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Effect of lattice vibrations on the ordering tendencies in substitutional binary alloys

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The effect of lattice vibrations on the ordering tendencies and phase stability of substitutional binary alloys is analyzed. The alloy Hamiltonian is cast onto an Ising-like Hamiltonian through a cluster expansion of the vibrational free energy computed in the harmonic approximation. The temperature dependence of the vibrational effective cluster interactions (VECI's) is found for a general d-dimensional alloy. Analytic results for the VECI's for $d=1$ are derived. It is argued that the vibrations can have pronounced effects on the phase diagram and on the short-range order at high temperatures.

The effect of the lattice vibrations on the phase stability of binary substitutional alloys can be drastic. Recent studies support this statement with both experimental and theoretical results. Anthony, Okamoto, and Fultz[1] measured the vibrational entropy of ordered and disordered Ni_3Al and showed that its contribution to the phase stability is comparable in magnitude to that of the configurational entropy. Theoretical computations of phase diagrams that include crude approximations to account for the lattice vibrations,[2–6] show that the predicted phase stability can be changed significantly when the vibrations are brought into the model, improving the agreement with experiment. In this paper, we develop the formalism to include the vibrations into the first-principle models to predict phase stability in substitutional alloys.

The energetics of the alloy can be modeled with an Ising-like Hamiltonian that results from mapping the alloy Hamiltonian onto a lattice model using a cluster-expansion technique.[7] In these lattice models, the occupancy of site n is labeled by a spinlike variable σ_n [$\sigma_n=+1$ (-1) when an A (B) atom is on site n]. The configuration (or substitutional state) of an N-site alloy is described by an N-dimensional vector $\{\sigma\}$ of 1's and -1's. The alloy Hamiltonian is

$$E(\{\sigma\})=\sum_{\alpha} V_\alpha \sigma_\alpha(\{\sigma\}) , \tag{1}$$

where the sum is over all clusters α of lattice points. The cluster function σ_α is the product of all the spin variables on cluster α and V_α is the effective cluster interaction (ECI). The free energy of this Hamiltonian can be computed with techniques like the cluster variation method[8] or Monte Carlo sampling[9] and the results can then be used to construct the phase diagram of the alloy system.

Values for the ECI's of a given system can be obtained by projecting the ground-state energy onto the cluster functions,[10,11] or by perturbing the local composition of a suitable chosen disordered reference medium.[12] In either case, the effective interactions only contain zero-temperature chemical information and no effect of vibrations or electronic excitations. However, different alloy configurations have different vibrational spectra and vibrational free energies. Therefore, lattice vibrations can influence the stability of ordered phases. The variation of the interactions caused by thermal expansion and electronic excitations will not be considered.

The behavior of a model alloy system that has both substitutional and vibrational degrees of freedom is characterized by two different time scales. The lattice vibrations take place in time scales of the order of 10^{-13} sec, while substitutional interchanges occur in time scales that are several orders of magnitude longer. If we assume the vibrational degrees of freedom are ergodic over the time scale of substitutional excitations, the alloy partition function can be coarse grained by integrating, for each substitutional configuration, over all vibrational states.[13] Since the only significant degrees of freedom left after this coarse graining are substitutional, the total free energy can be obtained in the phase space of a lattice model. The Hamiltonian of this lattice model includes the ground-state energy and vibrational free energy of a fixed atomic configuration $\{\sigma\}$. In analogy with (1), this temperature-dependent Hamiltonian can be expanded in cluster functions to get

