Ising-like Description of Structurally Relaxed Ordered and Disordered Alloys

C. Wolverton and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 27 April 1995)

We demonstrate the ability of generalized Ising-like cluster expansions to describe the energetics and thermodynamics associated with large atomic displacements in alloys. Although the expansion is constructed only from the energies of a few (small-unit-cell) ordered structures, it provides accurate predictions of the atomically relaxed *energies* of random, ordered, or partially ordered alloys, as compared with direct, large scale energy-minimizing simulations. Relaxed *energies* are obtained without having to compute relaxed *geometries*. Combination of the expansion with Monte Carlo simulations is shown to provide an efficient means for calculating thermodynamic properties.

PACS numbers: 71.10.+x, 05.50.+q, 64.60.Cn

One of the central problems in crystal and alloy physics is the prediction of the $T = 0$ lowest energy configurations and the thermodynamic evolution of these structures with temperature [1–3] Even for a binary A/B system on a lattice with a modest number of sites N, this is a formidable problem as the number 2^N of possible "configurations" σ (occupation pattern of each of the N sites by A or B) becomes enormous. Additionally, in each configuration the energy might be lowered by atomic displacements $\{\mathbf{R}_i\}$ ("relaxation") about the nominal lattice sites i, and the evaluation of the total energy of even one relaxation in a given configuration by first-principles quantum-mechanical means is currently limited to relatively small N by the computational effort of these techniques which currently scale as N^2 to N^3. Finding the ground state structure of an alloy can be described as an energy minimization problem $\min E[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ in the space of the configurational $\{\hat{S}_i\}$, positional $\{\mathbf{R}_i\}$, and volume V degrees of freedom. Here, $\hat{S}_i$ denotes the (pseudospin) occupation variable of site i with $\hat{S}_i = -1$ or $+1$ if site i is occupied by an A or B atom, respectively. All three types of variables ($\{\hat{S}_i\}$, V, and $\{\mathbf{R}_i\}$) are generally coupled. While molecular dynamics explorations of the energy surface $E[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ are suitable for finding the relaxed positions $\{\mathbf{R}_i\}$ of atoms in a *given* configuration σ (or in a class of configurations), this approach does not effectively probe the configurational space $\{\sigma\}$ itself. Conversely, representing $E[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ in terms of an Ising-like cluster expansion (CE) [4]

$$E_{\mathrm{CE}}(\{\hat{S}_i\}) = J_0 + \sum_i J_i \hat{S}_i + \sum_{j<i} J_{ij} \hat{S}_i \hat{S}_j + \sum_{k<j<i} J_{ijk} \hat{S}_i \hat{S}_j \hat{S}_k + \cdots \qquad (1)$$

lends itself (e.g., via Monte Carlo simulation) to efficient exploration of the *configurational* degrees of freedom, but typically does not shed light on the effect of positional relaxations. In Eq. (1), the J's are the interaction energies ("effective cluster interactions") and the first summation is over all sites in the lattice, the second over all pairs of sites, and so on. However, we now know that configurational and positional degrees of freedom can be strongly coupled and this coupling should not be ignored. For example, atomic relaxations have been shown to lower the miscibility-gap temperature in semiconductor alloys by several hundred or thousand degrees [5,6], alter the ground state structure of transition metal aluminides [7], and change the *sign* of the mixing energy [8] and cause large ($\sim$1 eV) shifts in the density-of-states peaks [9] for transition-metal alloys. A direct approach to the problem would involve minimizing $E[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ to find $T = 0$ ground states or to conduct on it Monte Carlo simulations with both configurational and positional degrees of freedom to obtain finite-T properties [5,10,11]. Such calculations, however, require the energy functional E to be sufficiently computationally inexpensive so that it can be practically evaluated for large cells [$O(10^3)$ atoms] for many [$O(10^6)$] trial configurations. This is currently possible only with simplified empirical energy functionals [5,10,11] but not first-principles methods.

