ECI's obtained is robust with respect to this choice.

Once a set of ECI's has been obtained, finite-temperature calculations can be performed using the cluster variation method (CVM).[24,36] In this method, one assumes that species

are only directly correlated over a given range specified by choosing one or more *maximal clusters* α_M.[37,38] The configurational entropy is then written as a sum of cluster entropies associated with observing various configurations of atoms on clusters of lattice sites. The CVM free energy can then be written as a functional of multisite *correlation functions*, which are thermodynamic averages of the cluster functions. The interested reader is referred to the more complete discussion of the ternary CVM in Refs. 27 and 28. The CVM free energy can be computed for any phase of interest, thus allowing the calculation not only of the phase diagram, but also the degrees of short- and long-range order for any of the phases. In the present paper, we restrict ourselves to an analysis of configurational order-disorder on the bcc lattice, and use the bcc tetrahedron approximation to the ternary CVM. In this approximation, there are 21 distinct correlation functions; hence the CVM free energy is a nonlinear functional of 21 independent variables. For the sake of brevity, the relevant quantities for a CVM calculation in this approximation will not be presented; they can be found in Ref. 28. Any effects due to magnetic, electronic, or vibrational excitations will not be considered in this paper, although these effects can have important effects on phase equilibria and could be included in principle.

III. PROTOTYPE CVM CALCULATIONS

Ternary CVM calculations were performed at stoichiometry A_2BC in systems that favor formation of the Heusler structure at this composition. Different sets of effective pair interactions (EPI's) were chosen to more accurately assess the factors controlling the relative stabilities of the $B2'$ and $L2_1$ phases. The bcc tetrahedron approximation to the CVM was used; hence EPI's are restricted to nearest- (NN) and next-nearest-neighbor (NNN) pairs. "Pseudobinary" effective pair interactions (PEPI's) $W_{pp'}^{IJ}$, were chosen for various combinations of ordering tendencies in the three binary systems. These PEPI's (a linear combination of the actual EPI's used in the expansion[28,29]) have a transparent interpretation. A pseudobinary EPI for binary system IJ ($I, J = A, B, C$; $I \neq J$) is defined as

$$W_{pp'}^{IJ} = \tfrac{1}{4}[\langle E_{II}\rangle + \langle E_{JJ}\rangle - 2\langle E_{IJ}\rangle], \qquad (3)$$

where $\langle E_{IJ}\rangle$ is the average energy of all *ternary* configurations with sites p and p' occupied by species I and J, respectively. A positive (negative) value of the pseudobinary EPI for binary IJ indicates that unlike (like) atoms are favored on sites p and p'. The system is said to possess "ordering" tendencies for sites p and p' if $W_{pp'} > 0$ and "clustering" tendencies if $W_{pp'} < 0$.

PEPI's were chosen for this study such that *at least* the following compounds are predicted to be ground states: $B2$ AB, $B2$ AC, and $L2_1$ A_2BC. Interactions that produced other ground states in addition to these were also considered suitable. No multiplet interactions were included in the prototype study, although these can affect the quantitative results (see Sec. IV C). The required ground states imply positive NN PEPI's for all binary systems; hence these PEPI's were held fixed for all calculations. PEPI values of (100, 100, and 50) were chosen for the AB, AC, and BC edges for simplic-

TABLE I. Transition temperatures as a function of various combinations of NN and NNN pseudobinary pair interactions for all binaries. Values for interactions and transition temperatures are given in kelvin. In addition to the transition temperatures to the $B2'$ and $L2_1$ phases (T_1 and T_2, respectively), the ratio of the two temperatures ($\tau = T_1/T_2$) is also given.

Set	$W_{NN}^{(AB)}$	$W_{NN}^{(AC)}$	$W_{NN}^{(BC)}$	$W_{NNN}^{(AB)}$	$W_{NNN}^{(AC)}$	$W_{NNN}^{(BC)}$	T_1	T_2	τ
I	100	100	50	-20	-20	125	862	588	1.47
II	100	100	50	-20	-20	100	824	482	1.71
III	100	100	50	-20	-20	75	786	367	2.14
IV	100	100	50	-20	-20	50	749	246	3.04
V	100	100	50	0	0	125	754	573	1.32
VI	100	100	50	0	0	100	715	474	1.51
VII	100	100	50	0	0	50	638	246	2.59
VIII	100	100	50	10	10	125	700	561	1.25
IX	100	100	50	10	10	100	660	468	1.41
X	100	100	50	10	10	50	582	245	2.38

ity. This removes any effects that would be caused by asymmetry in the NN pair interactions, which would affect both the sublattice occupations (see Sec. IV C) and the transition temperatures.

