PHYSICAL REVIEW B VOLUME 53, NUMBER 14 1 APRIL 1996-II

Contribution of the vibrational free energy to phase stability in substitutional alloys: Methods and trends

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(Received 21 November 1995)

Recent studies show that the effect of the lattice vibrations on predictions of phase stability can be important. Because complete computations of the phonon density of states from first principles are difficult, simpler models for the vibrational free energy have been used to incorporate these effects into phase diagram calculations. In this paper, we systematically investigate the accuracy of these approximations by studying model systems for which the vibrational free energy can be computed exactly in the harmonic approximation. We found that the Debye approximation, usually used in first-principles studies, fails to capture the configuration dependence of the vibrational free energy. We explain the reason for this failure. With the same model systems, we analyzed the effect of the lattice vibrations on the predicted phase diagrams as a function of size mismatch and chemical affinity. By fitting our results to the available experimental information, we find that the effect of vibrations on phase transition temperatures may be significant.

I. INTRODUCTION

Recent advances in theoretical models and computer power have made the first-principles calculations of alloy phase diagrams a powerful tool in materials science.[1,2] Precise control of external variables, attainability of extreme experimental conditions, and low cost make the computational models an attractive alternative to traditional laboratory experimentation for the design of new materials. In order to compete with ‘‘real’’ experiments, the computational models have to be reliable and capable of producing quantitative predictions. To achieve this goal, the theoretical models have to include all the important contributions to the alloy free energy.

In particular, methods to deal with substitutional disorder are well developed.[2] Quantum mechanics can be used to parametrize an Ising-like Hamiltonian for an alloy with any required accuracy. This lattice Hamiltonian allows one to compute the configurational entropy of a material and to evaluate its phase diagram. Although first-principles calculations based on this procedure have been successful in reproducing the topology of many real-alloy phase diagrams, the effect of neglecting other contributions to the free energy is unclear. Recently, Wolverton and Zunger[3] showed how the character of the short-range order in Ni-V and Pd-V is modified by the electronic entropy. The effects of lattice vibrations may be even more dramatic. It has been shown experimentally that for the Ni-Al, Fe-Al, Fe-Cr, and Cu-Au systems[4–8] the change of vibrational free energy in order-disorder and segregating phase transformations can be comparable in magnitude to the change in the configurational entropy. Some theoretical calculations,[9–12] based on simplified models for the vibrational free energy, support these conclusions, by showing that the inclusion of the vibrations in the theoretical models can significantly alter the predicted phase stability, bringing the predictions in closer agreement with experiment.

Despite this realization, very little has been done to justify the approximations used in the simplified models, and to study the trends of the effect of the lattice vibrations with size mismatch and chemical affinity. In this paper, we study model systems for which the vibrational free energy can be computed exactly within the harmonic approximation. This allows us to derive conclusions about the different approximations and the size and origin of the vibrational effect on alloy phase stability. In addition, we estimate the effect of vibrations on the transition temperatures in coherent transformations.

The rest of the paper is organized as follows. In Sec. II we briefly review the formalism used to study substitutional alloys and describe how a lattice model can accommodate the lattice vibrations. Simplified models that are usually used to address the problem are described in Sec. III. The model system used in the present study is presented in Sec. IV. Sections V and VI present the results of the exact approach and the simplified models, respectively. A discussion of possible approaches for first-principles calculations follows in Sec. VII. Rough estimates of the effect of the lattice vibrations on phase diagrams are reported in Sec. VIII. Section IX explores the roll of chemical affinity and atomic size in determining the effects of lattice vibrations on phase stability. Finally, the conclusions are summarized in Sec. X.

II. VIBRATIONAL FREE ENERGY AND ITS DEPENDENCE ON CONFIGURATION

The effect of the lattice vibrations on the phase stability of substitutional alloys can be studied with an Ising-like lattice model.[9,13] The only assumption needed for this transformation is that every microstate of the alloy can be uniquely mapped to a configuration of the atoms on a fixed lattice. This is achieved by, for every atom, finding the closest lattice site to its position. The mapping of the alloy problem to a lattice model breaks down close to displacive transitions, where the underlying lattice changes (e.g., from fcc to bcc). The lattice Hamiltonian can be properly defined by *coarse graining* the full Hamiltonian of the alloy system. The reduc-

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tion in the number of the degrees of freedom, from the quantum-mechanical continuous Hamiltonian to the lattice Hamiltonian, is achieved by integrating out the fastest degrees of freedom. For the case of a substitutional alloy, the configurational degrees of freedom evolve with much longer time scales than the vibrational or electronic degrees of freedom. That means that for every substitutional arrangement, there is a well-defined vibrational free energy. As our focus is on the vibrational free energy we ignore the electronic excitations. The lattice Hamiltonian contains the ''chemical'' energy of the relaxed ground state structure and its vibrational free energy. Therefore, the partition function of the system defined by this lattice Hamiltonian includes both configurational and vibrational degrees of freedom. In the harmonic approximation and for temperatures larger than the characteristic Debye temperatures of the system, the lattice Hamiltonian can be written as[11]

$$H(\vec{\sigma},T)=E_0(\vec{\sigma})+\langle\ln(\omega)\rangle(\vec{\sigma})k_BT+\frac{\hbar^2\langle\omega^2\rangle(\vec{\sigma})}{24k_BT}-\frac{\hbar^4\langle\omega^4\rangle(\vec{\sigma})}{2880k_B^3T^3}+\cdots, \tag{1}$$

where $\vec{\sigma}$ labels the configuration of the A and B atoms on the lattice, $\langle\ \rangle$ symbolizes averages (per atom) over the Brillouin zone, E_0 is the fully relaxed ground state energy, ω is the vibrational frequency of a phonon mode, and k_B and $\hbar$ are the Boltzmann and Planck constants, respectively. The terms that are not dependent on $\vec{\sigma}$ have been left out of the lattice Hamiltonian, as they do not contribute to the configurational thermodynamics.

We have shown[11] that the leading term $\langle\ln(\omega)\rangle k_BT$ in this high-temperature expansion is enough to accurately represent the vibrational free energy for temperatures of the order of, or higher than, the Debye temperatures of the system. Since most phase transformations occur in this temperature range, in the rest of the paper we will concentrate on this term, but most of the conclusions are also valid for the other terms in Eq. (1).

For systems described with classical potentials, the dynamical matrix is easily obtained from the second derivates of the total energy.[14] By diagonalizing this matrix, the values of the frequencies of the normal modes of the system can be obtained and the averages in Eq. (1) are easily computed. For systems that require a more complex, quantum-mechanical description, simplifications are necessary to get the moments of the frequency distribution (see Sec. III, below).