In this paper we show how one can construct a generalized cluster expansion of the form of Eq. (1) (i.e., integrating out the positional variables) so that its underlying ground state configurations and thermodynamic behavior reflect those of a given (first-principles or other) direct energy functional $E_{\mathrm{direct}}[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ *with fully relaxed geometries*. Once the J's are calculated, the effort to evaluate E scales linearly with the number of spin products, so Eq. (1) lends itself to efficient explorations of the configurational degrees of freedom. Thus, one can efficiently find *relaxed energies* of arbitrarily complex configurations without having to calculate the *relaxed atomic positions* $\{\mathbf{R}_i\}$ (via force minimization or molecular dynamics, processes that require numerous self-consistency as well as displacive iterations). We will further show the following: (i) the interaction energies in Eq. (1) can be calculated conveniently either from empirical or from first-principles energy functionals; (ii) Eq. (1) can be coupled with standard lattice theory statistical techniques [1–3] to compute alloy order-disorder transition temperatures, composition-temperature phase diagrams, enthalpies of formation, and short- and long-range order (SRO and

0031-9007/95/75(17)/3162(4)$06.00

LRO); and (iii) starting from the energies $\{E\}$ of a given set of *ordered* structures, one can predict accurately the energies of relaxed *random or partially ordered* alloys.

The cluster expansion technique used here has been evaluated previously for both GaP/InP and Cu/Pd [12] using first-principles local density approximation input of ~30 fully relaxed energies. While the results of these previous studies could be compared with experimental measurement, they could not be contrasted with thermodynamic calculations using $E_{\mathrm{LDA}}[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ directly. In the present work, we select a physically realistic yet computationally efficient energy functional $E_{\mathrm{direct}}[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ so that *direct* energy minimization and Monte Carlo simulations performed on it can be compared with the results of the cluster expansion, E_{CE} drawn from the same functional. We use the ternary valence-force-field (TVFF) as recently parametrized [5] for the semiconductor alloy, $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{P}$. In this alloy the cations Ga and In form a substitutional arrangement on one of the fcc sublattices of zinc blende, while the P anions occupy the other fcc sublattice. The basic properties of $E_{\mathrm{TVFF}}[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ are as follows: (i) It is fit (to within ~1–2 meV/atom to first-principles linear augmented-plane-wave calculations of formation energies for many ordered $(\mathrm{GaP})_m(\mathrm{InP})_n$ crystal structures [5]. (ii) It exhibits large and nontrivial atomic relaxation effects, e.g., the miscibility gap temperature is lowered by ≈2800 Kand the mixing energy is reduced by more than a factor of 4 due to relaxation. (iii) It includes pair as well as many-body effective cluster interactions of Eq. (1). (iv) The functional includes generic bond-stretching and bond-bending interactions, and thus it is characteristic of a large class of (covalent) materials. These features make the use of the TVFF a suitable and stringent test for our purpose.

We first calculate directly from the functional the *relaxed* formation energies of a few configurations σ:

$$\Delta H_{\mathrm{direct}}(\sigma) = E_{\mathrm{direct}}[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}] - [(1-x)E_{\mathrm{direct}}(A) + xE_{\mathrm{direct}}(B)], \tag{2}$$

where x is the concentration of B atoms in the configuration σ and $A \equiv \mathrm{GaP}$ and $B \equiv \mathrm{InP}$. For each structure σ, the relaxed formation energy is obtained by minimizing E_{direct} with respect to all coordinates $\{\mathbf{R}_i\}$ and V (via a conjugate gradient algorithm) with the condition that the relaxations preserve the symmetry of the structure. Unrelaxed formation energies are obtained by minimizing E_{direct} with respect to V, but leaving all atoms on ideal zinc-blende sites ($\{\mathbf{R}_i\} = 0$).

