Theoretical study of alloy phase stability in the Cd-Mg system

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A theoretical study of thermodynamic properties and of the phase diagram for crystalline hcp-based Cd-Mg alloys is presented. Many first-principles studies of phase diagrams for metallic alloys have considered only configurational contributions to the free energy, which arise from the effects of substitutional disorder on the entropy and enthalpy. In this paper, the additional effects of the vibrational free energy, the electronic entropy, and the energy associated with structural relaxations on the thermodynamic properties and calculated phase equilibria for Cd-Mg alloys are studied. Ground-state properties and the densities of states of stable and metastable Cd-Mg compounds with hcp-based structures have been calculated with the linear muffin-tin orbital (LMTO) method. The results of these LMTO calculations are combined with the cluster variation method to calculate the configurational free energy and electronic entropy of ordered and disordered alloys from first principles. The vibrational free energy is treated using the Debye model; the configurational dependence of the Debye temperature is obtained semiempirically from experimentally measured entropies of formation in combination with the resutls of the LMTO calculations. The energy associated with structural relaxations is estimated from experimentally measured lattice parameters and elastic constants. We find that, although the configurational free energy is the largest component of the total alloy free energy, nonconfigurational effects contribute significantly to thermodynamic properties, and hence appreciably affect the calculated Cd-Mg phase diagram.

I. INTRODUCTION

In order to understand the effect of thermodynamic variables on the physical properties of alloys, a knowledge of the equilibrium and metastable phases and how their relative stabilities depend on temperature, composition, pressure, etc., is required. Therefore, much theoretical research has been devoted to the study of phase stability in crystalline alloys. Electronic structure calculations provide an important tool in this field of study. From such calculations the total energies of pure elements and alloy compounds at 0 K can be determined from a knowledge of only the atomic numbers. Therefore, it has become possible to predict the equilibrium ground-state structures of many alloy systems and to determine lattice constants, heats of formation, and elastic properties from first principles which agree remarkably well with experimentally determined values.

As important as the first-principles, zero-temperature calculations mentioned above are, they cannot directly provide information about the effect of temperature (T) and composition (c) on the stability of alloy phases. To understand c-T phase diagrams, it is necessary to determine thermodynamic properties. In particular, if the temperature- and composition-dependent free energies can be calculated, then equilibrium phase boundaries can be obtained through standard common-tangent constructions. First-principles energy calculations must therefore be combined with statistical mechanical methods in order to calculate alloy phase diagrams.

In this paper we will be concerned with substitutional alloys for which atoms can be unambiguously associated

with the sites of a periodic crystal structure (e.g., fcc, hcp, bcc, etc.) which we shall refer to as the *parent structure*. For substitutional alloy systems, the phases differ by the type of configurational long-range order (or lack thereof) present, and by the type of parent structure upon which the alloy is based (more than one type of parent structure is generally present in substitutional alloy systems, as when the structures of the constituent elements differ, for example). The free energy of a substitutional alloy contains configurational, electronic, vibrational, and elastic contributions. The total energy of a given arrangement of atoms located on the sites of the ideal, rigid parent structure and the disorder associated with these configurations are the elements which contribute to the configurational free energy of a substitutional alloy. Elastic contributions arise from three effects in the case of a substitutional alloy: (1) global volume changes, (2) static displacements of atoms away from ideal lattice positions, and (3) structural relaxations. Dynamic vibrations of the atoms about equilibrium positions and electronic excitations give rise to vibrational and electronic contributions to the free energy, respectively.

The Ising model can be used to study configurational thermodynamic properties of substitutional alloys. In this model, the energy is expressed in terms of pairwise or, more generally, multiatom effective cluster interaction parameters (ECI's).[1,2] Recently it has become possible to derive these ECI's from first-principles calculations of the electronic structures of either ordered alloy compounds[3] or of disordered mixtures of atoms located at the sites of an ideal lattice.[4-6] For a given set of ECI's, statistical mechanical techniques such as the cluster variation

method[7] (CVM) or Monte Carlo simulation can be used to calculate configurational thermodynamic properties. Therefore, *ab initio* determinations of *c-T* phase diagrams are possible. Several such phase diagram computations for fcc- and bcc-based alloy systems have been undertaken recently (for a review of much of the work done along these lines, see Refs. 8 and 9).

One of the purposes of the present paper is to apply the techniques described in the previous paragraph to the study of an alloy system with hcp-based structures. Several studies of the ground-states of order[10–15] and prototype phase diagrams of the hcp Ising model[15–18] have been performed. However, very few first-principles calculations of phase diagrams for alloys containing hcp-based structures have been undertaken.[19] Another purpose of this paper is to analyze the effect of nonconfigurational free-energy terms on calculated phase diagrams and thermodynamic properties.

We have chosen to study Cd-Mg which is a prototype ordering hcp-based alloy system. In Fig. 1 the experimental Cd-Mg phase diagram as assessed by Moser *et al.*[20] has been redrawn. At high temperatures a continuous solid solution between hcp Cd and hcp Mg is found. As the temperature is lowered, three ordered phases with hcp-based structures are stabilized in composition ranges around the stoichiometries Cd_3Mg, $CdMg_3$, and $CdMg$. The Cd_3Mg and $CdMg_3$ phases form in the DO_{19} structure, while the $CdMg$ compound has the $B19$ structure (see Ref. 16 for a description of these hcp superstructures). Since the melting points of Cd and Mg, and the order-disorder transition temperatures of the Cd_3Mg, $CdMg$, and $CdMg_3$ phases are low, experimentally measured lattice parameters and thermodynamic properties are available for disordered and ordered alloys.[20–22]

In addition to the relative wealth of experimental information available for Cd-Mg, this system is also interesting because of the differences between elemental Cd and Mg. For example, since the Debye temperatures of Cd and Mg are significantly different (209 K and 400 K, respectively[23]), the vibrational contributions to the free energy of formation might be sizable. Furthermore, despite the fact that these elements are isovalent, the c/a ratio in elemental Mg is 1.623, close to the ideal value of $(\frac{8}{3})^{1/2} = 1.632\,993. . .$, whereas for Cd this ratio is highly nonideal at a value of 1.886.[24] The dependence of the c/a ratio on alloy concentration for disordered Cd-Mg alloys was measured by Hume-Rothery and Raynor,[22] and the results were explained according to a Brillouin zone stabilization mechanism. In this paper, the effect of c/a relaxation on the energy of Cd-Mg alloys will be shown to be very important in understanding the asymmetry in the measured peritectoid reaction temperatures, shown in Fig. 1, for the Cd_3Mg and $CdMg_3$ phases.

The remainder of this paper is organized as follows: In the following section it will be shown that the general expression for the total free energy of a nonmagnetic, metallic, substitutional alloy can be written in terms of
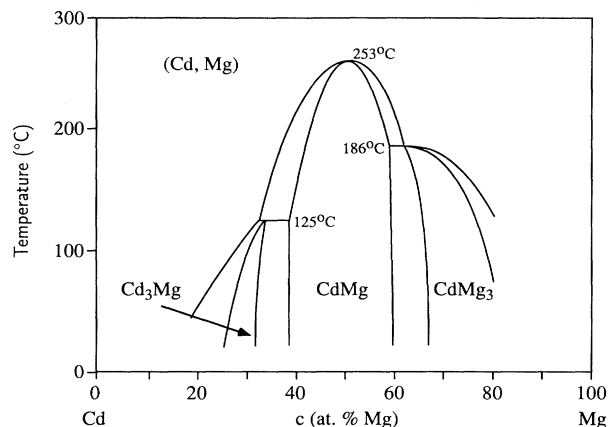

FIG. 1. The experimentally determined solid-state portion of the composition-temperature Cd-Mg phase diagram, as assessed by Moser *et al.* (Ref. 20). The horizontal axis corresponds to the concentration in atomic percent Mg: c (at. % Mg). The vertical axis gives the temperature in degrees centigrade. Equilibrium phase boundaries are indicated by solid lines and have be redrawn from Ref. 20. Temperatures of invariant reactions are indicated in the figure. (Cd,Mg) refers to the disordered, hcp-based solid solution. Regions of stability for ordered phases are indicated by the stoichiometries of the compounds: $CdMg$, Cd_3Mg, and $CdMg_3$.

configurational averages of the vibrational and electronic free energies, and the configurational and elastic energies. In Sec. III, we will show how the cluster expansion due to Sanchez, Ducastelle, and Gratias[1] and the CVM can be used to facilitate the calculation of these configurational averages. The approximations which will be made in describing electronic, elastic and vibrational contributions to the free energy will be discussed in Sec. IV where the method of calculating the cluster expansion coefficients for these different terms is also presented. Results of calculations of phase diagrams and thermodynamic properties will then be presented in Sec. V and compared to experimental measurements.[20,21] A comparison of our results with those of previous calculations[25,26] for the Cd-Mg system will be made in Sec. VI. Finally, in Sec. VII, a discussion of our results and some general conclusions will be presented.

II. THE ALLOY FREE ENERGY

A study of phase stability for alloys requires the calculation of thermodynamic properties, as mentioned above. In principle, all such properties can be obtained from the partition function. In particular, for a crystalline, binary, substitutional alloy with a single type of parent structure and an arbitrary concentration, at fixed pressure (P) and temperature, the partition function (Z) has the following form (what follows is closely related to the treatment given by de Fontaine[27] and by Ceder[28]):

$$Z(T,P,\mu) = \sum_{\sigma} \sum_{\tau} \exp\{-[E_s(\sigma,V) + E_T(\sigma,V,T,\tau) + PV - \mu c]/k_B T\} . \tag{1}$$

In Eq. (1), μ is the difference of the chemical potentials (per atom) for the two atomic species, V is the volume per atom, and k_B is Boltzmann's constant. The first sum in (1) is over all configurational "states" and σ specifies the arrangement of the different atoms on the sites of the parent structure of the alloy; the second sum is over all "excited" states (τ) of the alloy for a given configuration. The second two terms in the exponential in (1) are the familiar pressure-volume and chemical work terms which enter because we are working in a fixed P, T, μ ensemble. $E_s(\sigma, V)$ denotes the "static" total energy of the alloy at zero temperature and $E_T(\sigma, V, T, \tau)$ includes all of the effects of thermal excitations (e.g., vibrational modes, electronic excitations, etc.) on the alloy energy.