A. Results

The results of a series of calculations are given in Table I. The transition temperatures for the high-temperature $A2 \to B2'$ transition (T_1) and the lower-temperature $B2' \to L2_1$ transition (T_2) are given for each interaction set. The ratio of the transition temperatures $\tau = T_1/T_2$ ($0 < \tau < \infty$) is also given. A value of $\tau = 1$ indicates a direct transition from $A2$ to $L2_1$, whereas values greater than 1 are proportional to the size of the $B2'$ stability domain. From the CVM calculations, the $A2 \to B2'$ transition is second order, whereas the $B2' \to L2_1$ transition is *weakly* first order. The order of this transition could change for different interaction ratios, since both orders have been observed experimentally.[9]

Based on the transition temperatures as a function of interaction parameters, three basic conclusions can be drawn about the relative stability of the $B2'$ and $L2_1$ phases *in systems with bcc constituent binaries*. These observations are made based on the assumption that all NN pair interactions are of ordering type and that no other "unphysical" interactions are chosen (e.g., multiplet interactions that are significantly larger than the pairs or pair interactions that do not decay with increasing pair separation). In all cases, stability for a given phase is taken to be synonymous with a high decomposition temperature.

(I) Stability of the $L2_1$ phase is governed predominantly by the strength of BC NNN ordering, although AB and AC NNN interactions also play a role. The former effect can be seen by comparing the τ values for iteraction sets I–IV, where all interactions but W_{NNN}^{BC} are held fixed. The latter effect is observed in sets (I,V,VIII), (II,VI,IX), and (IV, VII,X).

(II) Stability of the $B2'$ phase is favored by NNN clustering in the AB and AC systems and NNN ordering in the BC

system. This follows from the data for interaction sets (I,V, VIII), (II,VI,IX), and (IV,VII,X), which fix W_{NNN}^{BC} and vary W_{NNN}^{AB} and W_{NNN}^{AC}

(III) The relative stabilities of the $B2'$ and $L2_1$ phases can vary continuously as a function of the interaction parameters. Three types of behavior can be observed: (1) The disordered phase transforms directly to the $L2_1$ structure ($\tau=1$), (2) a temperature range exists where the $B2'$ structure is an intermediate phase, and (3) the $L2_1$ phase is stable only at $T=0$ K ($\tau \rightarrow \infty$).

The $B32$ structure is favored by strongly ordering NNN pair interactions; if one assumes only NN and NNN interactions, $B32$ is energetically more stable than $B2$ for $W_{\mathrm{NNN}}/W_{\mathrm{NN}}>2/3$.[39] The $B2$ structure is favored with clustering NNN interactions, even though it can be stabilized for $W_{\mathrm{NNN}}/W_{\mathrm{NN}}<2/3$. Both structures are favored with ordering NN interactions. These facts lead to a simple conclusion based on statements (I) and (II): In a bcc-based ternary system, if the AB and AC binaries favor the formation of $CsCl$-like compounds, and if the BC binary possesses $B32$-like ordering tendencies, then a Heusler alloy of composition A_2BC is strongly favored. This is a sufficient condition for the formation of a Heusler compound at this stoichiometry, but it is not *necessary*. For example, it is possible within the range of NN and NNN interactions to have *three* binary $B2$ ground states *and* an A_2BC $L2_1$ structure. The reader should also note that it is difficult and possibly imprudent to apply these arguments to systems where some or all of the binary compounds at equiatomic composition are not bcc superstructures.

In this study, NN and NNN interactions were chosen such that the AB and AC binary systems are symmetric. These choices were made not out of limitations imposed by the calculations, but in order to reduce the size of the parameter space to investigate. Even within the range of NN and NNN interactions, there is a six-dimensional parameter space (three NN interactions, three NNN interactions). Asymmetry in the binary systems would probably not affect the conclusions of the present study significantly, although asymmetry does have an effect on sublattice occupations (see Secs. IV C and IV D). It is not really possible to draw general conclusions about the effects of adding *arbitrary* interactions. If interactions are added that are within the bcc tetrahedron, then no new ground states are introduced and the above conclusions are valid (see Ref. 40 for all of the ground states within the bcc tetrahedron approximation). Introduction of significant interactions beyond the bcc tetrahedron might stabilize new binary equiatomic ground states, which could complicate matters. A complete discussion of these issues is beyond the scope of the present work.

B. Comparison with previous analyses

All of the previous prototype analyses[11–13,15–20,41] used a Bragg-Williams (BW) approximation to the configurational entropy, whereas the present analysis uses the tetrahedron approximation to the CVM. In that sense, the results of this analysis are expected to deviate quantitatively from past work in that all CVM calculations differ from single-site mean-field methods (i.e., transition temperatures closer to their actual values). Aside from this somewhat superficial

quantitative difference, there are more substantive qualitative differences from these prior studies both in terms of the approximations made and in terms of the results.