We will map $E_{\mathrm{direct}}[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ for fully relaxed geometries onto a cluster expansion $E_{\mathrm{CE}}[\{\hat{S}_i\}]$ using the $\mathbf{k}$-space formulation of Laks *et al.* [13]. Rather than a cluster expansion of $\Delta H_{\mathrm{direct}}$, we will expand with respect to a reference energy, $\Delta E_{\mathrm{CE}}(\sigma) = \Delta H_{\mathrm{direct}}(\sigma) - E_{\mathrm{ref}}$. The reference energy is chosen to contain infinite-range real-space elastic interaction terms, namely, the *constituent strain energy* $\Delta E_{\mathrm{CS}}(\hat{k}, x)$ defined as the energy change when the bulk solids A and B are deformed from their equilibrium cubic lattice constants a_A and a_B to a common lattice constant $a_\perp$ in the direction perpendicular to $\hat{k}$. Subtracting these long-range terms from $\Delta H_{\mathrm{direct}}$ before cluster expanding removes the $\mathbf{k} \to 0$ singularity, and thus significantly enhances the convergence of the CE [13]. A convergent CE generally necessitates inclusion of both pair and many-body interactions. A large number of pair interactions with arbitrary separation, often required for convergence, may be conveniently summed using the reciprocal-space concentration-wave formalism, thus replacing an infinite sum over pairs with a discrete sum over a few $\mathbf{k}$ points. Typically only a few many-body interactions are required, and these may be efficiently summed in real space. Thus, we will separate the real space CE of Eq. (1) into two parts:

$$\Delta E_{\mathrm{CE}}(\sigma) = \sum_{\mathbf{k}} J(\mathbf{k})\,|S(\mathbf{k},\sigma)|^2 + \sum_f D_f J_f \overline{\Pi}_f(\sigma). \tag{3}$$

The first (reciprocal-space) summation includes all pair figures and the second (real-space) summation includes only nonpair figures. $J(\mathbf{k})$ and $S(\mathbf{k},\sigma)$ are the lattice Fourier transforms of the real-space pair interactions and spin-occupation variables, J_{ij} and $\hat{S}_i$, respectively. The function $J(\mathbf{k})$ is required to be a smooth function by minimizing the integral of the gradient of $J(\mathbf{k})$. The real-space summation in Eq. (3) is over f, the symmetry-distinct nonpair figures (points, triplets, etc.), D_f is the number of figures per lattice site, J_f is the Ising-like interaction for the figure f, and $\overline{\Pi}_f$ is a product of the variables $\hat{S}_i$ over all sites of the figure f, averaged over all symmetry equivalent figures of lattice sites.

The CE methodology relies on the choice of real-space figures $\{f\}$ and configurations $\{\sigma\}$ used to construct the quantities $J(\mathbf{k})$ and J_f. In our tests, we have used twenty pair interactions in the reciprocal-space portion of the CE and a real-space set of figures which includes the "empty" and point figures, as well as four triplet and four quadruplet figures. The energies $\Delta H_{\mathrm{direct}}$ [Eq. (2)] of 28 *short-period superlattices* (all contain ≤8 atoms/cell except two which have 16 atoms/cell) were used to fit the quantities $J(\mathbf{k})$ and J_f in Eq. (3). The fitting procedure leaves the energies of a large number of structures (not used in the fit) amenable to testing by comparing direct results ($\Delta H_{\mathrm{direct}}$) with CE predictions ($\Delta H_{\mathrm{CE}} = \Delta E_{\mathrm{CE}} + E_{\mathrm{ref}}$). Note that only the $T = 0$ K energies of structurally simple small-unit-cell ordered structures were used in the CE fit, whereas below we will use this CE to predict the energies of random alloys, complex structures with partial order (~1000 atoms/cell), and thermodynamic properties.