In this paper, the effects of atomic relaxations and chemical rearrangements on the $T=0$ K total energy of the alloy are treated separately. In other words, we split the first term in the exponential in (1) into two contributions:

$$E_s(\sigma, V) = E_c(\sigma, V) + E_r(\sigma, V) , \qquad (2)$$

where $E_c(\sigma, V)$ is the *configurational energy* defined as the total energy of an alloy for which the atoms are located on the sites of the ideal parent structure, and $E_r(\sigma, V)$ is the *relaxation energy* arising from symmetry-allowed deformations of the ideal lattice and from local atomic displacements, as we discuss further in Sec. IV B. For the present study we are concerned with nonmagnetic, metallic alloys for which electronic and vibrational excitations contribute to $E_T(\sigma, V, T, \tau)$. We neglect electron-phonon coupling, so that electronic and vibrational degrees of freedom are assumed to be independent. Therefore, the second term in the exponential of Eq. (1) can be written explicitly as

$$E_T(\sigma, V, T, \tau) = E_e(\sigma, V, T, \varepsilon) + E_v(\sigma, V, T, v) , \qquad (3)$$

where $E_e(\sigma, V, T, \varepsilon)$ is the change in the total energy of the alloy resulting from the excited state (ε) of the electron gas and $E_v(\sigma, V, T, v)$ is the contribution arising from the lattice vibrational state v. Inserting (2) and (3) into (1), we have the following approximate expression for the partition function:

$$Z(T, P, \mu) = \sum_\sigma \sum_\varepsilon \sum_v \exp\{-[E_c(\sigma, V) + E_r(\sigma, V) + E_e(\sigma, V, T, \varepsilon) + E_v(\sigma, V, T, v) + PV - \mu c]/k_B T \} . \qquad (4)$$

Following Ceder,[28] we can perform the second and third sums in (4) yielding

$$Z(T, P, \mu) = \sum_\sigma \exp\{-[E_c(\sigma, V) + E_r(\sigma, V) + F_e(\sigma, V, T) + F_v(\sigma, V, T) + PV - \mu c]/k_B T \} , \qquad (5)$$

where $F_e(\sigma, V, T)$ and $F_v(\sigma, V, T)$ are the electronic and vibrational *free* energies, respectively. The alloy free energy, in this case actually the *grand potential* [$\Omega(T, P, \mu)$], can be expressed as $-k_B T$ times the logarithm of (5) which can be written as follows:

$$\Omega(T, P, \mu) = \langle E_c(\sigma, V) + E_r(\sigma, V) + F_v(\sigma, V, T) + F_e(\sigma, V, T) \rangle_\sigma + k_B T \sum_\sigma \rho(\sigma, T, P, \mu) \ln\rho(\sigma, T, P, \mu) + PV - \mu c , \qquad (6)$$

where $\rho(\sigma, T)$ is the configurational density matrix defined as

$$\rho(\sigma, T, P, \mu) = \frac{1}{Z(T, P, \mu)} \exp\{-[E_c(\sigma, V) + E_r(\sigma, V) + F_e(\sigma, V, T) + F_v(\sigma, V, T) + PV - \mu c]/k_B T \} , \qquad (7)$$

which gives the probability of observing configuration σ for a given temperature, pressure, and chemical potential. In Eq. (6), the brackets with subscript σ ($\langle \ \rangle_\sigma$) indicate a configurational expectation value:

$$\langle E_c(\sigma, V) + E_\tau(\sigma, V) + F_v(\sigma, V, T) + F_e(\sigma, V, T) \rangle_\sigma = \sum_\sigma \rho(\sigma, T, P, \mu)[E_c(\sigma, V) + E_r(\sigma, V) + F_v(\sigma, V, T) + F_e(\sigma, V, T)]$$

$$(8)$$

and the second term in (6) is the temperature times the negative of the configurational entropy.

III. CLUSTER EXPANSION OF CONFIGURATIONALLY DEPENDENT FUNCTIONS AND THE CLUSTER VARIATION METHOD

In the last section it was shown that in order to evaluate the grand potential of a substitutional alloy (6), the configuration averages of the vibrational and electronic free energies, as well as of the configurational and relaxation energies, must be determined. In the first part of this section we will summarize the formalism of cluster expan-

sions[1,2] which can be used to express the configurational dependence of any function of σ. Several statistical mechanical techniques are available for performing the necessary configurational averages; in this paper we will use the CVM,[7] which is briefly described in the second part of this section.

A. Cluster expansions

By separating the configurational and relaxation energies according to Eq. (2), it is sufficient to let the variable σ denote the arrangement of atoms on the sites of the parent structure (for Cd-Mg alloys the parent structure is the hcp structure with an ideal axial ratio). In particular,

we define the pseudospin variable σ_p which, for a binary alloy, takes on values $+1$ or -1 depending on whether the site located at p is occupied by an atom of type A (Mg) or B (Cd). The configurational vector is composed of the N (N being the number of atomic sites on the parent structure) pseudospin variable for all sites p: $\sigma = (\sigma_{p_1}, \sigma_{p2}, \ldots, \sigma_{pN})$. Any function of the configuration $[f(\sigma)]$ for a binary substitutional alloy with a *given parent structure* can be rigorously expanded in terms of an orthonormal set of 2^N cluster functions as follows:[1,2]

$$f(\sigma) = \sum_\alpha f_\alpha \Phi_\alpha(\sigma) , \qquad (9)$$

where $\alpha = (p, p', \ldots, p'')$ is the set of atomic sites which will be referred to as a *cluster*. In (9), $\Phi_\alpha(\sigma)$ are the cluster functions which, for a binary alloy, are simply defined as products of the spin variables for each site in the cluster.[1,2] The f_α in (9) are the cluster expansion coefficients (CEC's) which are uniquely defined and are independent of the configuration.[1,2] It should be noted that the CEC's for $F_e(\sigma, V, T)$ and $F_v(\sigma, V, T)$ are *volume* and *temperature dependent*, whereas the coefficients for $E_c(\sigma, V)$ and $E_r(\sigma, V)$ are functions only of volume. The f_α have the full space-group symmetry of the parent structure[1] (in this case hcp) so that terms in (9) can be grouped together to yield

$$\frac{f(\sigma)}{N} = \sum_\alpha{}' m_\alpha f_\alpha \overline{\Phi}_\alpha(\sigma) , \qquad (10)$$

where the prime indicates that the sum is only over clusters distinct by symmetry, m_α is the multiplicity which is defined as the number of symmetry equivalent clusters divided by N, and the overbar on the cluster function indicates that it is averaged over all symmetry-related clusters. Using (10) the configurational average of any $f(\sigma)$ can be expressed as follows:

$$\frac{\langle f(\sigma) \rangle_\sigma}{N} = \sum_\alpha{}' m_\alpha f_\alpha \xi_\alpha , \qquad (11)$$

where the ξ_α are defined as the expectation values of the averaged cluster functions and are referred to as *correlation functions*.[1,29]

The expansion (9) is exact provided that all of the 2^N different terms are included. For the configuration energy $E_c(\sigma, V)$, the expansion coefficients have been shown to decay in magnitude rapidly (see, for example, Ref. 30). Therefore, it is, in practice, sufficient to retain only a small number of cluster expansion terms in order to accurately describe the configurational dependence of $E_c(\sigma, V)$.[30,31] In order to determine the coefficients for the different configurationally dependent alloy properties needed to compute the grand potential (6), we will use the structure inversion method (SIM) which was first applied to the study of (configurational) thermodynamic properties of transition-metal alloys by Connolly and Williams.[3] In the SIM it is assumed that clusters containing atomic sites, which are separated by more than a certain distance and/or which contain more than a given number of sites, have corresponding values of f_α which are negligible and

can therefore be ignored. As a consequence, expansion (10) is assumed to contain only a small number of terms (around 10), and the coefficients f_α are obtained from the values of $f(\sigma)$, m_α, and $\Phi_\alpha(\sigma)$ for a large number of configurations. In general, it is important to use more values of $f(\sigma)$ than the number of coefficients needed in order to check the convergence of the cluster expansion.[31,32]

B. The CVM and the configurational free energy

The configurational entropy term, and more generally the configurationally averaged quantities, in Eq. (6) will be calculated using the hcp tetrahedron-octahedron approximation[15,33] of the CVM.[7] Specifically, using the CVM, we can write

$$\sum_\sigma \rho(\sigma, T, P, \mu) \ln \rho(\sigma, T, P, \mu)$$

$$\approx \sum_{\beta \subseteq \alpha_M} a_\beta \sum_{\sigma_\beta} \rho_\beta(\sigma_\beta, T, P, \mu) \ln \rho_\beta(\sigma_\beta, T, P, \mu) , \qquad (12)$$

where $\rho_\beta(\sigma_\beta)$ is the reduced configurational density matrix[1] which gives the probability of observing configuration σ_β on cluster β for given values of T, P, and μ. The sum in (12) is over all of the clusters contained in the *maximal clusters* (α_M) which define the level of the CVM approximation. In this study, the tetrahedron and octahedron made up of points (1,2,5,7) and (1,2,3,4,5,6) in Fig. 2, respectively, are the maximal clusters. In (12) the coefficients a_β are geometrical quantities which are defined in Refs. 7 and 34, and values for the tetrahedron-octahedron approximation of the hcp structure are given by Gratias, Sanchez, and de Fontaine.[33]

The *cluster probability* $\rho_\beta(\sigma_\beta, T, p, \mu)$ can be expressed as a linear combination of the correlation functions corresponding to the subclusters of β.[29] The CVM expression for the configurational entropy (12) can therefore be combined with the cluster expansions of the configurational and relaxation energies and of the electronic and vibrational free energies to yield a grand potential which is a functional of the correlation functions. This functional
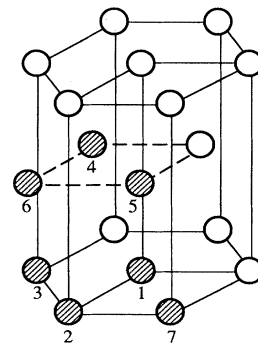

FIG. 2. The hcp structure. Shaded circles form the tetrahedron and octahedron clusters which are used in the CVM calculations. The terms used in the cluster expansion for the different free-energy contributions are those corresponding to subclusters of the tetrahedron and octahedron.

can be minimized for given values of T, P, and μ to yield a variational estimate of $\Omega(T,P,\mu)$ and other thermodynamic properties, provided the CEC's for $E_c(\sigma,V)$, $E_r(\sigma,V)$, $F_e(\sigma,V,T)$, and $F_v(\sigma,V,T)$ are known. In the next section we will discuss how these CEC's for the Cd-Mg system have been calculated.

IV. DETERMINATION OF CLUSTER EXPANSION COEFFICIENTS

In order to determine the CEC's we will use the SIM, whereby the expansion coefficients are obtained from values of the function of interest for a set of configurations. In this section we will discuss in detail how we have determined the coefficients for $E_c(\sigma,V)$, $E_r(\sigma,V)$, $F_e(\sigma,V,T)$, and $F_v(\sigma,V,T)$.

In Fig. 2, a schematic drawing of the hcp structure is shown on which a set of points are labeled. Nine terms will be included in the cluster expansions of $E_c(\sigma,V)$, $E_\tau(\sigma,V)$, $F_e(\sigma,V,T)$, and $F_v(\sigma,V,T)$. Eight of these terms correspond to the following symmetry nonequivalent clusters: the point, two nearest-neighbor pairs (1,2 and 1,5 in Fig. 1), the next-nearest-neighbor pair (2,4), three nearest-neighbor triangles (1,2,3 and 1,2,5 and 1,2,7), and the nearest-neighbor tetrahedron (1,2,5,7). The ninth term is the configurationally invariant one which is defined as the average of the function of interest over all configurations. As we discuss in Sec. IV E, these nine terms are sufficient to describe the configurational dependence of $E_c(\sigma,V)$, $E_r(\sigma,V)$, $F_e(\sigma,V,T)$, and $F_v(\sigma,V,T)$ in the Cd-Mg system.

In order to determine the CEC's for $E_c(\sigma,V)$, $F_e(\sigma,V,T)$, and $F_v(\sigma,V,T)$, the values of these properties for *ordered* hcp compounds will be used. In particular, the structures of the ordered compounds considered are nine of the ground states of the hcp Ising model with anisotropic nearest-neighbor pair interactions.[15,16] This set of structures consists of the pure hcp elements, an A_2B (AB_2) structure labeled by its space group $Cmcm$, the A_3B (AB_3) DO_{19} structure and three AB structures

denoted as $B19$, $Pmmn$, and $P\bar{6}m2$. In Refs. 15 and 16, the unit cells and space-group symmetry information of these structures are given. In Table I we list the values of the averaged cluster functions $[\bar{\Phi}_\alpha(\sigma)]$ for each structure and the values of the multiplicities (m_α). From Table I it can be seen that the averaged cluster functions for the two in-plane, nearest-neighbor triangles, (1,2,3) and (1,2,7) in Fig. 2, are the same for all of the ordered structures considered. For this reason we will assume in this work that the CEC's corresponding to these two triangles are always the same. In order to correct for this assumption using the SIM, one would need to determine properties of ordered structures for which the values of the averaged cluster functions for the two triangles are distinct. One such structure is the A_4B_3 ground state described in Ref. 15. However, the unit cell of this compound contains 14 atoms and is therefore difficult to consider in the band-structure calculations to be discussed below.