In the study of Matsuda,[11] expressions are derived for the energy based on NN and NNN interactions. Using these energy expressions and a BW formulation of the entropy, this author derives a set of necessary and sufficient conditions for the existence of the A_2BC phase in terms of the NN and NNN interactions. At least one of these conditions is in error, namely, that $16(W_{\mathrm{NN}}^{AC}-W_{\mathrm{NN}}^{AB})+6(4W_{\mathrm{NNN}}^{AC}-W_{\mathrm{NNN}}^{AB})=0$. One can imagine a completely symmetric case where the AB and AC binaries are equivalent (i.e., all of the interaction sets in the present analysis), in which case the above condition implies that $4W_{\mathrm{NNN}}^{AC}=W_{\mathrm{NNN}}^{AB}$ for an $L2_1$ transition to take place. This is clearly not the case, as is demonstrated by all of the results in the present study. In Matsuda's own study, the only way this problem was avoided was by setting $4W_{\mathrm{NNN}}^{AC}=W_{\mathrm{NNN}}^{AB}=0$. The other conditions are consistent with the current analysis. In addition to deriving these equilibrium conditions, Matsuda computes the order parameters as a function of temperature under the conditions that $W_{\mathrm{NN}}^{AB,AC}=V>0$, $W_{\mathrm{NN}}^{BC}=0$, $W_{\mathrm{NNN}}^{BC}=W$, and $W_{\mathrm{NNN}}^{AB,AC}=0$. Note that these interactions would tend to form $B2$ AB and AC structures and a $B32$ BC compound. Order parameters are computed for three different values of W/V, with results qualitatively consistent with the present study.

The study of Murakami *et al.*[12] is essentially an extension of the work performed by Matsuda, where these authors now allow for off stoichiometry. They derive the $A2 \rightarrow B2'$ transition assuming that $W_{\mathrm{NNN}}^{IJ}=0$ for all binary systems, yielding an $A2 \rightarrow B2'$ transition temperature T_1 that is a function of NN interactions *only*. They then derive the lower $B2' \rightarrow L2_1$ transition by assuming that sublattice 1 is completely occupied by A atoms at this transition. This yields a lower transition temperature (T_2) which is curiously *independent* of all interactions other than W_{NNN}^{BC}. Of course, the results for T_1 and T_2 are conceptually inconsistent, since, in the derivation of T_1, NNN interactions are assumed to be negligible, whereas for that of T_2 they are not only taken as nonzero, but are also shown to be dominant. The present study makes no assumptions about sublattice occupation and demonstrates clearly that T_2 is a function of *all* of the NNN interactions. In addition, the present work shows that when NNN interactions are included, they can have a pronounced effect on *both* transitions.

The work of Soltys and Kozubski[13,15–20] is a generalization of that of Wojciechowski.[41] The former studies contain results based on a variety of approximations. The first set of approximations used by Soltys involves the interactions used: NN,[13] NN and NNN,[16–20] and NN-3NN.[15] Most of these publications present derivations of the BW free energies, with only Refs. 13,15, and 18 providing transition temperatures, each of which is a function of the specific model chosen. The only work that contains any computations is Ref. 20. The second set of assumptions that Soltys makes concerns sublattice occupations, and these vary somewhat depending upon the specific publication (see, for example, Refs. 13 and 16).

The transition temperatures derived by Soltys and Kozubski are complex functions of the interaction parameters (see

Refs. 13,15,18) and these functions are not equivalent to those used by either Matsuda or Murakami. The formalisms of Soltys and Kozubski *are* consistent with these two authors in the sense that two sets of possible phase transitions are discussed (i.e., $A2 \rightarrow L2_1$ or $A2 \rightarrow B2' \rightarrow L2_1$). Aside from what has just been stated, it is difficult to compare the present investigation with those of Soltys and Kozubski.

The previous CVM work done on Heusler alloy phase transitions[9,21–23] involved the use of interactions that were either fit[9] or calculated[21–23] for the Ni_2TiAl system. The qualitative behavior of the transitions computed by these authors is consistent with the present study, but these authors made no effort to study the relative transition temperatures as a function of the interaction parameters. A further discussion of the methodology used and the results obtained by these authors will be given in Sec. IV D.

IV. APPLICATION TO THE Cd-Ag-Au SYSTEM

The Cd-Ag-Au system has a Heusler compound of composition Cd_2AgAu that disorders into a $B2'$ structure;[14] hence it is an ideal system to study using the above analysis as a starting point. Given the pivotal role that the binary systems play in the formation of the ternary compound, it is useful to examine the binary phase behavior at equiatomic compositions for Cd-Ag, Cd-Au, and Ag-Au.[42] In the Cd-Ag binary, there is an ordered bcc phase (crystal structure unspecified) that disorders at 523 K. The Cd-Au system has a $B2$ phase that melts at 902 K and a low-temperature $B19$ martensitic phase. The Ag-Au phase diagram reveals complete solid solubility for all measured temperatures, which seems reasonable given that Ag and Au are nearly size matched and are chemically quite similar. Thermodynamic data for this system indicate both short-range order[43] and a negative heat of mixing for solid solutions,[44] clearly showing that this system should order at low temperature. A series of linear augmented plane wave (LAPW) calculations by Lu *et al.*[45] indicate that on a fcc lattice, $L1_0$ AgAu is weakly stable, also indicative of ordering tendencies in this system. Kinetics may prevent the observation of such weakly stable ordered phases.