Figure 1 demonstrates the ability of the $\mathbf{k}$-space CE to accurately describe the energetics of atomic relaxations in ordered structures. Figure 1 contains both the relaxed and unrelaxed values of $\Delta H_{\mathrm{direct}}$, and contrasts these energies with the CE predictions. This comparison is illustrated for both structures which are used in the fitting of the CE [Fig. 1(a)] and those which are not used in the fit [Fig. 1(b)] and includes many low-symmetry structures with nontrivial relaxations. For clarity, not all the structures considered are depicted in Fig. 1, but the errors shown are typical: The average errors in the 28 fitted energies, 42 predicted energies, and maximum predicted error are 0.5, 1.1, and 2.6 meV/atom, respectively. The effects of relaxation on the energy of the ordered $(\mathrm{GaP})_m(\mathrm{InP})$ superlattices are quite large: The relaxed values of $\Delta H_{\mathrm{direct}}$ are $\sim$4 times smaller than the unrelaxed values. It may be seen from Fig. 1 that the prediction errors of the CE are insignificant compared with the energy gained upon relaxation.

Several anxieties may arise concerning the use of one "class" of alloy structures (e.g., small-unit-cell ordered structures as used here) to describe the energetics of a different class (e.g., random or partially ordered alloys). For instance, one might argue that the electronic structure of the random alloy is qualitatively different from that of small-unit-cell ordered structures, so that information drawn from the latter may not be legitimately used to describe the former. We address this issue in Fig. 2, which shows the directly calculated (both unrelaxed and relaxed) and CE (relaxed) [14] formation energies for *random* $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{P}$ alloys as a function of x. The directly calculated energies of random alloys were evaluated by configurationally averaging the energy E_{direct} of a 1000-atom box, in which the cations were placed on one of the fcc sublattices of zinc blende with random occupations. For unrelaxed energies, all atoms were placed at ideal zinc blende sites, whereas for relaxed energies all atoms were fully relaxed via a conjugate gradient algorithm. Averages were taken over 10–50 configurations, so that the statistical error was $\lesssim 0.1$ meV/atom. The CE uses as input only energies of simple ordered structures; however, the predicted values of the energies of random alloys closely mimic the direct calculations with fully relaxed geometries. The dramatic effect of atomic relaxation on the energy of random alloys is also shown in Fig. 2. As with the ordered alloys (Fig. 1), the formation energy of the random alloy is significantly reduced upon relaxation, and the error in the CE prediction (0.1 meV/atom at $x = 1/2$) is insignificant compared with the energy gained upon relaxation (59.1 meV/atom). Thus, we see that *a CE which is derived from the energies of small-unit-cell ordered structures is able to accurately predict the energies of atomically-relaxed random alloys.*

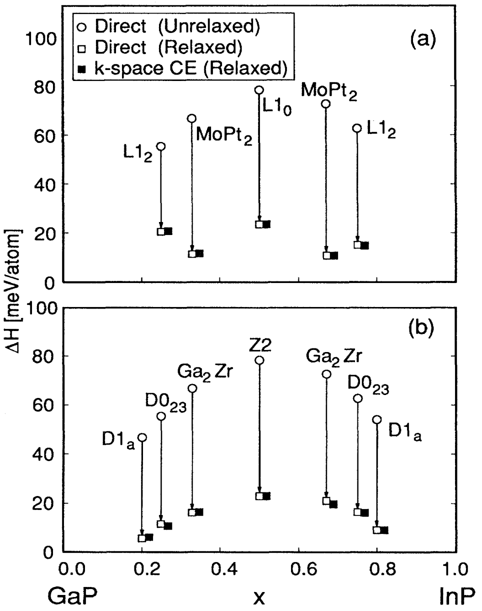

FIG. 1. Formation energies of several $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{P}$ compounds. Shown are directly calculated values and the results of the **k**-space CE for both (a) structures used in the fit and (b) structures not used in the fit. Structures are labeled by their Strukturbericht designation (where available). The amount of relaxation is indicated by the length of the arrows. The degree to which the **k**-space CE is able to describe the energetics of atomic relaxations is indicated by the comparison of the open and filled squares.