The eight distinct expansion coefficients (eight since we assume that the two in-plane triangle terms are equal) for the vibrational and electronic free energies, as well as for the configurational energy, are obtained by performing a least-squares fit of the truncated cluster expansion to the values of the nine ordered alloy compounds. For the relaxation energy, values of $E_r(\sigma,V)$ for disordered alloys, obtained from experimentally measured lattice parameters and elastic constants, will be used to obtain the CEC's also through a least-squares fit as described in Sec. IV B.

Before proceeding, a discussion of the volume dependence is needed. For given values of P, T, and μ, the equilibrium volume is determined as the value of V which minimizes the grand potential (6). For a pressure of one atmosphere, the PV term in (6) is negligible in the Cd-Mg system and we will, therefore, set $P=0$ in our calculations. The effect of V on the different terms in (6) can be incorporated in one of two ways: (1) volume dependence is considered explicitly in the cluster expansion by evaluating the volume dependence of the CEC's (in this case the grand potential is minimized with respect to V as

TABLE I. The number of clusters per atom (m_α) and average cluster functions of the ordered structures used to determine the CEC's. The clusters (α) listed in this table are those considered in the expansion of the configurational and relaxation energies, as well as the electronic entropy and vibrational free energy. The set of numbers listed for each cluster under the heading (α) correspond to the positions of the atoms which make up α according to Fig. 2.

α	m_α	hcp Cd	hcp Mg	DO_{19} Cd$_3$Mg	DO_{19} CdMg$_3$	$Cmcm$ Cd$_2$Mg	$Cmcm$ CdMg$_2$	$P\bar{6}m2$ CdMg	$B19$ CdMg	$Pmmn$ CdMg
		1	1	1	1	1	1	1	1	1
1	1	-1	1	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{3}$	$\frac{1}{3}$	0	0	0
1,5	3	1	1	0	0	$\frac{1}{9}$	$\frac{1}{9}$	-1	$-\frac{1}{3}$	$\frac{1}{3}$
1,2	3	1	1	0	0	$-\frac{1}{3}$	$-\frac{1}{3}$	1	$-\frac{1}{3}$	$-\frac{1}{3}$
2,4	3	1	1	1	1	$\frac{1}{9}$	$\frac{1}{9}$	-1	1	-1
1,2,5	6	-1	1	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{9}$	$-\frac{1}{9}$	0	0	0
1,2,7	1	-1	1	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	0	0	0
1,2,3	1	-1	1	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	0	0	0
1,2,5,7	2	1	1	-1	-1	$-\frac{1}{3}$	$-\frac{1}{3}$	-1	1	-1

well as the values of the correlation functions in a CVM calculation), or (2) the volume dependence is implicitly included through the dependence of V on σ. In the second case, the volume is fixed by the values of the correlation functions and the CEC's, can be determined with the SIM using the values of the functions of configuration at the volumes for which the energy of the alloy is minimized at $T=0$ K. This implicit treatment of the volume dependence is used to determine the CEC's in the present work (from now on, therefore, we will drop the explicit volume dependence in our notation for the different contributions to the free energy); we have analyzed the effect of including the volume dependence explicitly in our phase diagram calculations and we find that the differences are not significant.

A. The configurational energy

For the configurational energy, the CEC's will be determined from first-principles band-structure calculations of $E_c(\sigma)$ for the ordered structures discussed above. For each alloy compound, the total energy has been calculated within the local-density approximation[35] using the method of linear muffin-tin orbitals (LMTO) in the atomic sphere approximation (ASA).[36,37] Although the structures of the ordered compounds have sufficiently low symmetry so that the lattice parameters and atomic positions can relax away from the values corresponding to an ideal hcp structure, we have not included this effect in our band-structure calculations and we have optimized the total energy with respect to volume only. The effect of structural relaxation on the enthalpy will be included in the term $E_r(\sigma)$ which will be computed from experimentally determined lattice parameters[22] and elastic constants[44] as discussed in the next section. The LMTO calculated total energies are, therefore, for close-packed structures for which the ASA is most accurate.[36,37] For use in determining the CEC's for the electronic entropy, the density of states at the Fermi level is also computed at the calculated equilibrium volume.

The LMTO-ASA calculations were performed scalar relativistically and the exchange-correlation potential of von Barth and Hedin[38] was used. The combined correc-

tion terms[36,37,39] were included in the self-consistent calculation of the electronic potential and the muffin-tin correction[40] was used in the evaluation of Coulomb contributions to the total energy. The sphere radii of Cd and Mg were taken to be equal in the calculations since the relative sizes and bulk moduli of these elements are very similar.[37] All reciprocal-space summations were performed using the tetrahedron method[41] with sufficient numbers of k points to converge the energy to within 0.5 mRy/atom. The wave functions were expanded using orbitals with l less than or equal to 3.

In Table II, the calculated values of the equilibrium atomic volume (V_0), bulk modulus (B), configurational formation energy (ΔE_c), and density of states at the Fermi level (n_F) are listed. The configurational formation energy is defined as

$$\Delta E_c(\sigma) = E_c(\sigma, V_0) - cE_c(\text{Mg}) - (1-c)E_c(\text{Cd}) , \qquad (13)$$

where $E_c(\sigma, V_0)$ is the total energy of configuration σ at its equilibrium volume and similarly for $E_c(\text{Cd})$ and $E_c(\text{Mg})$; c denotes the atomic concentration of Mg. The bulk moduli and equilibrium volumes were calculated using a third-order polynomial fit to the total-energy versus atomic volume. In Table II, values of Debye temperatures are also given which were obtained in the manner described in Sec. IV D.

B. The relaxation energy

The relaxation energy, $E_r(\sigma)$, contains contributions from two distinct but related effects (note that the effect of global volume change is included in the configurational energy): symmetry-allowed distortions of the unit cell which cause the relative ratios of the lattice parameters to differ from those of an ideal hcp structure, and local displacements of atoms (which can occur in disordered phases as well as in perfectly ordered compounds for which the symmetry of the occupied Wyckoff positions allow atomic positional degrees of freedom). In principle, the relaxation energy in the alloy can be obtained from first-principles total-energy calculations of ordered alloy compounds.[42] We are currently using a full-potential

TABLE II. Calculated configurational formation energies (ΔE_c), molar volumes (V_0), bulk moduli (B), and density of states at the Fermi level (n_F) as derived from the LMTO-ASA for ideal hcp-based structures with unrelaxed geometries. The final column lists semiempirical Debye temperatures (θ) calculated according to the method described in Sec. IV D. The units of the different quantities are as follows: ΔE_c (mRy/atom), V_0 (cm^3/mol), B (Mbar), n_F (states/Ry atom), and θ (K).

Structure	Composition	ΔE_c	V_0	B	n_F	θ
hcp	Cd	0	12.34	0.68	4.1	209
hcp	Mg	0	13.31	0.40	4.8	400
DO_{19}	Cd$_3$Mg	-7.8	12.14	0.67	3.8	248
DO_{19}	CdMg$_3$	-7.2	12.46	0.49	4.14	352
$Cmcm$	Cd$_2$Mg	-8.0	12.10	0.63	3.6	253
$Cmcm$	CdMg$_2$	-7.5	12.32	0.52	3.9	322
$P\bar{6}m2$	CdMg	-5.2	12.44	0.55	4.1	267
$B19$	CdMg	-10.2	12.15	0.59	3.7	276
$Pmmn$	CdMg	-5.7	12.39	0.55	4.0	267

LMTO method[43] for this purpose. In the present study, however, the expansion coefficients of $E_r(\sigma)$ have been obtained from experimentally measured values of the lattice parameters for disordered alloys (in addition to those of elemental Cd and Mg) (Ref. 22) and of the elastic constants of the elements.[44]

In the Cd-Mg system, since the equilibrium volumes of the elements differ by only 5%, the effect of local atomic displacements on the total energy of the alloy should be small, and we have therefore not considered this effect. By contrast, axial (c/a) ratios differ greatly from the ideal value for Cd-rich alloys. Therefore, in this study $E_r(\sigma)$ will be taken to contain contributions solely from lattice parameter relaxations.

For disordered alloys at 500 °C, the lattice parameters have been experimentally determined using x-ray diffraction by Hume-Rothery and Raynor.[22] The measured values of the c/a ratio are given in Table III, where we also list the calculated value of the relaxation energy. $E_r(\sigma)$ is defined as the amount of energy required to change the ratio of the lattice parameters, at constant volume, from the ideal value [i.e., $c/a = (\frac{8}{3})^{1/2}$] to the experimentally measured equilibrium value. The relaxation energies given in Table III were calculated using the standard quadratic form:

$$E_r(\sigma) = \frac{V}{2} \sum_{i,j} C_{ij}(\sigma)e_i e_j \tag{14}$$

TABLE III. Experimentally measured (Ref. 22) c/a ratios for disordered alloys at $T=310$ °C and the corresponding calculated relaxation energies (E_r) as a function of the concentration (c). Relaxation energies were determined using formula (14) as discussed in Sec. IV B.

c (at. % Mg)	c/a	E_r (mRy/atom)
0	1.900	−3.4
5.65	1.870	−2.6
12.74	1.820	−1.7
17.96	1.771	−0.9
22.06	1.743	−0.6
23.74	1.735	−0.5
25.43	1.726	−0.4
27.49	1.710	−0.3
28.75	1.702	−0.2
31.00	1.694	−0.2
36.25	1.665	0.0
39.15	1.6578	0.0
40.57	1.6515	0.0
41.60	1.6515	0.0
40.91	1.6515	0.0
45.33	1.6437	0.0
48.51	1.6420	0.0
49.44	1.6400	0.0
54.20	1.6349	0.0
60.00	1.6320	0.0
65.00	1.6291	0.0
70.00	1.6280	0.0
80.00	1.6262	0.0
100.00	1.6235	0.0

in terms of the elastic constants $C_{ij}(\sigma)$, the strains e_i and e_j, and the experimentally determined atomic volume V.[22] Voigt notation has been used in Eq. (14) for indices i and j. For a distortion of the c/a ratio away from the ideal value, the only nonzero strains are e_1, e_2, and e_3, which can be obtained from the difference between the measured c/a ratio and the ideal one along with the requirement that the volume be preserved (imposing the constraint $e_1+e_2+e_3=0$).[45] In determining the relaxation energies in Table III we have assumed that the elastic constants depend linearly on the concentration

$$C_{ij}(\sigma)=cC_{ij}(\text{Mg})+(1-c)C_{ij}(\text{Cd}) , \tag{15}$$

where the pure element values of C_{ij} have been taken from Ref. 44.

For the stable ordered Cd-Mg compounds, the difference between the ratios of the experimentally measured lattice parameters[22] and the values of these ratios corresponding to an ideal hcp geometry is less than 2% for hexagonal Cd_3Mg and $CdMg_3$ and 5% for the orthorhombic CdMg structure. By contrast, the relaxation of the c/a ratio for pure Cd and Cd-rich disordered alloys amounts to nearly a 15% strain, indicating that the relaxation energy is an order of magnitude larger for Cd-rich disordered alloys. Therefore, we will assume that $E_r(\sigma, V)$ is zero for the CdMg, Cd_3Mg, and $CdMg_3$ compounds (and nonzero for elemental Cd and Mg and for disordered alloys).

In order to obtain CEC's for $E_r(\sigma)$, we will assume that short-range order is negligible for the alloys at 500 °C which were studied by Hume-Rothery and Raynor.[22] Therefore, the average cluster functions are approximated by the values for a completely random alloy:

$$\overline{\Phi}_\alpha(\sigma)=(2c-1)^{n_\alpha} , \tag{16}$$

where n_α is the number of atoms in cluster α. The values of the relaxation energies for the disordered alloys and the average cluster functions obtained from (16), as well as the assumed zero values of $E_r(\sigma)$ for the ordered compounds CdMg, $CdMg_3$, and Cd_3Mg, are used in a least-squares fit of the cluster expansion from which the CEC's are then determined.