A. Total energy calculations

In order to perform CVM calculations for Cd_2AgAu, a set of bcc effective cluster interactions (ECI's) need to be computed for the Cd-Ag-Au system. Linearized muffin-tin orbital (LMTO) calculations in the atomic sphere approximation[46] (ASA) were performed for a series of ordered bcc compounds containing Cd, Ag, and Au (including the bcc pure elements). In reality, Cd is hcp and Au and Ag are fcc, but we are interested in performing the CVM calculations on a bcc lattice, which necessitates an analysis of bcc energetics. Given our interest in the single Cd_2AgAu compound, a study of ordering on the bcc lattice should be sufficient.

LMTO-ASA calculations were performed for the 21 canonical bcc ground states within the tetrahedron approximation,[40] and all computations were done using equal-sized atomic spheres. Calculations were performed scalar relativistically using combined corrections; the exchange correlation of von Barth and Hedin[47] and a basis set

containing orbitals with $\ell = 0$, 1, and 2 were used. Total energies were converged to within 0.1 mRy/atom (0.131 26 kJ mol^{-1}) and 165 **k** points were sampled in the irreducible wedge of the Brillouin zone. No spin-polarized calculations were performed; it was assumed that magnetism could safely be neglected in this system since Cd_2AgAu is not magnetic. The results of the ASA calculations for all compounds of interest are given in Table II, where the equilibrium lattice constant (a_0), volume (Ω_0), bulk modulus (B), and formation enthalpy (ΔH_f) are listed. The formation enthalpy for a structure σ is defined as

$$\Delta H_f = E_\sigma(\Omega_{0,\sigma}) - c_A E_A(\Omega_{0,A}) - c_B E_B(\Omega_{0,B}) - c_C E_C(\Omega_{0,C}),$$
(4)

where $E_i(\Omega_{0,i})$ is the total energy of structure i at its equilibrium volume and c_i are the concentrations of species i in structure σ. A positive (negative) value of the formation enthalpy indicates that structure σ is unstable (stable) with respect to a mechanical mixture of its constituent elements *in their hypothetical bcc structures*.

The lattice constants, equilibrium volumes, and bulk moduli for all structures in Table II cannot be compared with experiment, since these are all hypothetical bcc structures. The lattice constants of Ag and Au are quite similar, consistent with the similarity in the experimental fcc lattice constants. The lattice constant for Cd relative to those of Ag and Au is also consistent with the experimental molar volumes for these compounds; i.e., Cd is larger than Ag and Au. There is some degree of size mismatch in this system, but as previously stated, this paper is only concerned with the configurational degrees of freedom of the order-disorder problem. A more complete treatment of atomic relaxations would not only necessitate calculations for additional structures (all included structures possess cubic symmetry without relaxations), but would probably require the use of a full-potential electronic structure method.

The qualitative behavior of the formation enthalpies for the binary compounds agrees well with experiment. Ordering in the Cd-Au compounds is strongest, followed by ordering in Cd-Ag and weaker ordering in Ag-Au. In the experimental diagrams, the stability trends in the former two systems are manifested in the stability of $B2$ CdAu (i.e., it melts before it disorders) and the disordering of bcc CdAg at 523 K. The most stable phases based on the these LMTO calculations can be found by constructing the convex hull of formation enthalpies, thus eliminating phases that are unstable with respect to a mechanical mixture of any combination of the constituent elements or compounds. In the binary systems, DO_3 compounds are stable in all systems, $B2$ compounds are stable in Cd-Au and Cd-Ag, and $B32$ is *slightly* favored over $B2$ in Ag-Au. All ternary compounds are stable with respect to decomposition into either a mixture of other ordered compounds or of the pure elements, with the most stable phases being $L2_1$ Cd_2AgAu, $L2_1$ $CdAu_2Ag$, and $F43m$ $CdAgAu_2$.

B. Effective cluster interactions

A set of volume-independent effective cluster interactions was computed using a structure inversion technique.[30,24] A least-squares fit using the technique of singular value decomposition was performed to determine the *set* of ECI's that

TABLE II. LMTO-ASA equilibrium lattice constants, volumes, bulk moduli, and formation enthalpies for 21 alloys in the Cd-Ag-Au system. Structures are given by their Strükturbericht designation where possible.