To study the thermodynamic properties of the alloy system, the actual dependence of H on the configuration $\vec{\sigma}$ is parametrized using a cluster expansion technique.[15] The occupancy of site i is labeled by a spinlike variable σ_i [$\sigma_i=+1$ (-1) when a B (A) atom is on site i]. The substitutional state (or configuration) of an N-site alloy, $\vec{\sigma}$, is then an N-dimensional vector of 1's and -1's. The alloy Hamiltonian is written as

$$H(\vec{\sigma},T)=\sum_{\alpha} V_\alpha(T)\sigma_\alpha(\vec{\sigma}), \tag{2}$$

where the sum is over all clusters α of lattice points. The cluster functions σ_α are defined as the product of the spin variables on cluster α, and V_α are the *effective cluster interactions* (ECI's). Once the ECI's are known, the thermodynamic properties of the alloy can be computed using any of the standard statistical mechanics techniques (e.g., Monte Carlo simulations, cluster variation method, low- and high-temperature expansions).

The techniques for obtaining the ECI's have been reviewed elsewhere.[16–19] In most cases, the ECI's can be obtained from the values of $H(\vec{\sigma},T)$ for a few (of the order of 10) ordered structures of the A and B atoms on the sites of the lattice. Given the above approximations, we would only need E_0 and $\langle\ln(\omega)\rangle$ for these configurations.

Because phase stability depends on differences in thermodynamic potentials, only the *formation* values of E_0, $\langle\ln(\omega)\rangle$, etc., are needed. For an ordered structure with composition c (atomic fraction of A), the formation value of a quantity Q is defined as

$$\Delta Q=Q-[cQ_A+(1-c)Q_B]. \tag{3}$$

It has been noted by several authors (see for example Ref. 20) that the value of $\Delta\langle\ln(\omega)\rangle$ for an ordered structure is independent of the masses of the A and B atoms. Also, $\Delta\langle\ln(\omega)\rangle$ is dimensionless, independent of the units used for ω, and invariant under a change in energy and length scales. These properties do not hold for the other moments of the frequency distribution in Eq. (1).

III. SIMPLIFIED MODELS

The calculation of $\Delta\langle\ln(\omega)\rangle$ for several ordered structures of a binary alloy from first principles is beyond the current computer power because it amounts to computing the full phonon dispersion relations for structures with complex unit cells. For this reason, simplified models have been developed in recent years to reduce these calculations to tractable schemes. In this section, we review some of these models.

A. Debye model

In the Debye model, the solid is considered as an elastic continuum with the same elastic constants as the true solid. The vibrational density of states is then parabolic, with a cutoff frequency ω_D given by the condition that the total number of frequencies should equal the $3N$ degrees of freedom. The Debye temperature is defined as $\theta_D=\hbar\omega_D/k_B$, and can be computed as[21]

$$\theta_D=\frac{2\pi\hbar}{k_B}\left(\frac{9}{4\pi}\frac{N}{V}\right)^{1/3}\left\{\int\left[\frac{1}{c_1^3}+\frac{1}{c_2^3}+\frac{1}{c_3^3}\right]\frac{d\Omega}{4\pi}\right\}^{-1/3}, \tag{4}$$

where c_1, c_2, and c_3 are the three speeds of sound in a given direction of propagation, N/V is the number density, and the integral is over all the possible directions. The speeds of sound can be easily computed if the elastic constants and density of the material are known.[21]

Assuming a Debye-like distribution of frequencies, the vibrational free energy of an ordered structure $\vec{\sigma}$ can be computed[22] once θ_D is known for that configuration. The resulting high-temperature limit of the vibrational free energy has the same form as Eq. (1) with

$$\langle \ln(\omega)\rangle_{\text{Debye}} = 3\ \ln\left(\frac{k_B\theta_D}{\hbar}\right) - 1. \tag{5}$$

Some of the effects of anharmonicity (e.g., thermal expansion) can be taken into account by using the Debye-Grüneisen model.[23] Since we are only evaluating the approximations to reproduce the harmonic behavior, these effects will not be considered.

In most studies where *ab initio* methods are used, computing all the elastic constants is very difficult and further approximations are necessary. Assuming constant transverse and longitudinal sound velocity, given by $c_l = (L/\rho)^{1/2}$ and $c_t = (S/\rho)^{1/2}$, where ρ is the density, and using empirical relationships between the bulk modulus and the shear (S) and longitudinal (L) moduli (valid for nonmagnetic cubic elements), Moruzzi, Janak, and Schwarz[23] derived the following approximation to Eq. (4):

$$\theta_D = 0.617(6\pi^2)^{1/3}\frac{\hbar}{k_B}\left[\frac{v^{1/3}B}{M}\right]^{1/2}, \tag{6}$$

where v is the average volume per atom, M is the average atomic weight, and B is the bulk modulus obtained from the binding curve as

$$B = v\,\frac{\partial^2 u}{\partial v^2}\bigg|_{v_0}, \tag{7}$$

where u is the energy per atom and v_0 is the equilibrium value of v.

We will refer to this scheme to approximate the Debye model as the Moruzzi-Janak-Schwarz (MJS) approximation. The MJS approximation has been widely used in studies of alloy thermodynamics. Studies of binary [Ag-Cu (Refs. 9 and 24), Co-Pt (Ref. 25), Au-Ni (Ref. 26), Ni-Al (Ref. 27), Ti-Al (Ref. 28), Au-Pd (Ref. 24), Au-Ag (Ref. 24), and Cd-Mg (Ref. 10)], pseudobinary [InP-InSb (Ref. 29), and GaAs-InAs (Ref. 30)], and ternary [Ru-Nb-Zr (Ref. 31)] alloys have been reported in the literature.

The popularity of the MJS scheme is due to its simplicity: The quantities needed (volume and bulk modulus) are byproducts of the calculation of the relaxed formation energies for the ordered structures. However, its validity for the calculation of *formation* free energies in alloys has not been demonstrated. For an ordered structure with composition c, the formation value of the coefficient of the leading term in Eq. (1) in the MJS scheme is

$$\Delta\langle \ln(\omega)\rangle_{\text{MJS}} = \frac{3}{2}\left[\ln\left(\frac{B}{B_A^c B_B^{1-c}}\right) + \ln\left(\frac{r}{r_A^c r_B^{1-c}}\right) + \ln\left(\frac{M_A^c M_B^{1-c}}{cM_A + (1-c)M_B}\right)\right], \tag{8}$$

where r is the average Wigner-Seitz radius of the structure (i.e., $v = 4\pi r^3/3$).