C. The electronic free energy

For the electronic free energy we will assume that the *energy* of the alloy is negligibly affected by electronic excitations, and we use the low-temperature expression for the *entropy* since we are concerned with temperatures which are below 1000 K in this study, and which are therefore much lower than the Fermi temperatures of the alloys. In particular, the low-temperature form of the electronic entropy is

$$S_e(\sigma, T) = \frac{\pi^2}{3} k_B^2 T n_F(\sigma) \tag{17}$$

in terms of the configurationally dependent density of states at the Fermi level $[n_F(\sigma)]$ at $T=0$ K. Using (17), the electronic entropy contribution to the alloy grand potential (6) can be determined from the configurational

dependence of $n_F(\sigma)$. The CEC's for $n_F(\sigma)$ are temperature independent [the T dependence of the entropy is contained explicitly in expression (17)]. The CEC's have been determined using the LMTO-ASA calculated values of the density of states at the Fermi level at $T=0$ K, given in Table II, in the same way as the expansion coefficients for the configurational energy were obtained. Specifically, the SIM was used to obtain the CEC's for $n_F(\sigma)$ through a least-squares fit of the eight-term cluster expansion for the density of states at the Fermi level to the values of $n_F(\sigma)$ for the ordered compounds which are listed in Table II.

D. The vibrational free energy

The vibrational free energy will be treated using the Debye model. Specifically, the vibrational internal energy and entropy take the form[46]

$$U_v(\sigma,T)=\tfrac{9}{8}k_B\theta(\sigma)+3k_BTD[\theta(\sigma)/T] \; ,$$

$$S_v(\sigma,T)=4k_BD[\theta(\sigma)/T]$$
$$\qquad -3k_B\ln[1-\exp(-\theta(\sigma)/T)] \; ,$$

(18)

and the free energy is expressed as

$$F_v(\sigma,T)=\tfrac{9}{8}k_B\theta(\sigma)-k_BTD[\theta(\sigma)/k_BT]$$
$$\qquad +3k_BT\ln[1-\exp(-\theta(\sigma)/k_BT)] \qquad (19)$$

in terms of the configurationally dependent Debye temperature $\theta(\sigma)$. The temperature dependence of the Debye temperature for a given configuration will be neglected in this work, and we will focus on the configurational dependence which is expected to be stronger. In Eqs. (18) and (19), $D[\theta(\sigma)/T]$ is the Debye function which is defined, for example, in Ref. 46 where tabulated values can also be found. In Eq. (18), the vibrational internal energy has been denoted $U_v(\sigma,T)$ in order to distinguish it from the energy of a vibrational state $E_v(\sigma,\nu)$, and the first term in Eqs. (18) and (19) is due to zero-point motion. In order to simplify the calculations of thermodynamic properties in this work, we have approximated the configurational expectation value of the vibrational free energy by the value of the free energy for the ensemble average of the Debye temperature:

$$\langle F_v(\sigma,T)\rangle_\sigma\approx F_v(\langle\theta\rangle_\sigma,T) \; . \qquad (20)$$

This approximation is valid to first order in the fluctuation of the Debye temperature about its ensemble average. We have estimated the leading correction to (20) and find it to be on the order of a tenth of a percent.

The Debye temperatures for ordered structures given in Table II were used to obtain the CEC's for $\theta(\sigma)$ through a least-squares fit of the cluster expansion, in the same manner as discussed above for $E_c(\sigma)$ and $n_F(\sigma)$. The values of the Debye temperatures listed in Table II were determined from a combination of experimentally determined and calculated information, as we now explain.

The values of the Debye temperatures for the pure elements listed in Table II were taken from experimental

measurements of heat capacities.[23] For the $B19$ CdMg and DO_{19} CdMg$_3$ and Cd$_3$Mg compounds, the values of $\theta(\sigma)$ have been obtained using entropies of formation at 298.15 K measured from calorimetry experiments;[21] the values of the entropies of formation in units of Boltzman's constant which are quoted by Hultgren, Anderson, and Kelley[21] are 0.10, 0.15, and -0.07 for the Cd$_3$Mg, CdMg, and CdMg$_3$ compounds, respectively. In order to extract the vibrational contribution to the experimentally measured entropies of formation for the compounds, we performed CVM calculations in which only the configurational and relaxation contributions to the free energy were included (in these calculations no electronic or vibrational terms were considered). From these calculations, the values of the *configurational* formation entropies were obtained at 298.15 K. The *electronic* formation entropies were then calculated from formula (17) at 298.15 K using the calculated densities of states at the Fermi level listed in Table II. The configurational and electronic contributions were then subtracted from the experimental values of the *total* formation entropies to give the *vibrational* entropy of formation. Next, using the Debye temperatures of the pure elements, the vibrational *formation* entropies were transformed into *total* vibrational entropies for the compounds [i.e., we determined $S_v(\sigma)$ as $S_v(\sigma)=\Delta S_v(\sigma)+cS_v(\text{Mg})+(1-c)S_v(\text{Cd})$]. The Debye temperatures of the $B19$ CdMg and DO_{19} CdMg$_3$ and Cd$_3$Mg compounds were then obtained numerically from these vibrational entropies $[S_v(\sigma)]$ using Eq. (18).

In order to obtain the CEC's for the Debye temperature, the values of $\theta(\sigma)$ for all nine of the compounds in Table II were needed. The procedure discussed in the previous paragraph only provided values for five configurations (the two pure elements as well as the $B19$ and two DO_{19} compounds). Since the values of $\theta(\sigma)$ for the additional, metastable compounds could not be determined directly from experimental data, information from the LMTO-ASA calculations were combined with approximate expressions for the Debye temperature to yield the values of $\theta(\sigma)$ for the $Pmmn$, $P\bar{6}m2$, and $Cmcm$ structures given in Table II. Specifically, the Debye temperature can be defined in terms of a Debye sound velocity (C_D) (Ref. 47) as follows (where h is Planck's constant):

$$\theta=\frac{h}{2\pi k_B}\left[\frac{6\pi^2N}{V}\right]^{1/3}C_D \; . \qquad (21)$$

The Debye sound velocity, in turn, can be written as follows:

$$C_D=\left[\frac{CV}{M}\right]^{1/2} \; , \qquad (22)$$

where C is a complicated function of the elastic constants[47] and $\overline{M}/V$ is the mass density. Following Moruzzi, Janak, and Schwarz,[48] we will assume that C is proportional to the bulk modulus (B), so that the Debye temperature for a Cd-Mg alloy with configuration σ and an average concentration (c) of Mg can be written as

$$\theta(\sigma) = \kappa(\sigma) \left[\frac{V_0^{1/3} B(\sigma)}{(1-c)M_{Cd} + cM_{Mg}} \right]^{1/2}, \qquad (23)$$

where M_{Cd} and M_{Mg} are the atomic masses of Cd and Mg, respectively, V_0 is the equilibrium volume per atom, and where $\kappa(\sigma)$ is a configurationally dependent parameter.

Assuming that $\kappa(\sigma)$ is only a function of the average concentration $[\kappa(c)]$, Eq. (23) can be used to determine the Debye temperatures for the $Pmmn$, $P\bar{6}m2$, and $Cmcm$ compounds. Specifically, the values of $\kappa(c)$ for 0, 25, 50, 75, and 100 at. % Mg can be obtained from the Debye temperatures, atomic volumes, and bulk moduli listed in Table II for Cd, DO_{19} Cd_3Mg, $B19$ CdMg, DO_{19} $CdMg_3$, and Mg, respectively. For the Cd_2Mg ($CdMg_2$) stoichiometry, $\kappa(c)$ was obtained by linearly interpolating between values at 25 and 50 (50 and 75) at. % Mg. The values of $\kappa(c)$ were used together with the calculated values of B and V_0 in Table II to obtain the Debye temperatures for the $Pmmn$, $P\bar{6}m2$, and $Cmcm$ compounds.

As discussed in detail by Grimvall,[47] a distinction should be made between the value of the Debye temperature which parametrizes the entropy and that which reproduces experimentally measured heat capacities; these values of θ are not generally equal since the vibrational spectrum of any real alloy is not exactly described by the Debye model. In the analysis of the vibrational entropy discussed above, the distinction between heat-capacity and entropy Debye temperatures was ignored, since values of θ derived from experimentally measured entropies for compounds were combined with those determined from heat-capacity measurements for the elements. Therefore, the values of the Debye temperatures given for the Cd-Mg compounds in Table II are meaningful only as a parametrization of the contribution of vibrations to the entropy of formation.

The estimated uncertainty in the measured entropies of formation, in units of Boltzmann's constant, is 0.06 which translates to a 5-K uncertainty in the calculated Debye temperature for the $B19$ CdMg and DO_{19} $CdMg_3$ and Cd_3Mg compounds. Of course, the error in the estimates of the *vibrational contribution* to the entropy of formation of the alloys may be larger than the experimental uncertainty in the measured *total* entropy of formation

because of possible inaccuracies in the calculated electronic and configurational entropies which were used to extract vibrational contributions. Therefore, our analysis of the configurational dependence of the vibrational entropy can only be expected to give an estimate of the relative magnitude of the vibrational contribution to the entropy of formation for Cd-Mg alloys.

E. Calculated cluster expansion coefficients

In Table IV, the calculated CEC's for $E_c(\sigma)$, $E_r(\sigma)$, $n_F(\sigma)$, and $\theta(\sigma)$, which are labeled E_α^c, E_α^r, n_α^F, and θ_α, respectively, are given. For the configurational energy (which is the dominant contribution to the energy of the alloy), we have analyzed the convergence of the cluster expansion in some detail. If only the configurationally independent term and the contributions from the point, two nearest-neighbor pair (1,2 and 1,5 in Fig. 2), the three nearest-neighbor triangle (1,2,3 and 1,2,5 and 1,2,7) and the nearest-neighbor tetrahedron (1,2,5,7) clusters are included in the cluster expansion, i.e., if only the terms for subclusters of the nearest-neighbor tetrahedron (1,2,5,7) and triangle (1,2,3) are included, the resulting fit to the configurational energies of the nine ordered compounds given in Table II is poor. Specifically, the calculated formation energies are only predicted by this truncated cluster expansion to within 1.5 mRy/atom, and the relative stabilities of the nine compounds (i.e., the ground states) are incorrectly reproduced. By contrast, when only the configurationally invariant term and the contributions of the point, two nearest-neighbor pair (1,2 and 1,5), and the *next-nearest-neighbor* pair (2,4) clusters are retained, the fit of the cluster expansion to the values of $E_c(\sigma)$ is much better. The error in the prediction of the formation energies is, at most, 0.5 mRy/atom and the correct ground states are obtained, showing clearly that the contribution of the second-neighbor pair to the expansion of $E_c(\sigma)$ cannot be neglected for Cd-Mg alloys, and that the magnitude of multiplet cluster and longer-ranged pair CEC's for the configurational energy are small.

In the remainder of this paper the nine-term cluster expansion, containing contributions from the second-neighbor pair as well as from all of the subclusters of the nearest-neighbor tetrahedron (1,2,5,7) and triangle (1,2,3),

TABLE IV. Calculated CEC's for the configurational energy (E_α^c), the relaxation energy (E_α^r), the density of states at the Fermi level (n_α), and for the Debye temperature (θ_α). The units for the different CEC's are as follows: E_α^c (mRy/cluster), E_α^r (mRy/cluster), n_α^F (states/Ry cluster), and θ_α (K/cluster).