Structure	a_0 (Å)	Ω_0 (cm^3 mol^{-1})	B (GPa)	ΔH_f (mRy/atom) [a]
bcc Ag	3.2195	10.05	138	0.0
bcc Au	3.2610	10.44	201	0.0
bcc Cd	3.4481	12.34	83	0.0
CdAu $B2$	3.3112	10.93	137	-20.4
CdAu $B32$	3.3123	10.94	138	-15.2
CdAu$_3$ DO_3	3.2852	10.67	161	-12.31
Cd$_3$Au DO_3	3.3481	11.3	89	-12.1
CdAg $B2$	3.2898	10.72	120	-11.8
CdAg $B32$	3.2951	10.77	114	-8.9
CdAg$_3$ DO_3	3.2526	10.36	123	-7.1
Cd$_3$Ag DO_3	3.3458	11.28	98	-6.8
AgAu $B2$	3.2423	10.26	157	-3.5
AgAu $B32$	3.2424	10.26	161	-3.9
AgAu$_3$ DO_3	3.2532	10.37	164	-2.6
Ag$_3$Au DO_3	3.2298	10.14	136	-3.0
Cd$_2$AgAu $L2_1$	3.2999	10.82	126	-17.6
CdAg$_2$Au $L2_1$	3.2623	10.45	136	-10.6
CdAgAu$_2$ $L2_1$	3.2744	10.57	146	-13.1
Cd$_2$AgAu $F43m$ [b]	3.3031	10.85	122	-13.3
CdAg$_2$Au $F43m$ [b]	3.2634	10.46	128	-11.7
CdAgAu$_2$ $F43m$ [b]	3.2733	10.56	148	-12.6

[a] 1 mRy/atom = 1.3126 kJ mol^{-1}.
[b] bcc [111] superlattice with layer stacking $AABC$.

best reproduces the formation energies from the LMTO ASA. In the present analysis, all structures were given equal weights ($\omega_i = 1$) and inversions were done for several collections of ECI's: (1) the first 9 ECI's (up to NNN pairs), (2) the first 15 ECI's (set 1 plus triplet interactions), (3) sets of between 16 and 19 ECI's that included a variety of quadruplet interactions, and (4) all 21 ECI's within the ternary bcc tetrahedron approximation. Tests were done based on two types of input structures, in order to determine how sensitive the inversion results are to this choice: (I) all 21 structures included and (II) all permutations with one structure excluded and the pure elements included. Structure set (I) gives an idea of the best fit that can be obtained, while the sets contained in (II) give an idea of the predictive capability of the cluster expansion for structures that are *not* included in the fitting procedure.

For inversions based on structure set (I) with different sets of ECI's, it was found that the rms errors in fitting structural energies used in the inversion were quite small when compared to the LMTO-ASA formation enthalpies (of the order of 0.5 mRy/atom) and they decreased as the number of ECI's in the inversion increased. Triplet and quadruplet interactions were found to be smaller than pairs, although some of these ECI's were significant. ECI's based on 9 and 21 cluster functions in the inversion are given in Table III. All interactions are with respect to the set of canonical basis functions $(1, \sigma, \sigma^2)$.[28]

Inversions based on structure sets (II) gave more revealing results. A total of 18 inversions were performed for sets of 20 structures (one excluded) that included the pure elements. As has been documented in other applications of the

structure inversion approach,[25,48] the most useful test of the validity of an inversion is to compare how well the ECI's can both fit the energy of structures that are included *and* predict the energy of those excluded from the fit. In the present study, the rms errors for structures included in the inversion decrease as the number of ECI's used in the inversion increases, as expected. The converse is true for the one structure excluded from the inversion; for sets containing more than 9 ECI's, the rms error in the exlcuded structure fluctuates by up to 2 mRy/atom depending on the structure. This seems to indicate that, for the 21 structures considered, the cluster expansion is not well converged for interaction sets that contain more than 9 ECI's (i.e., those sets that contain triplets or quadruplets). There is essentially a trade-off between accuracy of the fit for structures included in the expansion and predictive ability for structures not considered.

Local ground-state searches (see Ref. 24) using both 9 and 21 ECI's were performed in the bcc tetrahedron approximation. Each set of ECI's yielded the same set of 15 ground states: Cd, Ag, Au, $B2$ (CdAu, CdAg), $B32$ (AgAu), DO_3 (Cd$_3$Au, Cd$_3$Ag, CdAu$_3$, CdAg$_3$, Ag$_3$Au, AgAu$_3$), $L2_1$ (Cd$_2$AgAu, CdAgAu$_2$), and $F43m$ (CdAg$_2$Au). These ground states are the lowest-energy structures at their respective compositions from the LMTO-ASA data, and the binary structures are consistent with the formation of $L2_1$ Cd$_2$AgAu based on the arguments given in Sec. III.

C. CVM calculations

CVM calculations were performed for two different interaction sets based on an inversion with all 21 structures: (1) 9

TABLE III. Effective cluster interactions in the Cd-Ag-Au system. Two sets of ECI's are given: (I) inversion based on all ECI's up to and including pairs and (II) all ECI's within the bcc tetrahedron. Interactions are given without their multiplicities included.