Figure 3 further shows that a cluster expansion derived from completely ordered states (characterized by a LRO parameter, $\eta = 1$) can be legitimately used to predict the energies of states of *partial* order: $0 < \eta < 1$. Figure 3 contains a comparison of the CE and directly calculated energies of states with partial LRO of the $L1_0$, $L1_1$, and "40" [1] types. The direct calculations of states with partial LRO were performed for a fully relaxed 1000-atom simulation averaged over ten configurations (for each value of η), with the occupations of the cation sites being chosen consistent with the prescribed value of η. As was the case for ordered and random alloys, the CE also accurately predicts the energetics of states of partial LRO.

We next compare CE predictions with direct simulations for *finite-T thermodynamic properties.* The functional $\Delta H_{\mathrm{direct}}[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ used here has been used directly [5] (i.e., without the use of a CE) in Monte Carlo simulations with both spins $\{\hat{S}_i\}$ and positions $\{\mathbf{R}_i\}$ as dynamical variables. This calculation gave the

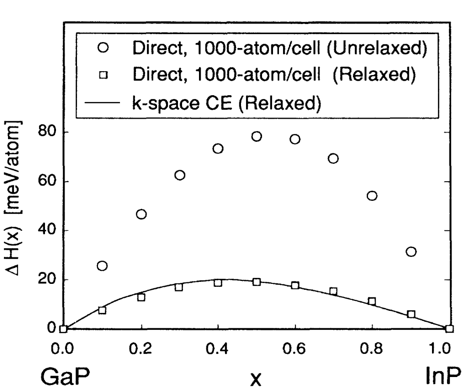

FIG. 2. Formation energies of random $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{P}$ alloys as a function of x. Directly calculated results for both relaxed and unrelaxed geometries are obtained from 1000-atom simulations.

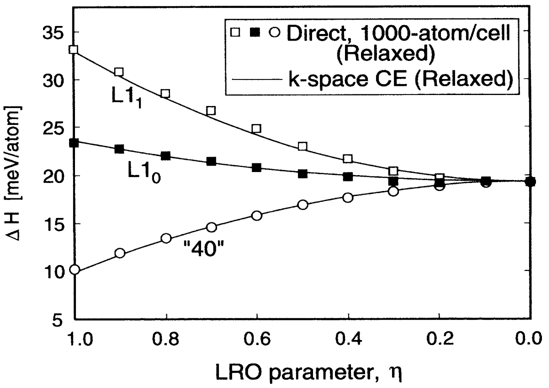

FIG. 3. Formation energies of $Ga_{0.5}In_{0.5}P$ alloys as a function of LRO parameter, η. Directly calculated results from 1000-atom simulations are shown as are the results of the **k**-space CE, using as input only $\eta = 1$ energies. $\eta = 1$ (0) indicates complete and perfect order (randomness).

composition-temperature phase diagram (open squares of Fig. 4). Here we apply the Monte Carlo algorithm to $\Delta H_{\rm CE}[\{\hat{S}_i\}]$ with only spin degrees of freedom, finding the CE prediction for the phase diagram (solid line in Fig. 4). The phase diagram computed using unrelaxed energies $\Delta H_{\rm direct}[\{\hat{S}_i\}; V; \{\mathbf{R}_i\} = 0]$ is also shown for comparison. In the Monte Carlo simulations using the CE, a cell of 1024 atoms with periodic boundary conditions was used. Simulations were performed in the Grand Canonical ensemble, 200–500 Monte Carlo steps were used for equilibration, and subsequently, averages were taken over 1000 steps. For each temperature, phase boundaries were determined from the discontinuity in concentration versus chemical potential. The effect of relaxation is drastic, as it lowers the miscibility gap temperature $T_{\rm MG}$ by ~2800 K. On this scale, the direct calculation and CE prediction for $T_{\rm MG}$ are in good agreement. One should note that the direct Monte Carlo calculations include vibrational effects whereas the CE results do not. Excluding vibrations in the direct simulations [5] raises $T_{\rm MG}$ by ~30 K, thereby bringing the direct and CE results even closer to each other. For $Ga_{0.5}In_{0.5}P$, we have also computed the nearest-neighbor Warren-Cowley SRO parameter α at $T = 1600$ K. SRO corresponds to correlations which exist in the disordered alloy, and hence pertains to a single, constant volume. Direct ($\alpha = -0.04$, with vibrations) and CE values ($\alpha = -0.02$, without vibrations) of SRO agree, with the negative signs indicating a very small tendency towards association of unlike (Ga-In) atom pairs. On the other hand, global stability or LRO corresponds [Eq. (2)] to the absolute stability of a given compound with respect to an equivalent amount of its constituents, and hence does not pertain to constant volume. Both CE and direct simulation show (Fig. 4) that the stable alloy LRO is phase separation.