α	E_α^c	$E_\alpha^c + E_\alpha^r$	n_α^F	θ_α
	−6.6824	−6.5437	3.9141	278.544
1	−0.3049	−0.7720	−0.3450	−99.745
1,5	1.2044	1.0021	0.0756	3.880
1,2	1.3655	1.1632	0.1201	2.292
2,4	−0.3061	−0.4228	−0.0080	5.023
1,2,5	0.0262	−0.0626	−0.0150	0.562
1,2,7	0.0738	−0.1927	0.0275	0.437
1,2,3	0.0738	−0.1927	0.0275	0.437
1,2,5,7	−0.0546	−0.1792	−0.0186	−3.821

will be used to describe the configurational dependence of $E_c(\sigma)$, $E_r(\sigma)$, $n_F(\sigma)$, and $\theta(\sigma)$. This cluster expansion contains the important pair terms for the configurational energy as well as multiplet interactions which are important for describing the asymmetry of the relaxation energy, in particular, about $c=0.5$. The CEC's listed in Table IV reproduce the values of $E_c(\sigma)$, $n_F(\sigma)$, and $\theta(\sigma)$ to within a maximum error of 2%. For $E_r(\sigma)$ the CEC's predict correct values to within 0.5 mRy/atom [which is 12% of the value of $E_r(\sigma)$ for Cd-rich alloys], indicating that the convergence of the cluster expansion for the relaxation energy is slower than for $E_c(\sigma)$, $n_F(\sigma)$, and $\theta(\sigma)$.

V. RESULTS

A. Ground states

In Fig. 3, the LMTO-ASA calculated configurational formation energies, defined by Eq. (13) in terms of total energies of *unrelaxed* structures, are plotted versus the concentration of Mg. Out of the nine structures considered in our LMTO-ASA calculations, those which are favored energetically at their stoichiometries and which are stable with respect to phase-separated mixtures of compounds with different compositions (based on the configurational energy alone) are connected by solid lines in Fig. 3. It is possible (although unlikely in this case, based on the experimental phase diagram for the Cd-Mg system) that the other terms in the $T=0$ K limit of the grand potential (6) can stabilize other structures, and that compounds not considered in our LMTO-ASA calculations are ground states (i.e., are stable at $T=0$ K).

In order to determine exactly the ground states out of all 2^N possible configuration of atoms, it is necessary to
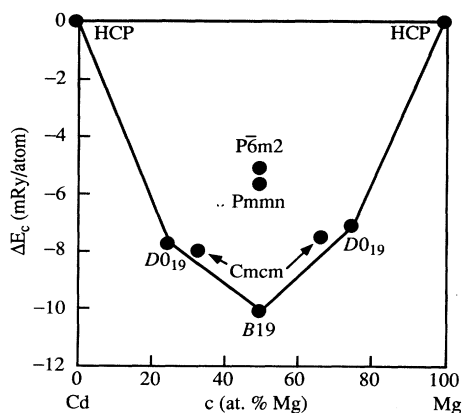
FIG. 3. LMTO-ASA calculated configurational formation energies (ΔE_c). ΔE_c is defined in Eq. (13) in terms of the energies of the alloy compounds with unrelaxed crystal structures. Solid circles indicate calculated values of ΔE_c and the solid lines connect those compounds which are energetically favored with respect to phase separation to the other compounds at different compositions and with respect to other compounds at the same composition. The structures are described in detail in Refs. 15 and 16.

find those arrangements of atoms on the hcp structure which minimize the following limit of the grand potential at $T=0$ K:

$$E_c(\sigma)+E_r(\sigma)+\tfrac{9}{k}k_B\theta(\sigma)$$
$$=\sum_{\alpha}{}'(E_\alpha^c+E_\alpha^r+\tfrac{9}{8}k_B\theta_\alpha)m_\alpha\overline{\Phi}_\alpha(\sigma)\ . \qquad (24)$$

In (24) the term proportional to the Debye temperature is due to zero-point motion, and we have used the cluster expansion of the configurational and relaxation energies and the Debye temperature on the right-hand side (rhs). The ground states can be determined from the values of $\overline{\Phi}_\alpha$ which minimize the rhs of (24) subject to a set of linear constraints on the cluster functions. These constraints arise because the $\overline{\Phi}_\alpha$ should describe physically realizable configurations of atoms on the lattice. The constraints are linear in the cluster function variables, as is the right-hand side of (24), and the determination of the ground states therefore reduces to a problem in linear programming for which global energy minima can be found. In this work we have used the cluster configuration polyhedron method[9,15] (CCPM) in which the constraints on the cluster functions are constructed by using the CVM formalism and requiring that the probabilities for observing each possible configuration on a cluster be between zero and one.

From the CCPM analysis, using the values of the cluster functions given in Table IV, we find that only hcp Cd and Mg as well as the $B19$ CdMg and the DO_{19} Cd$_3$Mg and CdMg$_3$ compounds are stable at $T=0$ K, in agreement with the experimental phase diagram shown in Fig. 1. The $B19$ CdMg and the DO_{19} Cd$_3$Mg and CdMg$_3$ compounds are also those which were found to be stable based on the configurational energy alone (Fig. 3), indicating that the relaxation energy and zero-point motion contributions introduce no new ground states. Furthermore, the second-neighbor and multiplet CEC's for the configurational energy are not sufficiently large to stabilize compounds which are not ground states for the hcp Ising model with nearest-neighbor pair interactions alone.[15,16]

B. Calculated phase diagrams

In Figs. 4(a)–4(c), the results of CVM calculations of phase diagrams for the Cd-Mg system are shown. In these calculations, the CEC's from Table IV were used and the grand potentials, Eq. (6), were calculated with the CVM for the disordered hcp phase as well as for the ground-state compounds: $B19$ CdMg and DO_{19} Cd$_3$Mg and CdMg$_3$. From intersections of the grand potentials, the phase boundaries in Figs. 4(a)–4(c) were determined.

Figure 4(a) shows the results of the phase diagram calculation when only the configurational contributions to the free energy are considered. The Cd$_3$Mg and CdMg phases are predicted to disorder congruently at roughly 420 °C, while CdMg$_3$ undergoes a peritectoid reaction to CdMg+(Cd,Mg) at approximately 380 °C. Therefore, the topology of the calculated phase diagram shown in Fig. 4(a) is in agreement with the experimentally determined
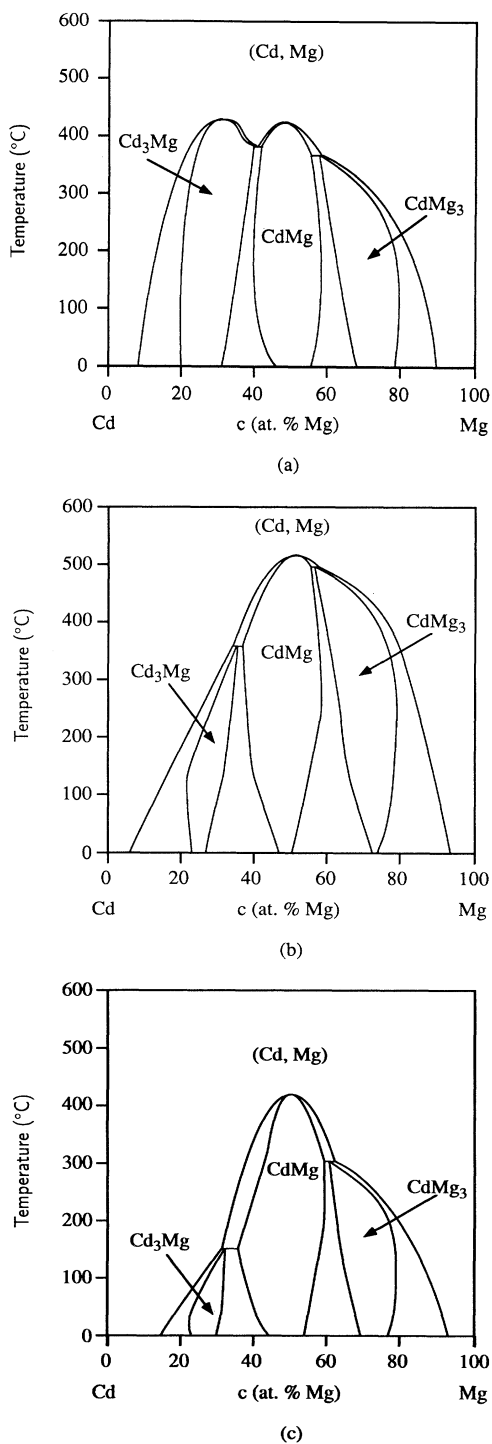
one[20] (Fig. 1) for Mg-rich alloys only. This is not surprising since the relaxation energy, which is largest for Cd-rich compositions, has not been included in this calculation.

The phase diagram shown in Fig. 4(b) has been calculated by taking into account both the relaxation and configurational contributions to the energy. The topology of this phase diagram is in better agreement with experimental measurements than the one in Fig. 4(a). Specifically, it is again found that the CdMg phase undergoes a congruent order-disorder transition at roughly 50 at. % Mg, but now both the Cd_3Mg and $CdMg_3$ phases undergo peritectoid reactions. The temperature of the reaction for $CdMg_3$ is calculated to be larger than for Cd_3Mg, in agreement with the experimental diagram (Fig. 1).

By comparing Figs. 4(a) and 4(b) it can be seen that the relaxation energy has the effect of stabilizing the disordered solid solution with respect to the Cd_3Mg compound. The stabilization of the disordered phase by $E_r(\sigma)$ is due to the fact that the ordered compounds have relaxation energies which are small (and were assumed to be zero in our calculations), while structural relaxation is large for Cd-rich disordered alloys. Although the overall topology of the phase diagram in Fig. 4(b) is correct, the temperatures of the invariant reactions are predicted to be too high. In fact, including the relaxation energy leads to calculated transition temperatures for the CdMg and $CdMg_3$ phases which are about 100 °C higher than those obtained from CVM calculations which take into account the configurational energy only [Fig. 4(a)]. For Mg-rich alloys, $E_r(\sigma)$ should be negligible for both ordered and disordered phases (see Table II), so the increase in the calculated transition temperatures is due to errors in the cluster expansion fit to $E_r(\sigma)$ which is on the order of 0.5 mRy/atom (~ 80 K).

Finally, the phase diagram in Fig. 4(c) was calculated by including all contributions to the free energy. The electronic entropy was found to have a negligible effect on calculated phase boundaries, and the differences between Figs. 4(b) and 4(c) are almost completely due to vibrational free-energy contributions. The dominant contribution to the free energy from vibrations comes from the vibrational entropy in this system, as we show below. By comparing Figs. 4(b) and 4(c), it can be seen that the effect of the vibrational entropy is to lower transition temperatures, and hence to stabilize the disordered phase. Therefore, the vibrational entropy is apparently larger for disordered than ordered phases.

It is encouraging that of all the calculated phase diagrams, the one which was computed using all contributions to the free energy [Fig. 4(c)] agrees best with the experimentally determined one (Fig. 1). Calculated reaction temperatures are roughly 30 °C too high for $Cd_3Mg \rightarrow CdMg + (Cd,Mg)$, 150 °C too high for $CdMg_3 \rightarrow CdMg + (Cd,Mg)$, and 170 °C too high for the congruent order-disorder transition of the CdMg phase. The discrepancy between calculated and experimentally measured reaction temperatures is partly due to inaccuracies in the description of the relaxation energy with the cluster expansion, as mentioned above. In the next sec-

FIG. 4. Phase diagrams calculated with the CVM using the CEC's listed in Table IV. Solid lines indicate calculated phase boundaries as determined by the intersections of the grand potentials for the disordered solid solution (Cd,Mg) and the ordered phases: Cd_3Mg, CdMg, and $CdMg_3$. In (a), only configurational contributions to the free energy were included, in (b) the configurational and relaxation contributions to the free energy were included, and in (c) all contributions to the free energy including the electronic entropy and vibrational free energy were included in the CVM calculations.

tions we will discuss further the reasons for the overestimation of the temperatures of the invariant reactions.