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

Although the expansion coefficients $V_\alpha(T)$ contain both chemical (ground-state) and vibrational effects, we will still use the term "effective cluster interaction" (ECI) to refer to them. The purely vibrational part of this interaction will be referred to as VECI (vibrational effective cluster interaction). Similar to the definition of the purely chemical ECI,[7] the nearest-neighbor VECI is defined as

$$\begin{aligned} V_{2,1} &= \tfrac{1}{4}(\langle F_{AA}^{\text{vib}}\rangle+\langle F_{BB}^{\text{vib}}\rangle-\langle F_{AB}^{\text{vib}}\rangle-\langle F_{BA}^{\text{vib}}\rangle) \\ &\equiv \Delta_{2,1}F^{\text{vib}} , \end{aligned} \tag{3}$$

where $\langle F_{MN}^{\text{vib}}\rangle$ is the average vibrational free energy of all configurations that have M- and N-type atoms at the sites of the pair cluster considered. The operator $\Delta_{2,1}$ is defined in (3) for convenience.

The low- and high-temperature limits of the vibrational free energy in the harmonic approximation for a given configuration of the binary alloy are given by[14]

$$\text{low } T \rightarrow F^{\text{vib}}(T) = \frac{\mu_1}{2} - \sum_{n=0,1,\ldots} \zeta(n+1) g_n T^{n+2} ,$$

$$\text{high } T \rightarrow F^{\text{vib}}(T) = -T \ln T + \mu_0 T + \frac{\mu_2}{24} T^{-1} - \frac{\mu_4}{2880} T^{-3} + \cdots , \tag{4}$$

where μ_n is the nth moment of the vibrational density of states (VDOS), with μ_0 defined as the logarithmic average of the frequencies, ζ is the Riemann zeta function,[15] and g_n is the nth derivative of the VDOS at the origin. The Boltzmann and Planck constants have been set to 1. In (4), only g_n and μ_n depend on the configuration of the alloy. Therefore, the leading high-temperature term, $-T \ln T$, does not contribute to the VECI.

After expressing the moments of the VDOS in terms of the dynamical matrix[16] and using (3) to get the VECI's, the final result is

$$\text{low } T \rightarrow V_{2,1}(T) = \frac{1}{2} \Delta_{2,1} \text{Tr} D^{1/2} - \sum_{n=0,1,\ldots} \zeta(n+1) \Delta_{2,1} g_n T^{n+2} ,$$

$$\text{high } T \rightarrow V_{2,1}(T) = \frac{T}{2} \Delta_{2,1} \ln \det D + \frac{1}{24T} \Delta_{2,1} \text{Tr} D - \frac{1}{2880 T^3} \Delta_{2,1} \text{Tr} D^2 + \cdots , \tag{5}$$

where D is the dynamical matrix.[14] These results can be easily generalized for any VECI (V_α) replacing the operator $\Delta_{2,1}$ by conveniently defined Δ_α's.[7] Expressions (5) are completely general for harmonic alloys, accounting even for relaxation of the atoms away from the ideal lattice sites (which have been recently proven to be important in the determination of phase stability; see, for example, Ref. 17).

We can already derive some conclusions. At $T=0$, the VECI's are determined by the zero-point vibration. The first power of T in the low-temperature limit is $d+1$ where d is the dimensionality of the system (because for $n<d-1$, g_n vanishes). At high temperature, the VECI's are linear in T, with the first correction being of the order of $1/T$. This fact will have important consequences for the transition temperatures of ordered alloys, and the short-range order at high T (see below).

If the force constants are known for a three-dimensional alloy on an arbitrary lattice, the terms in Eq. (5) can be computed numerically. We will now show that analytic results can be obtained for a simplified one-dimensional model. Although these results might not be quantitatively correct for higher-dimensional systems, they may still give insight into how the vibrations influence the configurational disorder.

Consider a one-dimensional alloy of A and B atoms of masses M_A and M_B. Each nearest-neighbor pair is connected with an ideal spring of constant γ_{AA}, γ_{BB}, or γ_{AB} depending on the occupation of the pair. The dynamical matrix is symmetric tridiagonal with elements

$$D_{ii} = (\gamma_{i-1,i} + \gamma_{i,i+1}) / M_i$$

and

$$D_{i,i+1} = -\gamma_{i,i+1} \sqrt{M_i M_{i+1}} .$$

To test the analytic results we obtained, we performed numerical calculations of the VECI's on chains of 10 000–50 000 atoms, averaging over 150 configurations.