As pointed out above, the exact value of $\Delta\langle\ \ln(\omega)\rangle$ is independent of the atomic masses of the A and B atoms. Both the Debye and MJS approximations fail to reproduce this property [see Eqs. (4) and (8)]. An *ad hoc* way of fixing this deficiency is to drop the last term in Eq. (8). We will refer to this scheme as the modified MJS (MMJS) approximation. To our knowledge the MMJS approximation has not been reported before.

B. Local harmonic model

In the local harmonic (LH) model,[32,33] every atom is assumed to vibrate independently from the other atoms, as if the rest of the structure were frozen at its equilibrium position. The vibrational density of states is then approximated by a set of δ functions at the Einstein frequencies of each atom. This is equivalent to neglecting the elements in the dynamical matrix outside the 3×3 block diagonal. With this simplification, the problem of diagonalizing the $3N\times3N$ dynamical matrix is reduced to the diagonalization of N 3×3 matrices. This model has been used to compute thermodynamic and structural properties of perfect crystals,[33] point defects,[34] grain boundaries,[33] interfacial segregation,[35] and phase transitions at surfaces.[36]

In the LH approximation the second moment of the vibrational density of states, $\langle\omega^2\rangle$, is obtained exactly. The second moment can be related to the trace of the dynamical matrix D through[14] $\langle\omega^2\rangle = \text{Tr}(D)/N$. The trace of D is preserved by the LH approximation making $\langle\omega^2\rangle_{\text{LH}} = \langle\omega^2\rangle_{\text{exact}}$. The other moments necessary to compute the free energy [most importantly $\langle\ln(\omega)\rangle$] are approximate in the LH model.

In the next section we define a model system for which $\langle\ln(\omega)\rangle$ can be computed accurately, while in the following sections we compare the exact results with those obtained using the approximations described in this section.

IV. MODEL SYSTEM

The model system we studied is a fcc Lennard-Jones (LJ) alloy, described by three LJ functions corresponding to the A-A, A-B, and B-B interactions. The functional form used is

$$V(r) = \epsilon[(R/r)^{12} - 2(R/r)^6]. \tag{9}$$

To simplify the calculations, the potential functions were truncated at $r = 2.5R$.

To analyze the effect of the lattice vibrations on the phase stability of the model system, we studied a set of 16 ordered structures with up to 8 atoms in the unit cell. Once the formation values of the chemical energy and the vibrational free energy are computed, a cluster expansion can be constructed to obtain a convenient parametrization of the configuration-dependent contributions to the lattice Hamiltonian.

TABLE I. Sets of Lennard-Jones parameters for the model alloy systems. In all cases, $\epsilon_{AA} = 1$ and $R_{AA} = 1$ without loss of generality. Set No. 1 corresponds to a simplified model of the Ar-Kr system (Ref. 38).

Set No.	ϵ_{AB}	R_{AB}	ϵ_{BB}	R_{BB}
1	1.437	1.003	1.371	1.062
2	1.185	1.031	1.371	1.062
3	0.813	1.031	1.371	1.062
4	0.813	1.000	1.000	1.000
5	1.000	0.974	1.000	1.000

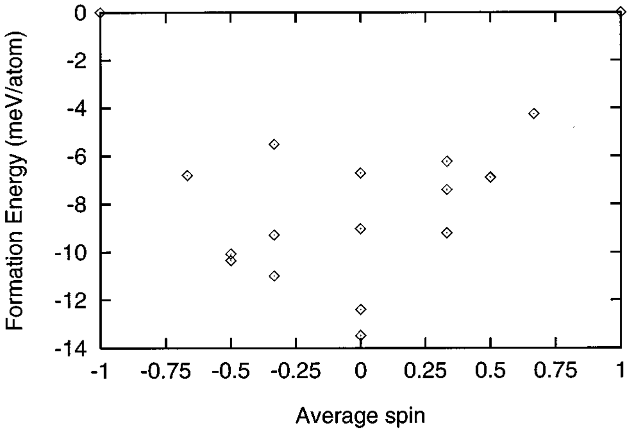

FIG. 1. Formation energy for the ordered structures for the first set of LJ parameters in Table I. Average spin of -1 (1) corresponds to pure A (B). The energy scale corresponds to $\epsilon_{AA}=9.83$ meV.

V. EXACT RESULTS

The values of the LJ parameters used in the calculations are summarized in Table I. The values of the atomic masses used were $M_A=39.95$ and $M_B=83.80$ (resembling Ar and Kr), unless otherwise stated. The geometry (unit cell shape and size, and the internal coordinates of the atoms) of all the ordered structures was optimized to minimize the energy.

To perform the integrals over the Brillouin zone to get $\langle\ln(\omega)\rangle$, we used the equivalent of 408 special fcc points obtained with the Chadi-Cohen scheme.[37] The resulting relative integration error in $\Delta\langle\ln(\omega)\rangle$ is less than 10^{-3}.

We first studied the system defined by the parameters in set No. 1 in Table I. These parameters correspond to a simplified model of the Ar-Kr system.[38] The computed values of ΔE and $\Delta\langle\ln(\omega)\rangle$ for the 16 ordered structures are shown in Figs. 1 and 2. With the parameters for the potentials used for these calculations, the system is of the ordering type ($\Delta E<0$). The positive values of $\Delta\langle\ln(\omega)\rangle$ imply that the transition temperatures computed with the vibrations in the lattice Hamiltonian will be lower than when the vibrations are neglected.

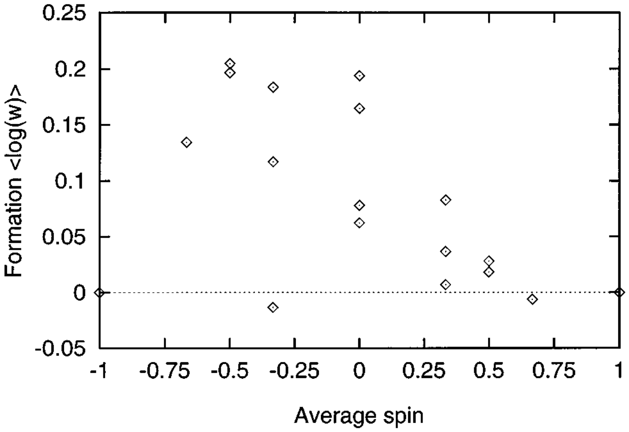

FIG. 2. Formation of the logarithmic average of the frequencies for the ordered structures for the first set of LJ parameters in Table I.