C. Thermodynamic properties

In order to understand the effect of the different contributions to the free energy on the stability of the phases in the Cd-Mg system, it is useful to analyze the calculated thermodynamic functions. In Figs. 5(a)–5(c) the calculated formation free energies ($\Delta G/k_B = [\Delta\Omega + \mu c]/k_B$), and formation enthalpies ($\Delta H/k_B = \langle \Delta E_c + \Delta E_r$

$+ \Delta U_v \rangle_\sigma/k_B$) along with the temperature times the negative of the entropies of formation ($-T\Delta S/k_B = -T[\Delta S_e + \Delta S_r + \Delta S_v]/k_B$), all in units of K, are plotted for the stable phases at 900 [Fig. 5(a)], 600 [Fig. 5(b)], and 300 [Fig. 5(c)] K. As in Eq. (13), ΔG, ΔH, and ΔS are all defined as the difference between G, H, and S for the alloy and the concentration-weighted average of the pure element values.

In Fig. 6(a), ΔG, ΔH, and $-T\Delta S$ at 900 K are shown for the disordered phase which is the only one stable at this temperature. The entropy and enthalpy contribu-
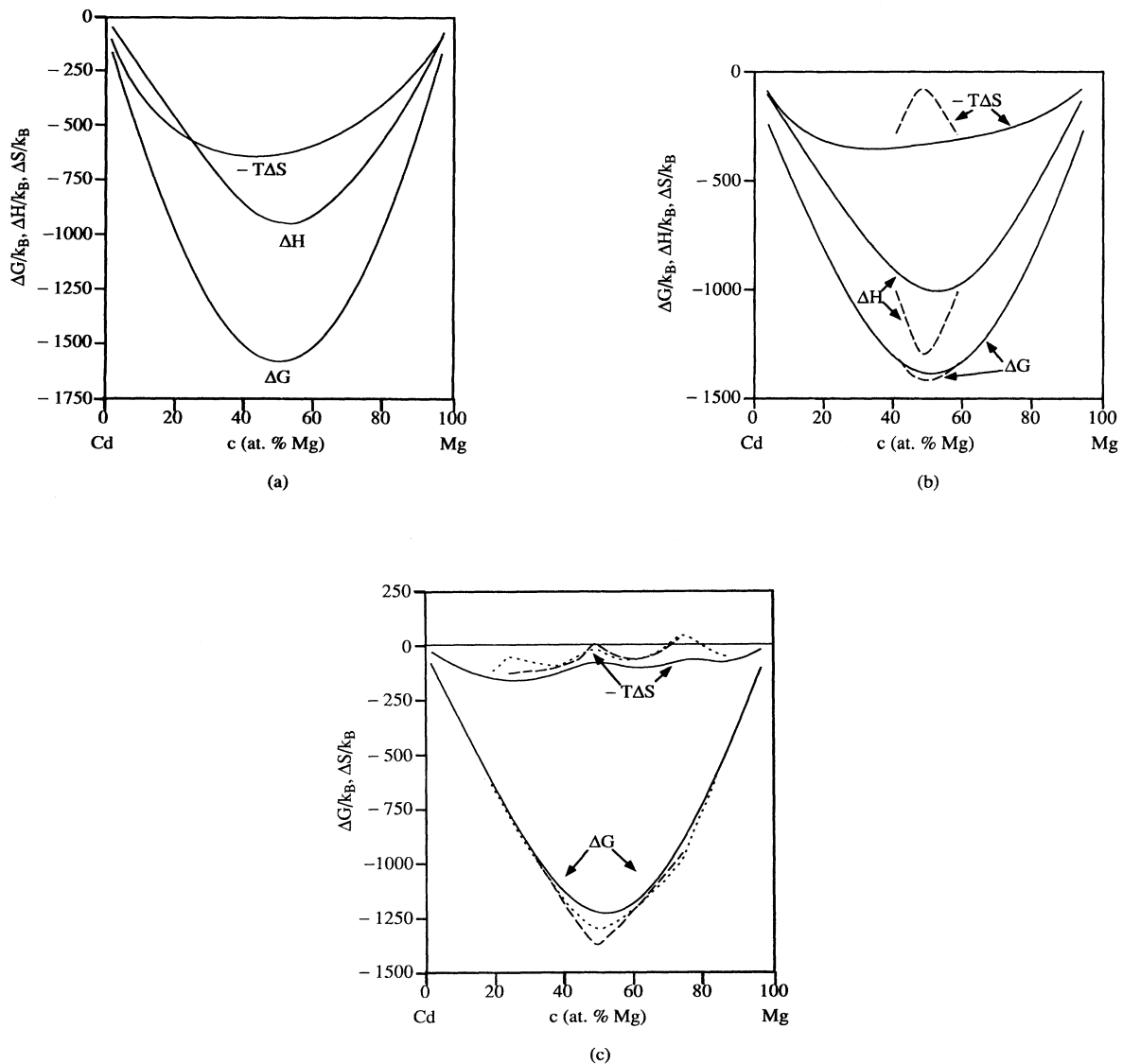
FIG. 5. Thermodynamic properties of Cd-Mg alloys as calculated with the CVM and the CEC's listed in Table IV for $T = 900$ K (a), 600 K (b), and 300 K (c). Free energies of formation are labeled as ΔG, enthalpies of formation by ΔH, and the negative of the temperature times the formation entropies by $-T\Delta S$. Solid lines indicate results for disordered alloys, dashed lines correspond to the CdMg phase with the $B19$ structure, and the dotted lines are for the Cd$_3$Mg and CdMg$_3$ phases with the DO_{19} structure. In (c), only the calculated curves for ΔG and $-T\Delta S$ are shown since the curve for ΔH at $T = 300$ K lies very close to that of ΔG.
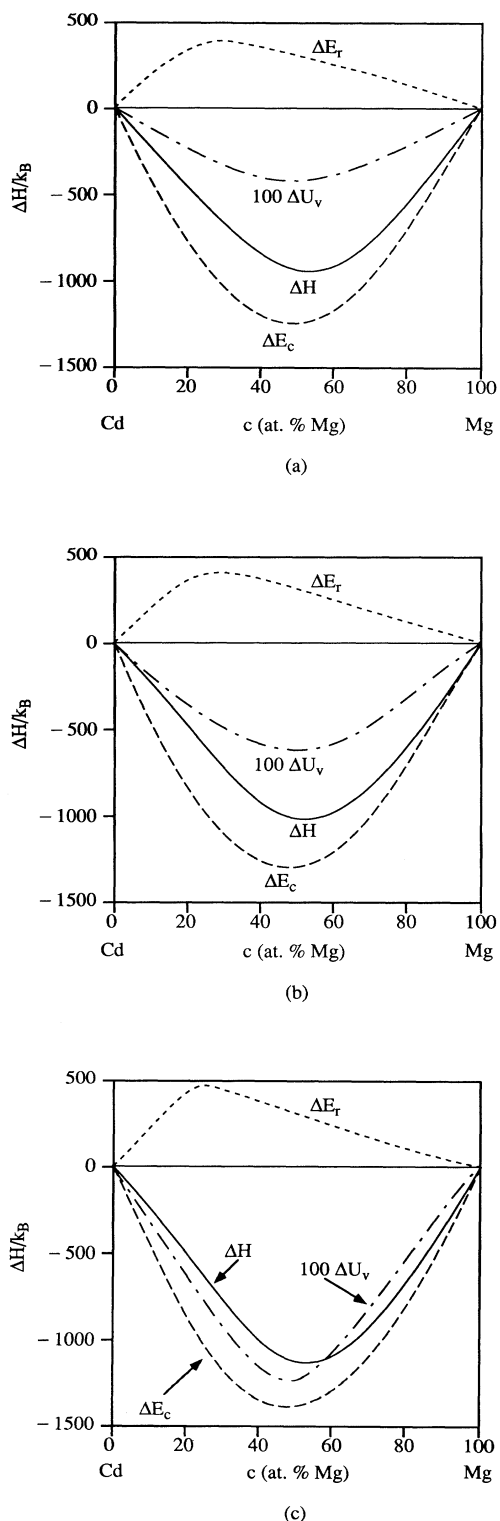
(a)

(b)

(c)

FIG. 6. CVM calculated contributions to and values of the total enthalpies of formation for disordered Cd-Mg alloys at $T=900$ K (a), 600 K (b), and 300 K (c). Solid lines correspond to total enthalpies (ΔH), dashed lines are for the configurational contributions (ΔE_c), dotted lines indicate the relaxation terms (ΔE_r), and the dash-dotted lines gives 100 times the vibrational enthalpies for formation (100 ΔU_v).

tions to the free energy of formation at 900 K are comparable.

At 600 K, the CdMg phase is stable in addition to the disordered solid solution. The thermodynamic functions for the ordered CdMg phase at 600 K are shown as dashed lines in Fig. 5(b). The entropy of the CdMg phase is smallest in magnitude at $c=50$ at. % Mg, which is the stoichiometry of the compound; the entropy increases nearly symmetrically as the concentration deviates to either side of 50 at. % Mg due to the disorder introduced by the occupation of the minority sublattice by increasing amounts of the majority species. In an analogous fashion, the enthalpy of formation of the CdMg phase is most negative near stoichiometry and decreases in magnitude as the number of unlike nearest-neighbor pairs increase. The equilibrium phase boundaries at 600 K for the calculated phase diagram shown in Fig. 4(c) can be obtained by applying the common tangent construction to the solid and dashed free-energy curves shown in Fig. 5(b). Since the differences in free energy are very small between the ordered and disordered phases in Fig. 5(b), it is clear that the computed phase boundaries are very sensitive to small errors made in the calculations of thermodynamic properties.

In Fig. 5(c), the thermodynamic functions for all of the ground states and the disordered phase at $T=300$ K are plotted. Dotted curves in Fig. 5(c) correspond to the phases with the DO_{19} structure, i.e., Cd_3Mg and $CdMg_3$, while the dashed line is again for the CdMg compound. The entropy terms for all of the ordered phases are smallest in magnitude at the stoichiometries of the compounds, as expected. Due to short-range order, the entropy of the disordered solid solution mimics that of the ordered phases, although the peaks in the values of $-T\Delta S$ which are less pronounced for the disordered phase. The entropy contributions are small at 300 K, so that the enthalpies and free energies of formation would practically lie on top of one another in Fig. 5(c); therefore, only the free energy and entropy of formation have been plotted in this figure. Based on the free energies, the ordered phases most and least stable with respect to the disordered solid solution are CdMg and Cd_3Mg, respectively, consistent with the calculated [Fig. 4(c)] and experimental (Fig. 1) phase diagrams.

In Figs. 6(a)–6(c), the different contributions to the formation enthalpies are plotted for the disordered phase. The configurational formation enthalpy (ΔE_c) is defined in Eq. (13). By analogy, ΔE_r and ΔU_v are defined as the differences between the values $E_r(\sigma)$ and $U_v(\sigma)$, respectively, for the alloy and the concentration-weighted averages of these quantities. It can be seen that ΔE_c is clearly the most important term of the total formation enthalpy. ΔE_c is found to increase in magnitude as the temperature is lowered due to short-range ordering in the disordered phase. The relaxation energy (ΔE_r) gives rise to an important contribution to the enthalpy of formation for Cd-rich alloys. ΔE_r is positive due to the fact that the values of $E_r(\sigma)$ are maximum for pure Cd and smaller for the alloys. As the temperature decreases, ΔE_r increases slightly since ordering tends to further decrease the values of $E_r(\sigma)$ for the alloys. The vibrational contribu-

tion to the enthalpy of formation is found to be 2 orders of magnitude smaller than the other terms, indicating that the effect of ΔU_v on phase stability in this system is negligible. We have also analyzed the different contributions to the enthalpy of formation for the ordered phases and we find that the relative contributions of the different terms are practically the same as for the disordered phase.

