Effective-pair interactions in transition-metal alloys: A supercell total-energy approach

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A new method is described for obtaining effective pair interactions (EPI) in transition-metal alloys from density-functional-theory total-energy calculations for supercell compounds. The calculated total energies are used to obtain explicit concentration-*independent* cluster interactions, through an inversion scheme [J. W. D. Connolly and A. R. Williams, Phys. Rev. B **27**, 5168 (1983)]. Using a truncated form for the higher-order interatomic correlation functions, the cluster interactions are resummed into concentration-*dependent* EPI. The EPI are interpreted within the established perturbation-theoretic framework. The method offers a treatment of electron-electron interactions that is more accurate than in existing perturbative methods, although the long-ranged oscillations in the EPI are much more difficult to obtain. Furthermore, the method can be used with density-functional calculations which supersede the muffin-tin approximation, and can generate a variety of types of EPI depending upon the particular truncation scheme employed. Results are presented for the Ni-Al and Nb-Y systems. In Ni-Al the EPI is strongly concentration dependent, with the ordering tendency much stronger at the Ni-rich end. The elastic strain energy contributes significantly to the ordering energy. In Nb-Y the EPI favors phase separation most strongly at the Nb-rich end of the phase diagram.

I. INTRODUCTION

A great deal of progress has been made over the past two decades in understanding the energetics of bulk and defective transition metals, largely because the advent of density-functional theory as a method for treating electron-electron interactions. However, existing theoretical techniques are still not capable of calculating transition-metal-alloy phase diagrams from first principles, except in very few cases. These phase diagrams involve complicated atomic configurations which necessitate the use of simplifying concepts such as effective interatomic potentials, instead of fully quantum-mechanical descriptions of the total energy. Existing methods for obtaining such potentials nonempirically are not yet sufficiently advanced to quantitatively treat incoherent phase diagrams. However, for coherent phase diagrams the simplification resulting from the periodicity of the underlying lattice allows one to define effective pair interactions (EPI), which describe only substitutional rearrangements on this fixed lattice, at a fixed concentration. The EPI are most straightforwardly obtained for cases in which the scattering potential (the difference between the effective one-electron potentials associated with the constituent atoms) is weak. They can, however, be obtained[1-4] even for systems with strong scattering potentials through the use of the "generalized perturbation theory" (GPT). In this method a completely random medium described by the coherent-potential approximation (CPA) is used as a starting point and concentration-dependent EPI are obtained by expansion of the total energy in powers of the various short-range-order parameters. The GPT was originally developed within the tight-binding approximation but was subsequently extended to include systems describable by

one-electron potentials of the muffin-tin form, using the Korringa-Kohn-Rostoker (KKR)-CPA formalism.[4] It is also possible to build on the KKR-CPA by treating concentration fluctuations to higher order[5] or by calculating energies associated with specific clusters[6] embedded in an effective medium defined by the KKR-CPA. To date, implementations of the CPA-based methods include only changes in the one-electron energy sum in the EPI, although the CPA treatment of the completely random medium includes electron-electron interactions in an averaged way. While the one-electron effects are undoubtedly the dominant contribution to the long-ranged oscillations in the EPI, the electron-electron terms can be important at small separations; for alloys with sufficiently weak EPI, the inclusion of these terms could actually change the sign of the EPI.

On the other hand, it has recently been shown[7] that by matching to the results of self-consistent supercell total-energy band calculations one can obtain physically reasonable cluster interactions which are concentration independent, except for the indirect concentration dependence mediated by lattice-constant changes. The price paid for the concentration independence of the interactions is that three-atom and higher-order terms must be included to obtain a reasonable description of the phase diagram. In this paper we establish an explicit connection between the concentration-*independent* cluster interactions and the concentration-*dependent* EPI, and use it to derive a new method for obtaining EPI. The connection is simply that the EPI are obtained by resumming the higher-order cluster interactions at fixed concentration, assuming a decoupled form for the higher-order interatomic correlation functions; this form corresponds to a lowest-order expansion of the total energy in powers of the short-range parameters. In fact, if sufficiently long-ranged cluster in-

teractions are taken into account, the interactions obtained by the resummation procedure are exactly the GPT EPI plus additional terms resulting from electron-electron interactions and higher-order terms not included in the GPT treatment of the random alloy response functions. It is thus possible to obtain accurate EPI's from cluster interactions, which are in turn obtained from ordered supercell total-energy calculations. The main strengths of the method are discussed in Secs. I A–I F.