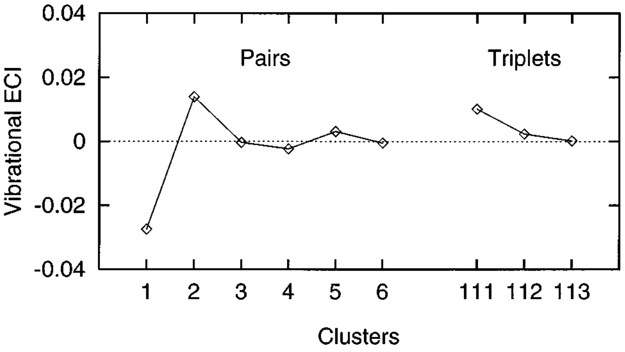

FIG. 3. Cluster expansion coefficients for $\Delta\langle\ln(\omega)\rangle$ (vibrational ECI's) computed with the Connolly-Williams (Ref. 16) method for the first set of LJ parameters in Table I. The pair clusters are labeled by the order of the pair, while the triplets are labeled by the pairs that form the triplet (e.g., "112" labels the triplet formed by two first nearest neighbor pairs and one second nearest neighbor pair).

We constructed a cluster expansion for $\Delta\langle\ln(\omega)\rangle$. The rms error of the cluster expanded values of $\Delta\langle\ln(\omega)\rangle$ is 0.03, indicating that the exact values are well reproduced by the cluster expansion. The values of the expansion coefficients (ECI's) are shown in Fig. 3. A rough estimate of the size of this effect can be computed using the method described in Sec. VIII. The vibrations will lower the transition temperatures by approximately 5% in this model system.

The ECI's are decaying with distance and number of sites in the cluster. This is a signature that the local environments determine the value of $\Delta\langle\ln(\omega)\rangle$. With the cluster expansion, the value of $\Delta\langle\ln(\omega)\rangle$ for any other structure can be easily computed. Although convergence studies for the cluster expansion of ΔE have been widely reported in the literature,[18,19,39–41] a comprehensive study of the convergence of the cluster expansion of $\Delta\langle\ln(\omega)\rangle$ is still lacking.

An interesting question to address is what part of the frequency spectrum is responsible for the reported values of $\Delta\langle\ln(\omega)\rangle$. To answer this question, we define for every structure the function

$$s(\omega)\equiv\ln(\omega)\Delta g(\omega), \tag{10}$$

where $\Delta g(\omega)$ is the formation value of the vibrational density of states (VDOS). Then the value of $\Delta\langle\ln(\omega)\rangle$ can be obtained as the area under the curve $s(\omega)$, i.e.,

$$\Delta\langle\ln(\omega)\rangle=\int_0^\infty s(\omega)d\omega. \tag{11}$$

The values of $s(\omega)$ were computed using the VDOS obtained with the equivalent to 408 fcc Chadi-Cohen k points and smoothed with a 0.02-THz-wide Lorentzian. The results are shown in Fig. 4.

It can be seen from these figures that the contribution of $s(\omega)$ to $\Delta\langle\ln(\omega)\rangle$ is, in most cases, larger in the high-frequency optical region of the spectrum than in the low-frequency acoustical modes. This is in agreement with recent experimental findings in the Fe-Al system.[6] This observation

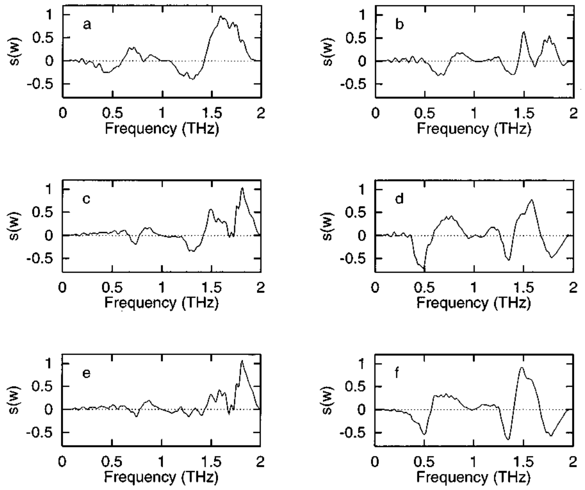

FIG. 4. Contribution to the formation value of the logarithmic average of the frequencies for some structures with the first set of LJ parameters in Table I. The plots correspond to the following structures in the Strukturbericht notation: (a) $L1_0$, (b) $L1_1$, (c) A-rich $L1_2$, (d) B-rich $L1_2$, (e) A-rich DO_{22}, and (f) B-rich DO_{22}. The frequency scale corresponds to $\epsilon_{AA}=9.832$ meV and $R_{AA}=3.87$ Å.

has important consequences for the applicability of some of the approximate methods (see Sec. VI).

To condense the results for the other sets of LJ parameters in Table I, we computed the averages of ΔE and $\Delta\langle\ln(\omega)\rangle$ for the 16 ordered structures studied. These values are shown in Table II.

VI. EVALUATION OF SIMPLIFIED MODELS

For the set of ordered structures used in Sec. V, we computed $\Delta\langle\ln(\omega)\rangle$ using the Debye, MJS, MMJS, and LH models. Figure 5 shows a detailed comparison of the performance of these models for the first set of LJ parameters in Table I. A summary of the results for the other sets of LJ parameters is shown in Table III.

It can be seen from Table III that the performance of the models varies between the various sets of LJ parameters. However, the local harmonic model systematically outperforms the other models, for the fcc LJ alloys studied. The magnitude of the LH error in $\Delta\langle\ln(\omega)\rangle$ is acceptable (compare Tables II and III) for a first attempt at including the lattice vibrations in the free energy models. However, the implementation of the LH model with first-principles approaches is not straightforward. In fact, the calculation of the Einstein frequencies of the atoms in the unit cell of a given structure is almost as difficult as the calculation of all the spring constants [from which, the exact value of $\langle\ln(\omega)\rangle$ can be obtained].

The LH model is a very useful technique to approximate the vibrational properties of nonperiodic systems (e.g., defects, surfaces, interfaces) modeled with classical potentials. In these cases, the dynamical matrix is easily obtained, while finding its eigenvalues is difficult because of the lack of periodicity. The LH model greatly facilitates this diagonalization as described in Sec. III.B. In the case of simple ordered

TABLE II. Average values of ΔE and $\Delta\langle\ln(\omega)\rangle$ for the 16 ordered structures considered, using the sets of LJ parameters of Table I. The energies are in units of ϵ_{AA}.