The different contributions to the entropies of formation of the disordered phase at 900, 600, and 300 K are shown in Figs. 7(a)–7(c). The Δ symbols again indicate formation quantities, defined as the difference between the function for the alloy and the concentration-weighted average value. At all temperatures the contribution from the electronic entropy (ΔS_e) is an order of magnitude smaller than the total formation entropy and, therefore, ΔS_e affects the phase stability *in this system* very little. By contrast, the configurational entropy ($\Delta S_c \equiv S_c$) gives rise to the largest contribution to the total entropy of formation at all temperatures. The strong effect of short-range order on the total entropy of formation at 300 K is found to be due almost entirely to the configurational term, as shown in Fig. 7(c). The vibrational entropy of formation (ΔS_v) is comparable to the configurational entropy, particularly at lower temperatures. ΔS_v depends on the temperature much more weakly than does ΔS_c, as can be seen by comparing values in Figs. 7(a)–7(c). Furthermore, ΔS_v is not strongly affected by short-range order.

In Figs. 7(a)–7(c), ΔS_v starts out positive for Cd-rich compositions, reaches a maximum value between 40 and 50 at. % Mg, decreases and even becomes negative at lower temperatures as the concentration of Mg is increased, and finally goes to zero for pure Mg. Due to the uncertainties in the calculated values of ΔS_v, we cannot conclusively way whether or not the change in the sign of ΔS_v at low temperatures [Fig. 7(c)] is meaningful. However, based on the results of our calculations, we can conclude that the contribution of ΔS_v to the total entropy of formation is positive for near equiatomic alloys. We have compared the vibrational entropies for ordered and disordered phases at the same compositions and temperatures, and we find that ordering has the effect of decreasing ΔS_v; this result is consistent with the fact that including the contribution of the vibrational entropy in the phase diagram calculations results in a decrease in the transition temperatures of the ordered compounds [compare Fig. 4(b) and 4(c)]. In Sec. VII, we discuss in more detail the effect of atomic ordering on the vibrational entropy.

In Figs. 8(a) and 8(b), calculated values of thermodynamic properties are compared with experimental measurements.[21] In Fig. 8(a), the solid and open squares are the calculated and experimentally measured total enthalpies of formation, respectively, for the ordered compounds at 298 K. It is found that the calculations overestimate the magnitude of ΔH by as much as 550 K (~ 3 mRy/atom). The dashed line and open circles in Fig. 8(a) represent calculated and experimentally measured values, respectively, of the enthalpy of formation for disordered alloys at 543 K. The calculated values of ΔH are again found to be too exothermic for the disordered alloys, this
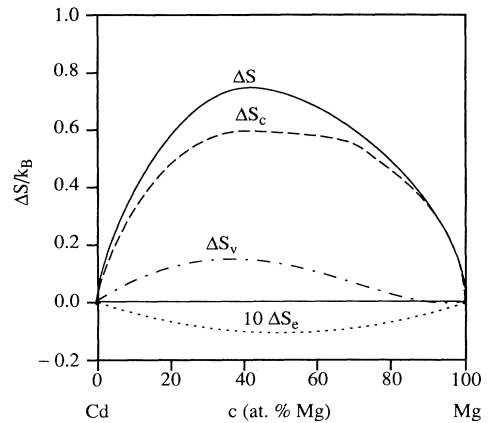
(a)
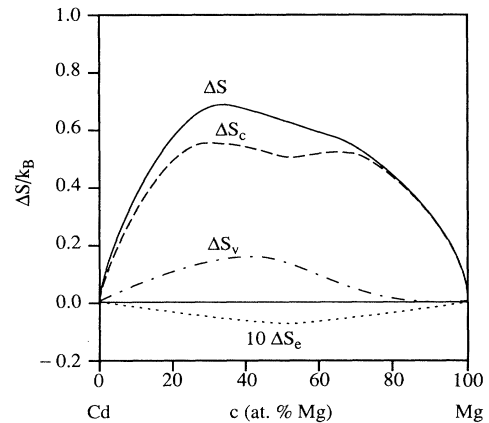
(b)
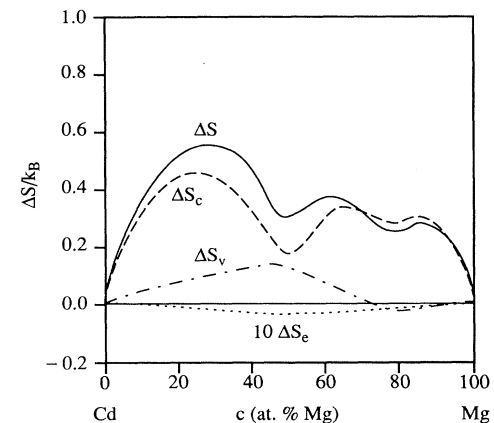
(c)

FIG. 7. CVM calculated contributions to and values of the total entropies of formation for disordered Cd-Mg alloys at $T = 900$ K (a), 600 K (b), and 300 K (c). Solid lines correspond to total entropies of formation (ΔS), while the dashed lines are for the configurational contributions (ΔS_c), the dotted lines indicate 10 times the electronic entropies of formation (10 ΔS_e), and the dash-dotted lines give the contribution of the vibrational entropies of formation (ΔS_v).
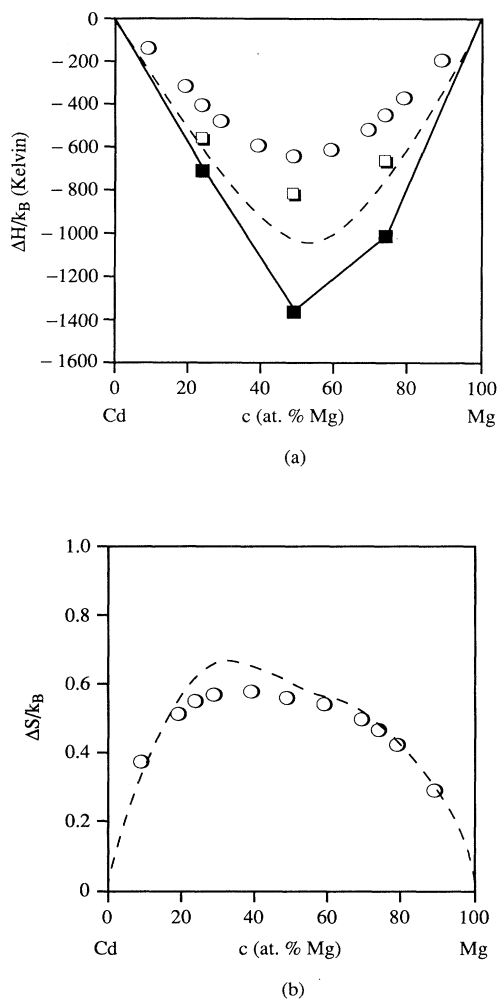
(a)

(b)

FIG. 8. Calculated and experimentally measured (Ref. 21) heats of formation (ΔH), in (a), and entropies of formation (ΔS), in (b). Open circles and dashed lines represent experimentally measured and calculated values, respectively, at $T = 543$ K for disordered alloys. In (a), open and solid squares represent experimentally measured and calculated values, respectively, for the enthalpies of formation for the ordered phases at $T = 298$ K.

time by as much as 400 K (~ 2 mRy/atom).

The calculated order-disorder transition temperatures for the phase diagrams in Figs. 4(a)–4(c) are primarily affected by *differences* between ΔH for ordered and disordered alloys at the same composition. From Fig. 8(a), it is found that the absolute agreement between theory and experiment is better when comparing *differences* in enthalpies for ordered and disordered phases with the same composition than it is for values of the formation enthalpies themselves. Specifically, the differences between the calculated values of the high- and low-temperature enthalpies of formation are only 0.2 mRy/atom smaller for Cd_3Mg, 1 mRy/atom larger for CdMg, and 0.3 mRy/atom larger for $CdMg_3$ than the corresponding differences in the experimentally measured

values. These errors in the calculated differences of formation enthalpies are, therefore, largest for CdMg and smallest for Cd_3Mg. Similarly, the calculated temperatures for the invariant reactions in Fig. 4(c) are overestimated the most for the CdMg phase, less for $CdMg_3$, and the least for the Cd_3Mg phase. Therefore, it appears that the discrepancies between the calculated and experimentally determined phase diagrams [Figs. 4(c) and 1] can be largely attributed to the errors in the calculated enthalpies of formation.

In Fig. 8(b), the calculated and experimentally measured[21] total entropies of formation are shown to be in almost perfect agreement for all compositions except those near 30 at. % Mg, where the entropy is overestimated by, at most, 10%. Since our calculated entropies are derived from parameters which were fit to experimentally measured values at 298 K, the good agreement between theory and experiment in Fig. 8(b) is not surprising. Nevertheless, the plotted values in Fig. 8(b) show that our assumption that the T dependence of the Debye temperature is not as strong as the configurational dependence, when the entropy of formation is considered, appears to be a valid one. Furthermore, the results of Fig. 8(b) suggest that our estimates of the individual contributions to the entropy shown in Figs. 7(a)–7(c) are reasonable.

VI. COMPARISON WITH PREVIOUS CALCULATIONS

In Refs. 25 and 26, Leung *et al.* present calculated thermodynamic properties[25] and order-disorder transition temperatures[26] for Cd-Mg alloys. These authors use pseudopotential theory[49] combined with a variational principle based on the Gibbs-Bogoliubov inequality[50] to determine Helmholtz free energies from which related thermodynamic properties are obtained. The Einstein approximation is used to treat lattice vibrations and to define the reference system required to obtain a variational free-energy expression. Chemical short-range-order effects are neglected by these authors (i.e., perfectly random disorder was assumed) allowing configurational averages to be performed analytically. Accordingly, the configurational entropy is treated using the regular solution and Bragg-Williams approximations for disordered and ordered alloys, respectively. The method of Leung *et al.*,[25,26] therefore, should not be applied to the calculation of the entire phase diagram of the Cd-Mg system since the Bragg-Williams approximation is known to predict phase boundaries with unphysical topologies in frustrated systems (such as the hcp Ising model with antiferromagnetic coupling).[27,51]

By minimizing the free energy with respect to the Einstein temperatures for Cd and Mg, and with respect to the order parameter corresponding to the DO_{19} structure, an estimate of the order-disorder transition temperature (T_{ord}) for Cd_3Mg and $CdMg_3$ is obtained by Leung[26] as the lowest temperature for which the order parameter is found to be zero. The calculated value of T_{ord} is underestimated by roughly 30 K for $CdMg_3$, while for Cd_3Mg it is correctly found to lie in the middle of the two-phase region at 25 at. % Mg in Fig. 1. The Bragg-Williams approximation is known to overestimate order-disorder

transition temperatures,[51] so if a more accurate treatment of the configurational entropy was used by Leung,[26] both transition temperatures would have been underestimated. Interestingly, however, it is found by Leung[26] that vibrational effects accounted for a lowering of the calculated transition temperatures by roughly 15%, in agreement with our calculations where the peritectoid reaction temperatures in Fig. 4(c) are lower than in Fig. 4(b).

Calculated excess entropies by Leung, Stott, and Young[25] for disordered alloys at 543 K correctly reproduce the experimentally measured concentration dependence of this quantity. However, the quantitative agreement between calculated and measured entropies found by Leung, Stott, and Young[25] is not as good as found in our calculations, which is to be expected since our entropy expression was fit to low-temperature data. Enthalpies of mixing calculated by Leung, Stott, and Young[25] are found to be sensitive to the choice of the zeroth Fourier component of the pseudopotentials and could not be compared with our results. Calculated heat capacities by Leung[26] for the ordered $CdMg_3$ phase are underestimated when compared to experimental measurements, a fact which is attributed to the neglect of short-range order by Leung.[26] In other words, Leung concludes that a more accurate evaluation of the configurational averages than are given by the Bragg-Williams approximation are required to obtain better quantitative results.