Type	Number	Set I: ECI (meV)	Set II: ECI (meV)
Empty	0	0.8769	0
Point	1	-284.14	-274.25
	2	-121.42	-111.52
NNN pair	3	12.001	8.4174
	4	1.108	-0.3936
	5	11.8459	13.5065
NN pair	6	19.0784	13.6606
	7	14.3723	10.7745
	8	34.8842	36.0668
Triplet	9	0	3.1194
	10	0	1.4473
	11	0	0.9614
	12	0	0.0891
	13	0	-0.0901
	14	0	0.9026
Quadruplet	15	0	-2.0622
	16	0	-0.4707
	17	0	-0.4202
	18	0	-0.3325
	19	0	-0.5174
	20	0	-0.5873

ECI's and (2) all 21 ECI's in the bcc tetrahedron. The bcc tetrahedron approximation to the entropy was used and calculations were done using the canonical basis.[28] The analysis was performed in exactly the same manner as that in the prototype study, except calculations were also done in a pseudobinary (vertical) section of the ternary phase diagram (the section $Cd_2Ag_{2-2x}Au_{2x}$ for $0 < x < 1$).

The order parameter and sublattice occupations as a function of temperature are given in Figs. 3 and 4, respectively, for CVM calculations based on 9 ECI's. Results for calculations involving 21 ECI's are qualitatively similar. The $B2'$ and $L2_1$ transitions based on 9 ECI's were found to occur at 1473 and 308 K ($\tau = 4.8$), respectively; less reliable calculations based on 21 ECI's found these transitions at 1522 and 388 K ($\tau = 3.92$), respectively. The large difference between the transitions for 9 and 21 ECI's is probably due to the presence of large multiplet interactions in the set of 21 ECI's. Even though some of these interactions are small in magnitude compared to the pairs, their effects are increased by the higher multiplicity of these clusters (i.e., more clusters per lattice point). Qualitatively, the two interaction sets reveal very similar behavior: a very stable $B2'$ structure that disorders at very high temperature and an $L2_1$ structure that is weakly stable and appears only at low temperature.

The sublattice occupations given in Fig. 4 for 9 ECI's reflect the asymmetric ordering tendencies in the constituent binary systems, where ordering in Cd-Au is much stronger than in Cd-Ag. As a result of this asymmetry, in the $B2'$ phase region, there is a preference for Au on sublattices 2 and 3 and for Ag on sublattice 1. The strong ordering in Cd-Au favors the formation of Cd-Au NN pairs, which thus
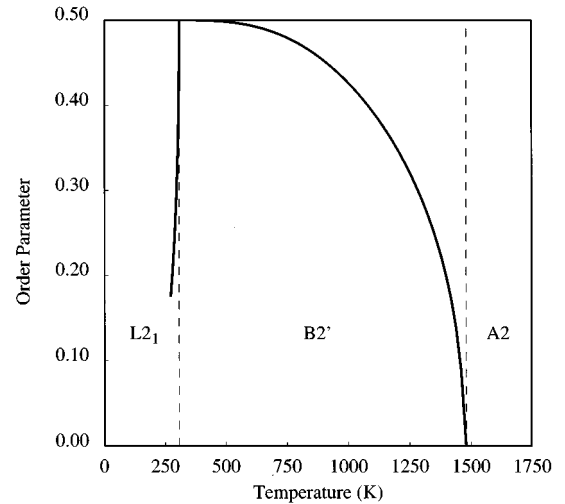

FIG. 3. Order parameter $\eta = \langle \sigma_1^2 \rangle - \langle \sigma_3^2 \rangle$ as a function of temperature calculated using the CVM with 9 ECI's. A transition to the $B2$ phase occurs near 1500 K, followed by a low-temperature transition to the Heusler structure. Note that for the order parameter as defined, a value of 0.5(0) in the $B2$ (Heusler) structure indicates perfect order. From this fact, it is clear that the $B2$ phase is nearly perfectly ordered well before a transition to the Heusler structure takes place.

enriches sublattices 2 and 3 with Au and depletes them of Ag. Note also that sublattice 1 is completely occupied by Cd *before* the $L2_1$ transition occurs, emphasizing the weak tendency towards the formation of the Heusler alloy in this system.

The vertical section of the phase diagram was calculated by assuming that both the high- and low-temperature transitions are second order. This assumption was made to simplify the calculation, since otherwise data would have to be taken at other compositions to locate any tie lines outside the section. Alternatively, one could assume that the vertical section is *quasibinary* (i.e., that the tie lines lie inside the plane of the section), as was done by Burton *et al.*[21–23] Such assumptions were avoided in the present work to retain the ternary spirit of the calculations. The isopleth connecting $B2$ CdAu and $B2$ CdAg was computed and is given in Fig. 5. Experimental data from Petzow and Effenberg[49] have been superimposed on the CVM results. Immiscibility between the $B2$ and $L2_1$ phases was not considered in the calculations, although it would presumably occur at low temperatures.[22] This simplification was made to avoid the same difficulty with tie lines outside the section of the diagram. The bcc $A2 \rightarrow B2'$ transition lines in theory and experiment follow the same general trend, indicative of the stronger ordering tendencies in Cd-Au. The experimental transition line disappears due to melting, however. The low-temperature $B2' \rightarrow L2_1$ transitions as given by theory and experiment agree fairly well, with a similar quantitative error in the CVM prediction for transitions at different compositions.