Set No.	Average ΔE	Average $\Delta\langle\ln(\omega)\rangle$
1	-0.8610	0.0931
2	0.0735	-0.0816
3	1.4379	-0.3270
4	0.6887	-0.1345
5	0.0038	0.0218

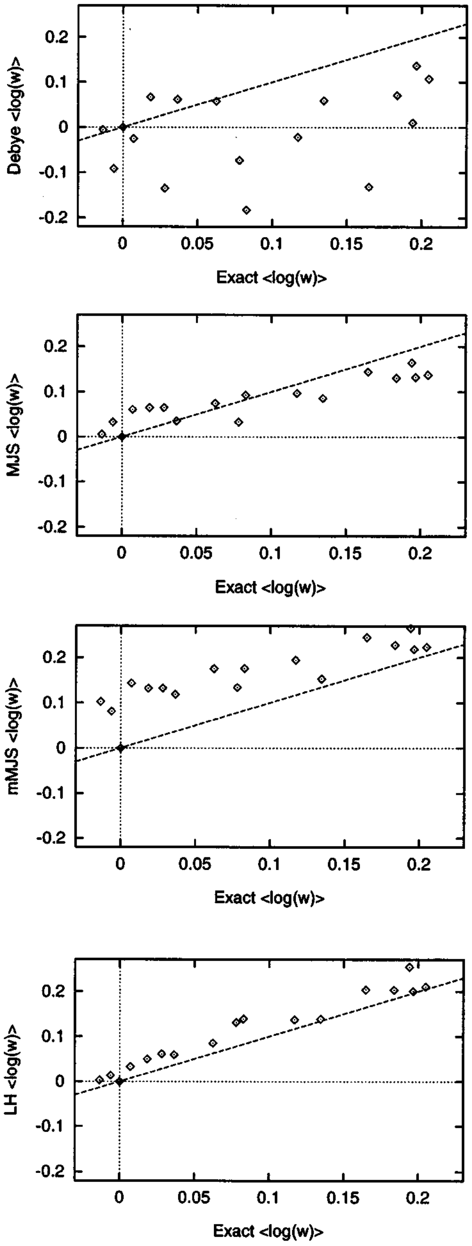

FIG. 5. Comparison of the exact value of $\Delta\langle\ln(\omega)\rangle$ with the prediction of the Debye, MJS, MMJS, and LH models for the 16 ordered structures. The closer the points lie to the dashed line, the better the approximation.

TABLE III. Root mean square (rms) error of the prediction of the value of $\Delta\langle\ln(\omega)\rangle$ for 16 ordered structures using the Debye, MJS, MMJS, and LH models, for the sets of LJ parameters shown in Table I.

	rms error of approximations			
Set No.	Debye	MJS	MMJS	LH
1	0.1378	0.0403	0.0848	0.0321
2	0.1036	0.0255	0.0780	0.0190
3	0.1442	0.0524	0.0907	0.0280
4	0.0891	0.0877	0.0050	0.0026
5	0.1047	0.0744	0.0175	0.0092

structures of binary alloys, modeled with first-principles methods, the difficult part of the problem is to obtain the dynamical matrix, while its diagonalization is simplified by the aid of Bloch's theorem. For all these reasons, the LH model, although quite accurate, is not practical for first-principles calculations of vibrational properties of alloys.

The performance of the approximations based on the Debye model (Debye, MJS, and MMJS) is not as good as the LH model (see Table III). The errors are comparable in magnitude to $\Delta\langle\ln(\omega)\rangle$. Although the MJS and MMJS models are approximations to the Debye model, the former perform systematically better than the latter for the cases studied. We do not understand this behavior.

We identified three sources of error in the Debye and MJS models: contribution of high-frequency vibrations to $\Delta\langle\ln(\omega)\rangle$, lack of sampling of certain spring constants, and mass effects.

As noted in Sec. V the high-frequency part of the vibrational spectrum makes a very important contribution to $\Delta\langle\ln(\omega)\rangle$. Since the Debye and MJS models are based on the elastic properties, they lack information about this part of the spectrum. On the other hand, the LH model is a better approximation to the optical modes. This could explain the better performance of the LH model.

The value of the bulk modulus used as input in the MJS model does not depend on some of the atomic spring constants. For example, in a cubic structure, the bulk modulus only depends on the central spring constants, but not on the off-diagonal elements of the spring constant tensors. In cases where these off-diagonal elements contribute significantly to $\Delta\langle\ln(\omega)\rangle$, the MJS model will fail to capture the essential features of the system.

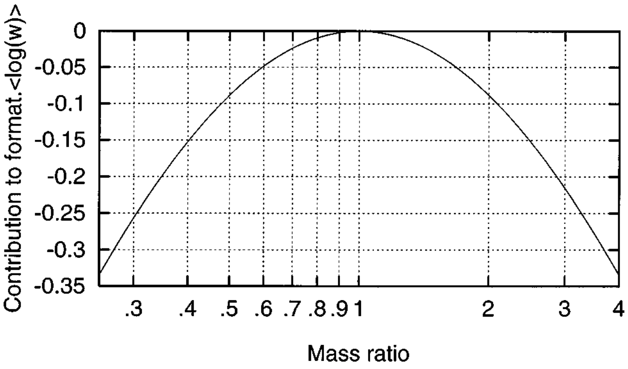

FIG. 6. Contribution of the masses to the value of $\Delta\langle\ln(\omega)\rangle$ in the MJS and Debye models, for an alloy of composition 1/2, as a function of the mass ratio M_A/M_B.

The third source of error in the Debye and MJS models is the dependence of $\Delta\langle\ln(\omega)\rangle$ on the atomic masses of the constituent atoms. As pointed out in Sec. II, the exact value of $\Delta\langle\ln(\omega)\rangle$ is independent of M_A and M_B, while the predicted value in the Debye and MJS models depends on the masses through Eqs. (4) and (8). It can be shown that the contribution of the masses in both models has exactly the same form. Figure 6 illustrates the size of this effect for an alloy at composition 1/2 as a function of the mass ratio. It can be seen that for an alloy of mass ratio 2 (roughly the Ar-Kr case) the effect of the masses is of the order of the total value of $\Delta\langle\ln(\omega)\rangle$ (see Table II), making the predictions of these models unreliable. The *ad hoc* correction introduced in the MMJS model improved the results for some cases, but it is not consistently better than the MJS model.

VII. ALTERNATIVE FRAMEWORKS FOR FIRST-PRINCIPLES CALCULATIONS

We showed in Sec. VI that neither the local harmonic nor the Debye-like models provide the framework for first-principles calculations of the effect of lattice vibrations on the phase stability of alloys. The LH model is relatively accurate, but its implementation in first-principles calculations is difficult, whereas the Debye-like models are of very easy implementation, but the predictions they make are not reliable. Therefore, alternative approaches are needed. In this section we explore methods that could make the calculations both feasible and accurate.

Frozen phonon calculations for a few high-symmetry k points are feasible with first–principles methods and have been reported for several systems (see for example Ref. 42). An important question to answer is how many k points are needed to obtain a converged value for $\Delta\langle\ln(\omega)\rangle$. To address this question, we computed the k point convergence of $\Delta\langle\ln(\omega)\rangle$ for some of the structures studied in previous sections for the first set of LJ parameters in Table I.