VII. DISCUSSION

A method for taking into account contributions to the free energy of a binary substitutional alloy arising from electronic and vibrational excitations, as well as from configurational disorder, has been presented. Under the assumption that electron-phonon interactions can be ignored, the contributions of the vibrational and electronic states to the total partition function can be summed over independently for a given configuration of atoms as discussed in greater detail by Ceder.[28] The remaining configurational averages, which must be performed to obtain thermodynamic properties, can be handled using the formalism of cluster expansions[1] combined with the CVM. Specifically, the configurational dependence of the vibrational free energy and the electronic entropy, as well as the configurational and relaxation energies, can be rigorously expanded in terms of a complete orthonormal set of multisite cluster functions with expansion coefficients which are generally temperature [in the case of $F_v(\sigma)$ and $S_e(\sigma)$] and volume dependent, as is also discussed by Sanchez, Stark, and Moruzzi[52] and Ceder.[28] The values of the ensemble averages of the cluster functions, and therefore of $F_v(\sigma)$, $S_e(\sigma)$, $E_c(\sigma)$, and $E_r(\sigma)$, are obtained by minimizing the CVM free-energy (grand potential) functional.

For the configurational energy, the present study and numerous others show that the cluster expansion of the configurational energy is rapidly convergent for many alloy systems and that only a small number (~ 10) of terms are needed to describe accurately the configurational dependence of $E_c(\sigma)$. By contrast, it appears from this

work and that of Laks et al.[42] that real-space cluster expansions of elastic contributions to the total energy converge somewhat more slowly. For the vibrational free energy and electronic entropy, more work is needed to establish the convergence properties of the cluster expansion. However, the present results for Cd-Mg alloys and the work of Sanchez, Stark, and Moruzzi[52] for Cu-Ag (in which vibrational effects, but not electronic entropy contributions to the free energy, were taken into account) seem to indicate that the configurational dependence of $F_v(\sigma)$ and $S_e(\sigma)$ can be accurately parametrized in terms of a small number of cluster expansion terms.

The advantages of a cluster expansion approach in studying phase stability and thermodynamic properties of substitutional alloys are discussed in detail by de Fontaine.[27] These advantages include the ability to take into account the full configurational dependence of all contributions to the free energy; the values of these contributions for a configurational state of arbitrary partial order can be determined within the cluster framework. Furthermore, the ground states of all of the possible 2^N configurations for a given alloy system (characterized by a given set of CEC's) can be exactly determined using the cluster expansion by solving a linear programming problem.[9] The stability of the ground states at finite temperature can then be studied in the framework of a generalized Ising model using the CVM or Monte Carlo simulation, for example. The cluster expansion formalism provides a formal definition of the Ising model interaction parameters. Therefore, there are, in principle, no approximations made in using the Ising model to describe the configurational dependence of substitutional alloy properties, as shown clearly by Ceder.[28]

In this paper the cluster expansion approach and the CVM have been applied to the study of phase stability in the Cd-Mg system. From the results of the calculations of phase diagrams, shown in Figs. 4(a)–4(c), and thermodynamic properties, Figs. 5–7, we find the following: (1) The structural relaxation of the c/a ratio away from its ideal value gives rise to an important contribution to the enthalpy of formation for Cd-rich disordered alloys; the relatively low temperature for the peritectoid transition to the Cd_3Mg phase can only be reproduced in our calculations if the contribution of $E_r(\sigma)$ to the free energy is taken into account. (2) Vibrational states primarily affect thermodynamic properties through their contribution to the entropy of Cd-Mg alloys; the vibrational entropy is larger at a given composition and temperature for disordered than for ordered phases. (3) Electronic excitations give rise to negligible contributions to thermodynamic properties for Cd-Mg alloys. (4) Calculated phase boundaries are very sensitive to the values of thermodynamic functions as can be seen by examining the effect of small differences of the free energy (ΔG) on the common tangents of the ΔG curves in Figs. 5(a)–5(c). We conclude that nonconfigurational contributions to the free energy are not negligible, and must be considered in any theoretical study of phase stability which hopes to obtain accurate, quantitative results.

In Figs. 6(a)–6(c), we show that the most important contribution to the enthalpy of formation comes from the

configurational energy. However, the contribution of the relaxation energy is sizable and cannot be neglected for Cd-rich alloys. The experimentally measured and calculated values of the enthalpies of formation are significantly different, as shown in Fig. 8(a). In the present study the ASA has been used to calculate the configurational contribution to ΔH, and relaxation effects were treated in a semiempirical and somewhat approximate manner. By using a full-potential band-structure approach the configurational and relaxation contributions to ΔH can be calculated more accurately, and we expect that the agreement between experiment and theory for ΔH can be improved. Phase boundaries are primarily affected by differences of ΔH, rather than by the values themselves. Calculated and experimentally measured differences between the values of ΔH for disordered and ordered compounds differ only slightly (by at most 1 mRy/atom), as shown in Fig. 8(a). Therefore, the errors made in the calculation of ΔH appear to largely cancel when subtracting values for phases with the same composition. Although the discrepancies between calculated and experimentally measured differences of enthalpies of formation are small, they are sufficient to explain the errors in the calculated reaction temperatures (when compared to the measured values given in Fig. 1) shown in Fig. 4(c) (since 1 mRy/atom = 160 K).

For disordered alloys, we find that the dominant contribution to the entropy of formation comes from the configurational entropy as shown in Figs. 7(a) and 7(b). $S_c(\sigma)$, however, is strongly affected by short-range and long-range ordering; the effect of short-range order is clearly shown in Figs. 5(c) and 7(c). Consequently, for long-range- or strongly short-range-ordered phases, $S_c(\sigma)$ is smaller and the vibrational entropy gives rise to a contribution to the total entropy of formation as important as the configurational entropy contribution. $S_v(\sigma)$ is less sensitive than $S_c(\sigma)$ to ordering and, therefore, has a relatively smaller effect on calculated transition temperatures.

The electronic entropy in the Cd-Mg system gives rise to a negligible contribution to the total entropy of formation. The relatively small magnitude of ΔS_e is due to the fact that density of states near the Fermi level contains contributions from s and p electrons only, so that $n_F(\sigma)$ is small for all Cd-Mg alloys. It would be interesting to study the effect of $S_e(\sigma)$ on phase stability and the thermodynamic properties of transition-metal alloys for which the densities of states contain more structure and are larger in magnitude near the Fermi level. Several investigators[53-55] have shown that the contribution of S_e to the entropy difference between close-packed and bcc structures of elemental transition metals is as large as that of the vibrational entropy. For a given parent lattice in a substitutional transition-metal alloy, $S_e(\sigma)$ might also differ significantly for ordered and disordered phases. For transition metals at reasonably high temperatures, Eriksson et al.[55] have shown that the low-temperature expression for the electronic entropy (17) is not accurate. In order to apply the cluster expansion formalism to the study of the effect of electronic entropy on phase stability in transition-metal alloy systems, it is therefore necessary

to expand $S_e(\sigma, T)$ at each temperature independently. The temperature-dependent CEC's for the vibrational entropy can be obtained from the values of $S_e(\sigma, T)$ for ordered compounds, which, in turn, can be calculated by numerically integrating the zero-temperature densities of states using the temperature-dependent Fermi function.

By comparing the calculated vibrational entropies for stable ordered compounds and the disordered phase, we find that atomic ordering at a given composition and temperature leads to a decrease in S_v. Therefore, vibrational entropy contributions to the free energy give rise to a 20% decrease in the calculated order-disorder transition temperature of the CdMg phase, and an even greater decrease in the calculated peritectoid reaction temperatures for the Cd_3Mg and $CdMg_3$ phases. In agreement with our results, Leung[26] finds that the effect of vibrational entropy is to decrease the order-disorder transition temperatures for Cd_3Mg and $CdMg_3$. Sanchez, Stark, and Moruzzi[52] find that the vibrational entropy has an effect of similar magnitude on the calculated critical temperature (T_c) for phase separation in the Cu-Ag system: a 10% increase in T_c occurs when the effect of vibrational modes on the alloy free energy is included. In a recent Monte Carlo study of order-disorder transitions for the Ising model on the simple-cubic lattice, Tuijn and Bakker[56] studied the effect of vibrational entropy on the calculated transition temperature at zero field. The contribution of $S_v(\sigma)$ to the free energy of the Ising model was obtained using an analytical expression in terms of the force constants between AB, AA, and AB neighbors. For a reasonable ratio of the AB coupling constant to the geometric average of those for AA and BB neighbors (this ratio was taken to be greater than 1, appropriate for ordering systems), Tuijn and Bakker found that at constant volume the effect of vibrational entropy was to decrease the transition temperature by as much as 50%. Therefore, our results and those of Leung[26] for the Cd-Mg system, as well as those of Sanchez, Stark, and Moruzzi[52] and Tuijn and Bakker[56] clearly show that the effect of vibrational entropy on calculated phase diagrams can be sizable.

The effect of ordering on the vibrational entropy at fixed composition and temperature depends on the effect of local environments on the vibrational frequencies. Moraitis and Gautier[57] have studied the entropy of formation for several substitutional alloy systems at high temperatures using a semiempirical model, and they find that ΔS_v is sensitive to the local atomic environment. Consider the expression for the Debye temperature given in Eq. (22). For an alloy system where atomic ordering is energetically favorable, we expect that the force constants between unlike neighbors are larger in magnitude than the average of those for like neighbors. Upon ordering an increase in the value of the elastic moduli, and hence of C in Eq. (22), is expected. Thus, for an alloy system where compound formation is energetically favorable, provided that the volume changes very little, ordering would tend to lead to an increase in the value of the Debye temperature, and would tend to decrease the vibrational entropy, consistent with our results and those of Leung[26] for the Cd-Mg system and the results of the

model calculation of Tuijn and Bakker.[56] In principle, however, for an alloy system where ordering is favorable, a large decrease in the volume upon ordering might cause the Debye temperature (22) to decrease, leading to an increase in the vibrational entropy. Therefore, whether the vibrational entropy will tend to increase or decrease order-disorder transition temperatures appears to be system dependent.

In the present study, an estimate of the effect of vibrations on thermodynamic properties and phase stability was obtained using experimentally measured entropies at low temperatures[21] where the configurational contributions were expected to be small. In general, of course, reliable experimental data are not always available and it is of interest to apply first-principles techniques to the study of vibrational entropy in substitutional alloys. Once again, what is needed is a way of calculating CEC's for the vibrational entropy. One way of deriving the CEC's is from calculated temperature-dependent vibrational entropies of ordered compounds according to the SIM, as was done in the present study and in the work of Sanchez, Stark, and Moruzzi.[52] In order to calculate from first principles the vibrational entropy of an ordered compound, an extremely efficient method was proposed by Moruzzi, Janak, and Schwarz.[48] This method makes use of Debye-Gruneissen theory, and an empirical expression for the Debye temperature in terms of the bulk modulus which holds for cubic nonmagnetic metals. It is not clear whether Moruzzi's method can be extended to lower symmetry structures such as hcp, of interest in the present study. In general, it may be necessary to use more accurate, but computationally heavy, techniques which are available for calculating phonon frequencies and densities of states of alloy compounds (see, for example, Refs. 58–67) to determine the required vibrational entropies.

In summary, we have presented a theoretical study of thermodynamic properties and phase equilibria in the Cd-Mg alloy system. When only configurational contributions to the free energy are taken into account, calculated transition temperatures for the Cd-Mg compounds are predicted to be too high and the topology of the phase diagram is correct for Mg-rich alloys only. The relaxation energies associated with distortions of the c/a ratios of disordered Cd-rich alloys are found to be responsible for the lower peritectoid reaction temperature of the Cd_3Mg phase when compared to that of the $CdMg_3$ phase. We find that the vibrational energy is larger for disordered than ordered phases, causing calculated transition temperatures to decrease when the contributions of vibrational modes to the free energy are considered. When all contributions to the alloy free energy are taken into account, the types of invariant reactions found in the c-T phase diagram are correctly predicted and transition temperatures are only slightly higher than those measured experimentally. In conclusion, while the configurational free energy is the dominant contribution to the total alloy free energy, nonconfigurational effects are significant and appreciably affect the calculated phase diagram for Cd-Mg alloys.

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