The high-temperature form of the VECI's can be solved exactly, using (5) and the dynamical matrix for the linear chain defined above. After lengthy algebra, the final result for the nearest-neighbor VECI is

$$\text{high } T \rightarrow V_{2,1}(T) = \frac{1}{8} \ln \left[\frac{\gamma_{AA} \gamma_{BB}}{\gamma_{AB}{}^2} \right] T + \frac{1}{48} \left[\frac{\gamma_{AA}}{M_A} + \frac{\gamma_{BB}}{M_B} - \gamma_{AB} \left[\frac{1}{M_A} + \frac{1}{M_B} \right] \right] \frac{1}{T} - \frac{1}{5760} \left[3 \left[\frac{\gamma_{AA}}{M_A} \right]^2 + 3 \left[\frac{\gamma_{BB}}{M_B} \right]^2 - 2\gamma_{AB}{}^2 \left[\frac{1}{M_A{}^2} + \frac{1}{M_B{}^2} + \frac{1}{M_B M_A} \right] \right] \frac{1}{T^3} + \cdots . \tag{6}$$

The first term in the rhs of (6) was already obtained by Bakker[18] and Matthew *et al.*[19] The numerical results we obtained agree with (6) within numerical precision. Similar derivations show that all the other VECI's vanish in the infinite-temperature limit. As a consequence, the cluster expansion is convergent at high temperatures.

The low-temperature coefficients cannot be solved exactly but a good approximation can be obtained by analyzing the elastic limit. We replace the binary chain by a monatomic one with the same elastic properties. The values of μ_1 and g_n can then be expressed in terms of the lattice-averaged cluster functions on the point cluster ($\langle \sigma_1 \rangle$) and the nearest-neighbor cluster ($\langle \sigma_{2,1} \rangle$). After linearizing μ_1 and g_n around the chain with random occupation ($\langle \sigma_1 \rangle = 0$, $\langle \sigma_{2,1} \rangle = 0$) we obtain

$$\text{low } T \rightarrow V_{2,1}(T) = -\frac{2}{\pi} \frac{\alpha_-}{\alpha_+^{3/2}} \frac{1}{\sqrt{M}} - \frac{\zeta(0)}{4\pi} \frac{\alpha_-}{\alpha_+^{1/2}} \sqrt{M} T^2 - \frac{3\zeta(2)}{64\pi} \alpha_- \alpha_+^{1/2} M^{3/2} T^4 + \cdots , \tag{7}$$

where

$$\alpha_\pm = \frac{1}{\gamma_{AA}} + \frac{1}{\gamma_{BB}} \pm \frac{1}{\gamma_{AB}} , \quad M = (M_A + M_B)/2 ,$$

$$\zeta(0) = 1.645 , \quad \zeta(2) = 1.082 .$$

To test the two approximations made to obtain the low-temperature result (7), i.e., the elastic limit and the linearization, we computed $V_{2,1}(T=0)$ numerically for 137 different sets of the parameters of the system (M_A, M_B, γ_{AA}, γ_{BB}, γ_{AB}). In Fig. 1 the numerical results are compared with those in (7). Reasonable agreement is obtained. Formula (7) fails to predict the ordering tendencies at low T of isotopic disordered chains, i.e., those chains for which all the spring constants are equal.

To estimate the temperature range for which Eq. (6) and (7) are valid, we computed $V_{2,1}(T)$ numerically for a linear chain with $\gamma_{AA}=1$, $\gamma_{BB}=3$, $\gamma_{AB}=1.2$, $M_A=1$, $M_B=1.5$. Figure 2 shows the results. The Debye temperatures for pure A, pure B, and ordered AB structures are shown in the temperature axis. The slight difference in the slope at high T is due to numerical errors, while the differences at low T are due to approximations introduced to derive (7). It can be seen that two terms in the high-T limit and two terms in the low-T limit suffice to represent the temperature dependence of the VECI at all temperatures.