For the pure elements, the k points were chosen according to the Chadi-Cohen scheme.[37] For the ordered structures, the k points corresponded to the equivalent set of k points in reciprocal space. Of course, due to the different symmetry and unit cell of the ordered structures, the actual number of *distinct* k points varied with the ordered structures. Table IV summarizes the number of distinct k points for the ordered

TABLE IV. Number of k points for the different ordered structures as a function of the iteration number in the Chadi-Cohen scheme.

Chadi-Cohen iteration	Structures				
	fcc	$L1_0$	$L1_1$	$L1_2$	DO_{22}
1	2	2	4	1	1
2	10	12	15	4	3
3	60	80	102	20	20
4	408	576	748	120	144

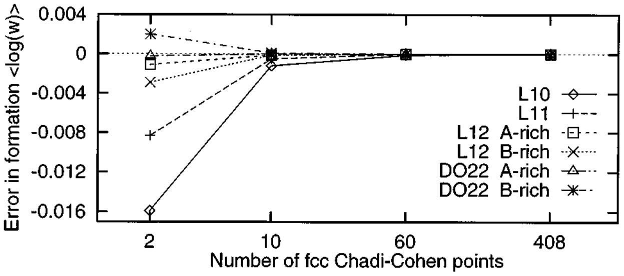

FIG. 7. Convergence error in $\Delta\langle\ln(\omega)\rangle$ as a function of the number of fcc Chadi-Cohen k points.

structures for different numbers of iterations in the Chadi-Cohen scheme.

We computed $\Delta\langle\ln(\omega)\rangle$ for some of the ordered structures as a function of the iteration in the Chadi-Cohen scheme to select the k points. The convergence results are shown in Fig. 7. It can be seen that convergence of the formation values within 1% is achieved for the third set of k points. However, if only the first iteration is used, the convergence error in $\Delta\langle\ln(\omega)\rangle$ is less than 0.016. This corresponds to less than 20% of the average value of $\Delta\langle\ln(\omega)\rangle$. The simplicity of the Lennard-Jones system studied precludes the extrapolation of this convergence property to more complex systems, for which a quantum-mechanical method is necessary. However, if the fast convergence of $\Delta\langle\ln(\omega)\rangle$ is a general feature, it will open the road for first-principles frozen phonon calculations at a very few high-symmetry k points, for the calculation of vibrational free energy of alloys.

A second possibility to use first-principles approaches is to exploit the recent advances in linear response methods,[43,44] based on the pseudopotential method (for a review see Ref. 45). For systems where the pseudopotentials of the two atoms forming the alloy are similar enough, the identity of the atoms can be treated as a perturbation. The reference state is a virtual crystal formed by a "virtual" atom sitting at the ideal lattice sites. The virtual atom is described with a pseudopotential equal to the arithmetic average of the pseudopotentials of the real atoms. The method allows the calculation of geometries of relaxed structures, formation energies, and phonon frequencies of ordered and disordered configurations. It has been successfully applied to the Si-Ge system.[46] The similarity of the pseudopotentials of Si and Ge allowed these calculations.

In most cases, however, the pseudopotentials of the two species are not similar enough for a perturbative treatment of the atomic identity. This is the case, for instance, in transition-metal alloys and oxide mixtures. The linear response method can still be used to compute the phonon frequencies of specific ordered structures, but the linear response function has to be computed for each configuration of atoms separately. The current computing power would allow only calculations of this sort for very few high-symmetry ordered structures. For simple systems, where a few ordered structures are enough to obtain a reliable cluster expansion of $\Delta\langle\ln(\omega)\rangle$, this method can provide a viable approach for first-principles calculations.

A third option for first-principles calculations would involve an extension of the method recently proposed by Wei and Chou.[47] This method obtains the real-space spring constant tensors by computing the forces on atoms of perturbed unit cells and inverting the resulting set of equations. This approach has been very successful in computing the phonon frequencies and thermodynamic properties of elemental semiconductors.[47–49] It is very computer intensive because it requires the calculation of forces for several low-symmetry large unit cells, in order to obtain *all* the non-negligible spring constants. These unit cells would become even larger and of lower symmetry for ordered configurations of an alloy. However, the knowledge of *all* the spring constants is not really necessary for the calculation of $\Delta\langle\ln(\omega)\rangle$. In fact, $\Delta\langle\ln(\omega)\rangle$ is an integrated quantity over the density of states and therefore does not depend on the fine details of the phonon dispersion relations. Exploiting this fact, we developed a hierarchy of approximations to get $\Delta\langle\ln(\omega)\rangle$. Preliminary results for the Si-Ge system suggest that the effort needed to compute $\Delta\langle\ln(\omega)\rangle$ for an ordered structure is, in fact, much less than that required to obtain the complete set of spring constant tensors.

VIII. ESTIMATE OF THE EFFECT OF THE LATTICE VIBRATIONS ON THE PREDICTED PHASE STABILITY

A rough estimate of the effect of the lattice vibrations on the phase diagram of a substitutional binary alloy can be obtained by assuming that only the nearest neighbor pair ECI is nonzero in the Hamiltonian of the alloy,

$$H(\vec{\sigma},T)=(V_{\text{chem}}+V_{\text{vib}}k_BT)m_2\langle\sigma_2\rangle, \tag{12}$$

where V_{chem} and V_{vib} are the chemical and vibrational ECI's obtained by cluster expanding E_0 and $\langle\ln(\omega)\rangle$, respectively, $\langle\sigma_2\rangle$ is the lattice average of the cluster functions on the nearest neighbor pairs of the lattice, and m_2 is the number of nearest neighbor pairs per lattice site (e.g., $m_2=6$ for fcc and $m_2=4$ for bcc). The transition temperatures at composition 1/2 for systems with only nearest neighbor ECI's are given by $T_c=\alpha|V|/k_B$, where α is a numerical constant that only depends on the underlying lattice and on whether the system is ordering or segregating. For the fcc lattice, $\alpha=1.7$ for ordering systems and $\alpha=9.8$ for segregating systems, while for bcc, $\alpha=6.5$ regardless of the ordering tendency (the bcc lattice is not *frustrated* in the nearest neighbor approximation).