D. Discussion

The CVM predictions for the $B2' \rightarrow L2_1$ transition are somewhat lower than the experimental result of 523 K found
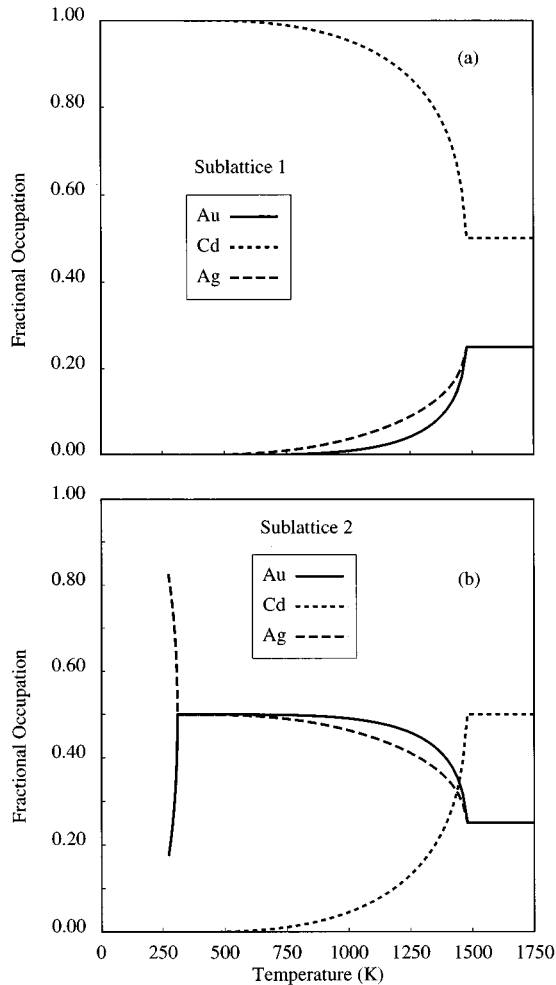
FIG. 4. Fractional occupation of sublattices 1 (a) and 2 (b). In the disordered phase, fractional occupations are constant and given by the average concentration. In the $B2$ phase, sublattice 2 becomes enriched by Au, indicative of the asymmetry in the system. At low temperature, sublattice 2 fills with Ag as expected for the Heusler structure. Sublattice 3 occupations are equivalent to sublattice 2, except at low temperature, where the Ag and Au occupations are reversed.

in Rothwarf and Muldawer.[14] The agreement is excellent, however, given that it was obtained essentially with only a knowledge of the atomic numbers of the elements. The high-temperature $B2' \to A2$ transition does not occur at all compositions in the experimental system since $B2'$ $Cd_2(Ag,Au)$ melts at 923 K before it disorders at the equiatomic composition. The underestimation of T_2, the low-temperature transition, is most likely due to the fact that the pair interactions indicate NNN ordering in Cd-Au and Cd-Ag that is too strong and NNN ordering in Ag-Au that is too weak. The strength of the NN ordering tendencies leads to the very stable $B2'$ phase and is probably the dominant factor in the overestimate of the $B2' \to A2$ transition. It appears that no site-substitution studies have been done in Cd-Ag-Au, so that the prediction of preferential sublattice occupation cannot be compared with experiment. However, given the asymmetry in the ordering tendency of the binary Cd-Au and Cd-Ag systems, it seems unlikely that experiment would reveal a qualitatively different picture. To the authors' knowledge, no
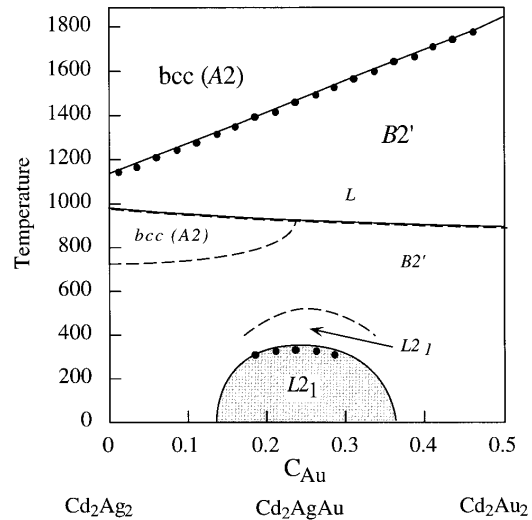

FIG. 5. Calculated isoplethal section of the Cd-Ag-Au phase diagram. All transitions were assumed to be second order, and two-phase equilibria between the $B2$ and Heusler structures at low temperature were not considered. Experimental data from Ref. 49 are superimposed with dotted lines; these phase fields are indicated with smaller italicized letters.

previous studies have made predictions concerning sublattice occupation in Heusler compounds.