Most of the important features of alloy phase diagrams occur at temperatures that are generally of the order or larger than the Debye temperatures of the system. From Fig. 2 we then expect that the first term in the high-T expansion will dominate the VECI's. The value of the VECI for this example is a sizable fraction of the temperature (recall $k_B=1$), and therefore will significantly effect the phase diagram.

The leading term of the VECI at high T is independent of the masses of the atoms for the linear chain [see (6)]. This is also a well-known result for an alloy in any dimensions. From the leading term in (6), we see that if the spring constant between the A and B atoms is smaller than the *geometrical average* of the spring constants between like atoms, the vibrations will induce ordering in the alloy, while phase separation will be favored otherwise. On the other hand, an arithmetic average for γ_{AB} would induce ordering. The importance of the results obtained can be illustrated by considering two examples: the change in the predicted transition temperatures for ordering and phase-separating systems and the limit of the short-range order (SRO) parameter at infinite temperature.

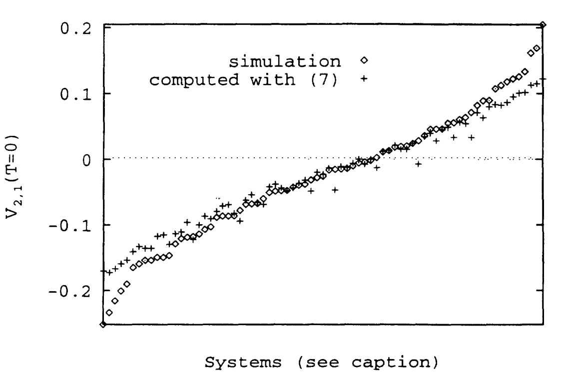

FIG. 1. Comparison of the zero-temperature VECI computed with Eq. (7) and numerical results. The 137 different systems scan the sets of parameters $0.3<\gamma_{BB}, \gamma_{AB}<3$, and $1<M_B<3$, while keeping $\gamma_{AA}=1$ and $M_A=1$. The systems are ordered in the horizontal axis in increasing value of $V_{2,1}$ as obtained numerically. It can be seen that Eq. (7) underestimates the absolute value of the VECI for large VECI's.

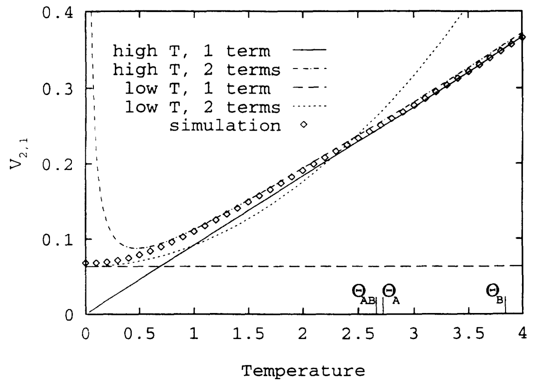

FIG. 2. Nearest-neighbor VECI as a function of temperature for a linear chain with $\gamma_{AA}=1$, $\gamma_{BB}=3$, $\gamma_{AB}=1.2$, $M_A=1$, $M_B=1.5$. Debye temperatures for different configurations are also indicated.