The size of the effect of the lattice vibrations can be expressed as the ratio between the transition temperatures computed with and without considering the vibrations as

$$\frac{T_c^{\text{chem+vib}}}{T_c^{\text{chem}}}=\frac{1}{1\mp\alpha V_{\text{vib}}}, \tag{13}$$

where the "$-$" and "$+$" correspond to ordering and segregating systems, respectively. Due to the linear dependence on temperature of the leading term in Eq. (1), the result in Eq. (13) only depends on the sign of V_{chem} (i.e., on the ordering tendency of the system) and not on its actual value. In other words, for a rough estimate of the relative change in transition temperatures with lattice vibrations, it is enough to compute the vibrational ECI's V_{vib}. The predicted values of the relative change in transition temperatures, $(T_c^{\text{chem+vib}}$

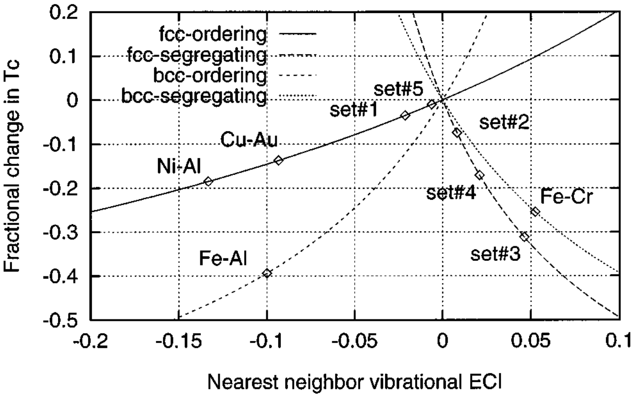

FIG. 8. Rough estimate of the effect of lattice vibrations on the predicted phase stability for some alloys systems. The labels "set No." correspond to the set of LJ parameters in Table I, while the vibrational ECI's for the other systems were estimated from experimental measurements of vibrational entropy.

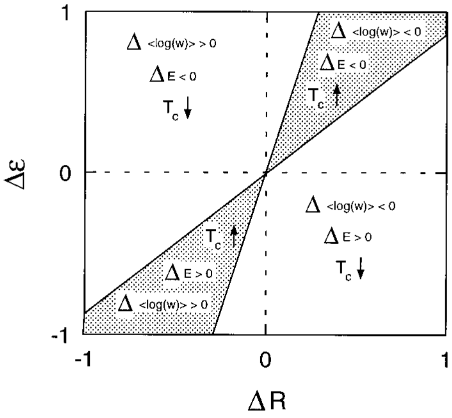

FIG. 9. Trends in the effect of lattice vibrations on phase stability. The shaded region corresponds to the set of LJ parameters that define systems in which the lattice vibrations tend to increase the transition temperatures.

$-T_c^{\mathrm{chem}})/T_c^{\mathrm{chem}}$, according to Eq. (13) are shown in Fig. 8 as a function of V_{vib} for fcc and bcc alloys.

We used Eq. (13) to estimate the effect of the lattice vibrations on the phase stability of the LJ systems described in Table I. The predicted relative change in the transition temperatures is shown in Fig. 8 (labels "set No. 1" – "set No. 5"). For this rough estimate, the nearest neighbor vibrational ECI's were obtained by fitting a cluster expansion with only this ECI (and an empty and point terms) to the values of $\Delta\langle\ln(\omega)\rangle$ of the 16 ordered structures.

Estimates of the effect of vibrations on the phase stability of real materials can be made using the experimental results of Fultz and co-workers.[4–8] They measured differences in vibrational entropy between different configurations of several alloys. These differences allow us to obtain an estimate for the value of the nearest neighbor vibrational ECI's, assuming a short-range cluster expansion, and recalling that $\Delta S_{\mathrm{vib}} = -k_B \Delta\langle\ln(\omega)\rangle$ in the high-temperature limit. The resulting estimates for the change in transition temperature at composition 1/2 are shown in Fig. 8. Note that for the alloy systems studied, all transition temperatures are reduced by the lattice vibrations (this includes both ordering and segregating systems).

It is clear from Fig. 8 that the effect of lattice vibrations on the transition temperatures can be significant. Although using only nearest neighbor interactions makes this a rough estimate, the truncation of the cluster expansion is not expected to bias the estimate towards larger effects. Therefore, lowering transition temperatures by 30% might not be uncommon. In the next section we analyze whether the trend of *lowering* the transition temperatures in Fig. 8 can be explained.

IX. TRENDS

The simple model system of Sec. IV allows us to analyze how the effect of the lattice vibrations on phase stability changes, when changing the size mismatch and chemical affinity of the alloy species. In principle, this is achieved by systematically varying the parameters that define the Lennard-Jones potentials (i.e., ϵ_{AA}, R_{AA}, ϵ_{AB}, R_{AB}, ϵ_{BB}, and R_{BB}) and computing the vibrational effective interactions for different sets of parameters. For simplicity, we computed $\Delta\langle\ln(\omega)\rangle$ for just one ordered structure ($L1_0$). The results obtained may not be valid for more complex systems, but provide a guideline for analyzing simple cases.

Without losing generality, we can set $\epsilon_{AA}=1$ and $R_{AA}=1$ [recall that the value of $\Delta\langle\ln(\omega)\rangle$ is independent of the energy and length scales]. A power expansion of $\Delta\langle\ln(\omega)\rangle$ for $L1_0$ can be constructed numerically around $\epsilon_{AB}=1$, $R_{AB}=1$, $\epsilon_{BB}=1$, and $R_{BB}=1$. The linear term of the expansion does not depend on the four variables independently, but only on $\Delta\epsilon=\epsilon_{AB}-(\epsilon_{AA}+\epsilon_{BB})/2$ and $\Delta R = R_{AB}-(R_{AA}+R_{BB})/2$:

$$\Delta\langle\ln(\omega)\rangle_{L1_0} \approx 0.84\Delta\epsilon - 2.86\Delta R. \tag{14}$$

For an ordering system, a positive value of $\Delta\langle\ln(\omega)\rangle$ reduces the ordering tendency of the system. A similar expression can be computed for the formation *energy* of $L1_0$:

$$\Delta E_{L1_0} \approx -4.70\Delta\epsilon + 4.05\Delta R. \tag{15}$$

A negative value of ΔE_{L1_0} corresponds to an ordering tendency. Equations (14) and (15) divide the parameter space $(\Delta\epsilon,\Delta R)$ in four areas (see Fig. 9). In the unshaded areas, ΔE_{L1_0} and $\Delta\langle\ln(\omega)\rangle_{L1_0}$ have opposite sign and the effect of the lattice vibrations is to reduce the (ordering or segregating) transition temperature. The behavior in these areas is consistent with the intuitive understanding of the vibrational effect: In ordering systems, *A*-*B* bonds have lower energy than the average of the *A*-*A* and *B*-*B* bonds. Usually lower energy means stiffer bonds and therefore lower vibrational entropy. This lower entropy will make the ordered structure less stable and hence its transition temperature will be lower. A similar argument can be applied to segregating systems with the same conclusion. In a small area of parameter space (shaded areas in Fig. 9) vibrations increase the transition temperature, indicating that the simple picture described above breaks down.