The previous CVM studies by Tso and Sanchez[9] and Burton et al.[21-23] differ from the present work in several respects. In the study of Tso and Sanchez, the CVM tetrahedron approximation was used to study $B2' \to L2_1$ transition in Ni_2TiAl; NN and NNN interactions were fit to the binary phase diagrams to achieve this end. No sublattice occupations were computed by these authors, second-order transitions were assumed as in the present study, and high-temperature transitions between the disordered and $B2'$ phase were not considered. In the work of Burton et al., quasibinary sections of the ternary phase diagram were computed in the cube approximation (CA) to the *binary* simple cubic (sc) CVM. This allowed for facile computation of immiscibility between the $B2'$ and $L2_1$ phases, since it reduces the phase equilibria to a binary problem. In addition, these authors computed the $B2' \to L2_1$ transition *at stoichiometry* using the octahedron approximation (OA) to the ternary bcc CVM.[23] They found substantial differences between the ternary bcc-OA and binary sc-CA calculations of the $B2' \to L2_1$ transition. This indicates that the introduction of even a small amount of disorder on the A-site sublattice can have a large effect on the transitions. In the present paper, complete ternary disorder is allowed; hence any errors introduced with respect to a quasibinary approximation are avoided. The latter are likely to be larger than any errors introduced by assuming that the transitions are second order.

The discrepancy between the experimental and theoretical transition temperatures could be remedied by a variety of factors. An increase in the stability of the Cd-Ag and Cd-Au $B2$ compounds relative to $B32$ AgAu would most likely lead to weaker NNN ordering in the former binary systems. An increase in the stability of the $B32$ AgAu phase implies stronger NNN ordering in this system. These two effects will yield a more stable Heusler structure. It might also seem

beneficial to compute formation enthalpies relative to the elements in their *true* crystal structures. This, however, would only change the formation enthalpies by a linear function of composition, which in turn can only effect the empty and point cluster interactions.[50] At a fixed composition, these interactions do not affect the energy when the configuration is changed; hence they could not affect the results presented here. Finally, inclusion of vibrational and electronic contributions to the free energy would most likely improve the quantitative agreement, although would probably not change the qualitative results.

The atomic sphere approximation in the electronic structure calculations is another possible source of error. The ASA was used as an initial method to see if reasonable qualitative results could be obtained for this system. It could no doubt be improved, at least quantitatively, in any number of ways. The simplest possibility would be to allow for variations in sphere radii for different atoms. A more accurate solution would be to perform costly full-potential calculations (using LAPW or full-potential LMTO, for example). This would avoid approximations associated with the ASA, and would also allow a better treatment of atomic relaxations. Given the qualitative success of the present results, these lengthy calculations were not undertaken, although it may be necessary for other systems in the future.

V. CONCLUSIONS

The complex ordering phenomena in bcc-based Heusler alloys can be treated quite well using accurate ternary cluster variation method calculations. The series of order-disorder phase transitions that occur in these systems cannot only be reproduced, but also information about the nature of the transitions, the degree of long-range order, and sublattice occupations can be obtained. In addition, it is plausible to perform such calculations for prototype systems and for *real* systems using effective cluster interactions obtained from first principles.

Prototype studies revealed several qualitative features about the nature of the phase transitions in these systems. The formation of a Heusler compound of stoichiometry A_2BC is favored most if the binary systems AB and AC favor $B2$ compounds, and if the BC system favors a $B32$

compound. The relative stabilities of each of the compounds in the binary systems then plays a role in determining the quantitative nature of the phase transitions seen at the Heusler composition. Specifically, it was found that the NNN ordering tendencies in the three binary systems are a controlling factor for the relative temperatures at which the $A2 \rightarrow B2'$ and $B2' \rightarrow L2_1$ transitions occur.

CVM calculations were done using input from a series of LMTO-ASA calculations of Cd-Ag-Au alloys. The CVM analysis with 9 ECI's revealed both high- and low-temperature transitions in Cd_2AgAu, in agreement with experiment. A vertical section of the Cd-Ag-Au phase diagram was also computed and agreed qualitatively with experiment, despite the melting transition that occurs in the real system. Asymmetry of the ordering tendencies in the Cd-Au and Cd-Ag systems also leads to a prediction of preferential sublattice occupation in the $B2'$ phase, something that has yet to be verified experimentally in this system. Such calculations could prove useful in other systems where information is needed about the types of substitutional antisite defects present.

In this study, the effect of multiplet cluster interactions was not examined in detail, but the results for the set of 21 ECI's in Cd-Ag-Au clearly indicate that these interactions can play a significant role in the degree of $L2_1$ stability. Such quantitative effects *cannot* be obtained by extrapolation from the binary edges, thus rendering techniques based only on binary information limited in their predictive ability. The present first-principles analysis of the Heusler compound Cd_2AgAu does not suffer from these limitations, and it amply demonstrates the viability of a first-principles methodology in the study of complex ternary order-disorder problems.

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