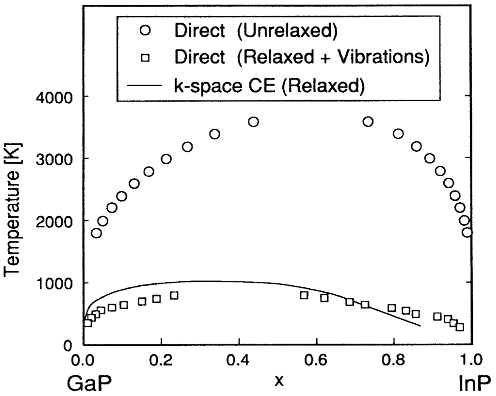

FIG. 4. Composition-temperature phase diagram of $Ga_{1-x}In_xP$. The squares indicate the the results of performing Monte Carlo calculations directly on $\Delta H_{\rm direct}[\{\hat{S}_i\}; V; \{\mathbf{R}_i\}]$ including random spin flips and a atomic displacements while the line is the result of applying Monte Carlo to $\Delta H_{\rm CE}[\{\hat{S}_i\}]$ including spin flips only.

This work was supported by the Office of Energy Research (Division of Materials Science of the Office of Basic Energy Sciences), U.S. Department of Energy, under Contract No. DE-AC36-83CH10093.

---

[1] F. Ducastelle, *Order and Phase Stability in Alloys* (Elsevier, New York, 1991).

[2] A. Zunger, in *Statics and Dynamics of Alloy Phase Transformations,* edited by P. E. A. Turchi and A. Gonis, NATO ASI Series (Plenum, New York, 1994).

[3] D. de Fontaine, Solid State Phys. **47**, 33 (1994).

[4] J. M. Sanchez, F. Ducastelle, and D. Gratias, Physica (Amsterdam) **128A**, 334 (1984).

[5] A. Silverman, A. Zunger, R. Kalish, and J. Adler, Phys. Rev. B **51**, 10 795 (1995).

[6] S.-H. Wei, L. G. Ferreira, and A. Zunger, Phys. Rev. B **41**, 8240 (1990).

[7] D. M. Nicholson, *et al.* in *High Temperature Ordered Intermetallic Alloys III,* edited by C. T. Liu, *et al.* Mater. Res. Soc. Symp. Proc. **133**, 17 (1989).

[8] C. Amador and G. Bozzolo, Phys. Rev. B **49**, 956 (1994).

[9] Z. W. Lu, S.-H. Wei, and A. Zunger, Phys. Rev. B **45**, 10 314 (1992).

[10] S. Foiles, in *Surface Segregation Phenomena,* edited by P. A. Dowben and A. Miller (CRC Press, Boca Raton, 1990), p. 79.

[11] P. C. Kelires and J. Tersoff, Phys. Rev. Lett. **63**, 1164 (1989); B. Dunweg and D. P. Landau, Phys. Rev. B **48**, 14 182 (1993).

[12] Z.-W. Lu, D. B. Laks, S.-H. Wei, and A. Zunger, Phys. Rev. B **50**, 6642 (1994).

[13] D. B. Laks, L. G. Ferreira, S. Froyen, and A. Zunger, Phys. Rev. B **46**, 12 587 (1992).

[14] We also find that a CE using as input *unrelaxed* energies accurately predicts the direct simulations of the energy functional for *unrelaxed* geometries.