Consider the phase stability of substitutional binary alloys on the fcc and bcc lattices with nearest-neighbor ECI's and nearest-neighbor central force constants. If the transition temperatures are higher than the Debye temperatures of the system, only the first term in the high-temperature VECI needs to be kept. Then, the total nearest-neighbor effective pair interaction becomes $V_{2,1}=V_C+TV_V$, where V_C is the chemical ECI and $V_V=\frac{1}{2}\Delta_{2,1}\ln\det D$. From numerical experiments, we have found that for 3D lattices a good estimate for

$$V_V \text{ is } \frac{3}{8}\ln(\gamma_{AA}\gamma_{BB}/\gamma_{AB}^2)$$

(this result is exact in simple cubic lattices with nearest-neighbor central force constants[20]). Table I summarizes the transition temperatures for fcc and bcc alloys with composition $\frac{1}{2}$ as a function of the VECI (generalization to arbitrary composition is straightforward). We can see that a relatively small force constant disorder will have a pronounced effect on the transition temperatures. Due to the high transition temperature for phase separating fcc alloys, the result of vibrations will be noticed best in these systems: for alloys where $\gamma_{AA}\gamma_{BB}/\gamma_{AB}^2=1.3$ (which is a reasonable value), vibrations lower the transition temperature by a factor 2 from the value one would get neglect-

TABLE I. Transition temperatures for equiatomic alloys on the fcc and bcc lattices with nearest-neighbor chemical (V_C) and vibrational (TV_V) effective cluster interactions. $V_{2,1}=V_C+TV_V$ is the total nearest-neighbor effective cluster interaction.

Lattice	Segregation ($V_{2,1}<0$)	Ordering ($V_{2,1}>0$)
fcc	$\frac{T_C}{\lvert V_C\rvert}\cong\frac{9.8}{1+9.8V_V}$	$\frac{T_C}{V_C}\cong\frac{1.7}{1-1.7V_V}$
bcc	$\frac{T_C}{\lvert V_C\rvert}\cong\frac{6.5}{1+6.5V_V}$	$\frac{T_C}{V_C}\cong\frac{6.5}{1-6.5V_V}$

ing the vibrations. The frustrated geometry of the fcc lattice will make the effect less pronounced for ordering systems. For the bcc lattice, the magnitude of the effect is the same for ordering and segregating alloys. In lattice dynamic studies of binary alloys, it is sometimes assumed that $\gamma_{AB}=\sqrt{\gamma_{AA}\gamma_{BB}}$ when better estimates are not available. We can see from our results that this is a risky assumption when studying phase stability, because a small deviation in the value of γ_{AB} induces a big change in the predicted phase diagram.

Another manifestation of the temperature dependence of the ECI's will show up in the average atomic configuration at infinite temperature. It is generally assumed that in this limit the Warren-Cowley SRO parameter (α) vanishes, based on the fact that the completely disordered state has the highest *configurational* entropy. This is valid only when the ECI's approach a constant value at high T. From the derivation above, we see that if the lattice vibrations are considered, the *vibrational* entropy introduces a linear T dependence in the ECI's at high T. It can be easily shown that, in that case, α will approach a finite nonzero value when $T \rightarrow \infty$. This value can be predicted if the leading high-temperature term of the VECI's is known [see (5)]. This possible behavior of the SRO was already pointed out by Miller[21] and some experimental evidence to support it is available for Ni-Fe and Ni-Cu alloys.[22,23]

To summarize, the contribution of the lattice vibrations to the free energy can be included in the calculation of phase diagrams using the formalism developed in this paper. By integrating out the vibrational degrees of freedom, we obtain an Ising-like Hamiltonian with temperature-dependent effective interactions. When the dynamical matrix as a function of the alloy substitutional state $\{\sigma\}$ is known, (5) provides the general procedure to get the temperature-dependent vibrational ECI's that have to be added to the chemical ECI's to compute phase diagrams. For temperatures larger than the Debye temperatures of the system, the vibrational ECI's become linear in temperature. For a one-dimensional alloy with nearest-neighbor spring constants, analytic expressions have been obtained for the high- [see (6)] and low- [see (7)] temperature forms of the vibrational ECI on the nearest-neighbor pair. For this simplified model, the cluster expansion of the vibrational free energy is rapidly convergent at high temperatures. The vibrational contributions to the ordering tendencies should be included in future phase diagram computations, as their effect could be comparable to that of chemical effective interactions.

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