X. CONCLUSIONS

The configurational dependence of the vibrational free energy can be expanded with a short-range Ising-like Hamiltonian. This makes it possible to compute the *total* free energy for the alloy system, including the effects of substitutional and vibrational excitations. Fits of this Hamiltonian to experimental data indicate that the effect of vibrations on transition temperatures may be significant.

The computation of this quantity from first principles will be difficult. In our model system, we find that the major contribution to the formation value of the vibrational free energy comes from the intermediate and high frequencies of the phonon spectrum. This prohibits the use of simplified models for the vibrational free energy which are based solely on information of the elastic constants. The Debye approximation, in particular, fails because it does not contain information about the important high-frequency part of the spectrum, may not sample all the spring constants, and depends on the masses of the atomic species. We proposed alternative schemes that may be feasible to use with first-principles approaches, and still retain enough information about the system to produce reliable results. Although we confirmed the general trend of the lattice vibrations lowering the transition temperature, we identified cases where the opposite effect is expected.

ACKNOWLEDGMENTS

This work was supported in part by the MRSEC Program of the National Science Foundation under Award No. DMR-9400334 and by the Charles Reed Fund at MIT.

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[1] F. Ducastelle, *Order and Phase Stability in Alloys* (North-Holland, Amsterdam, 1991).

[2] D. de Fontaine, Solid State Physics **47**, 33 (1994).

[3] C. Wolverton and A. Zunger, Phys. Rev. B **52**, 8813 (1995).

[4] L. Anthony, J. K. Okamoto, and B. Fultz, Phys. Rev. Lett. **70**, 1128 (1993).

[5] B. Fultz *et al.*, Phys. Rev. B **52**, 3315 (1995).

[6] L. Anthony, L. J. Nagel, J. K. Okamoto, and B. Fultz, Phys. Rev. Lett. **73**, 3034 (1994).

[7] B. Fultz *et al.*, Phys. Rev. B **52**, 3280 (1995).

[8] L. J. Nagel, L. Antony, and B. Fultz, Philos. Mag. Lett. **72**, 421 (1995).

[9] J. M. Sanchez, J. P. Stark, and V. L. Moruzzi, Phys. Rev. B **44**, 5411 (1991).

[10] M. Asta, R. McCormack, and D. de Fontaine, Phys. Rev. B **48**, 748 (1993).

[11] G. D. Garbulsky and G. Ceder, Phys. Rev. B **49**, 6327 (1994).

[12] A. Silverman, A. Zunger, A. Kalish, and J. Adler, Phys. Rev. B **51**, 10795 (1995).

[13] G. Ceder, Comput. Mater. Sci. **1**, 144 (1993).

[14] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press, New York, 1963).

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

[16] J. W. D. Connolly and A. R. Williams, Phys. Rev. B **27**, 5169 (1983).

[17] H. Dreyssé, A. Berera, L. T. Wille, and D. de Fontaine, Phys. Rev. B **39**, 2442 (1989).

[18] D. B. Laks, L. G. Ferreira, S. Froyen, and A. Zunger, Phys. Rev. B **46**, 12587 (1992).

[19] G. D. Garbulsky and G. Ceder, Phys. Rev. B **51**, 67 (1995).

[20] G. Grimvall and J. Rosen, Int. J. Thermophys. **4**, 139 (1983).

[21] G. A. Alers, in *Physical Acoustics* (Academic Press, New York, 1965), Vol. III-B, p. 1.

[22] D. C. Wallace, *Thermodynamics of Crystals* (John Wiley & Sons, New York, 1972).

[23] V. L. Moruzzi, J. F. Janak, and K. Schwarz, Phys. Rev. B **37**, 790 (1988).

[24] T. Mohri, S. Takizawa, and K. Terakura, J. Phys. Condens. Matter **5**, 1473 (1993).

[25] C.-S. Oh, T. Mohri, and D. N. Lee, Mater. Trans. JIM **35**, 445 (1994).

[26] C. Colinet *et al.*, J. Phys. Condens. Matter **6**, L47 (1994).

[27] I. A. Abrikosov, A. V. Ruban, D. Ya Kats, and Y. H. Vekilov, J. Phys. Condens. Matter **5**, 1271 (1993).

[28] W.-T. Tseng and J. P. Stark, Philos. Mag. B **70**, 919 (1994).

[29] K. Nakamura and T. Mohri, Model. Simul. Mater. Sci. Eng. **1**, 143 (1993).

[30] T. Mohri, Prog. Theor. Phys. Suppl. **115**, 147 (1994).

[31] J. D. Becker and J. M. Sanchez, Mater. Sci. Eng. A A **170**, 161 (1993).

[32] R. LeSar, R. Najafadabi, and D. J. Srolovitz, Phys. Rev. Lett. **63**, 624 (1989).

[33] A. P. Sutton, Philos. Mag. A **60**, 147 (1989).

[34] L. Zhao, R. Najafabadi, and D. J. Srolovitz, Model. Simul. Mater. Sci. Eng. **1**, 539 (1993).

[35] H. Y. Wang, R. Najafabadi, D. J. Srolovitz, and R. Lesar, Interface Sci. **1**, 7 (1993).

[36] R. Najafabadi and D. J. Srolovitz, Surf. Sci. **286**, 104 (1993).

[37] D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).

[38] M. L. Klein and J. A. Venables, *Rare Gas Solids* (Academic Press, London, 1976).

[39] R. Magri, S. H. Wei, and A. Zunger, Phys. Rev. B **42**, 11388 (1990).

[40] L. G. Ferreira, A. A. Mbaye, and A. Zunger, Phys. Rev. B **37**, 10547 (1988).

[41] G. Ceder, G. D. Garbulsky, and P. D. Tepesch, Phys. Rev. B **51**, 11257 (1995).

[42] K. M. Ho, C. L. Fu, and B. N. Harmon, Phys. Rev. B **28**, 6687 (1983).

[43] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).

[44] S. de Gironcoli, Phys. Rev. B **51**, 6773 (1995).

[45] M. C. Payne *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).

[46] S. de Gironcoli, Phys. Rev. B **46**, 2412 (1992).

[47] S. Wei and M. Y. Chou, Phys. Rev. Lett. **69**, 2799 (1992).

[48] S. Wei, C. Li, and M. Y. Chou, Phys. Rev. B **50**, 14587 (1994).

[49] S. Wei and M. Y. Chou, Phys. Rev. B **50**, 221 (1994).