A. Improved treatment of electron-electron interactions

Since the electron-electron interactions are treated fully self-consistently in the supercell calculations their effects on the EPI are included (within the particular approximation for exchange and correlation effects used in these calculations), in the sense that an atomic species is allowed to have several different charge states with relative weights determined by the local environment, which in turn depends on the short-range order. Even if one assumes that the Madelung energy in the completely random system is small, the Coulomb contribution to the EPI contains the *derivative* of the Madelung energy with respect to the short-range-order parameters and can thus be appreciable. This effect has been included in tight-binding-model calculations[8] but not in more sophisticated treatments of EPI. While a disordered metallic alloy environment undoubtedly contains a continuum of charge states for each atom, the discrete approximation corresponding to the use of a finite number of supercell total energies is an improvement over the use of only a single, short-range order-independent, average charge state.

B. Ability to supersede the muffin-tin approximation

The only inputs for the method are the supercell total-energy calculations, which can be performed with any band-theoretical formalism. The full-potential linear augmented-plane-wave and pseudopotential methods provide results superior to muffin-tin results many cases, such as highly anisotropy systems and open structures; at present, no way is known of implementing the GPT within these methods. This feature will be particularly useful in studies of surfaces and layered structures.

C. Inclusion of additional terms in perturbation expansion

As will be discussed in Sec. II, the method described here includes the EPI a large number of terms which appear in higher order in the GPT expansion.

D. Flexible treatment of local lattice strain effects

In the supercell calculations the atoms can be allowed to relax in such a way as to minimize the total energy. While the relaxation effects are small in closely packed alloys, they are larger in open crystal structures. Furthermore, this way of treating atomic relaxation effects may provide useful insight into systems not directly modeled by the calculations, such as liquid alloys.

· E. Flexible treatment of higher-order interatomic correlation functions

By the simple expedient of using a variety of truncation procedures to obtain the approximate higher-order correlation functions used in resumming the cluster potentials, one can obtain a variety of potentials applicable to different types of problems. For example, the high-temperature expansion used in the present calculations could be replaced by a product form, which would presumably give more accurate results at temperatures where the high-temperature approximation breaks down.

F. Conceptual simplicity

Since one only performs ordered supercell total-energy calculations, there is no need for an elaborate treatment of disorder effects. The use of calculations for periodic systems to model disordered systems is best justified for total-energy calculations, such as those described here, which average over the electronic density of states and are not sensitive to the spatial behavior of particular wave functions. If one were interested in Fermi surface properties such as conductivity, one would expect poorer convergence since periodic calculations contain no mechanism for broadening the Fermi surface.

The price paid for these strengths is, of course, that one must use very large supercells to obtain the large separation behavior of the EPI. This is a serious problem; in the fcc structure, a four-atom supercell yields only the nearest-neighbor EPI, while an eight-atom supercell includes third neighbors. Since the computing time increases faster than the square of the size of the unit cell, increasing the range of the calculated EPI by a small amount can be very costly in computer time. However, because of the growing availability of supercomputer time, the treatment of large supercells is becoming a less onerous task. In fact, the speed of these computers means that a premium is placed on conceptual simplicity rather than minimization of CPU time. The present method is in sense complementary to the GPT: the short-range behavior of the EPI, which is sensitive to the electron-electron terms, is obtained more accurately by the supercell method, while the long-ranged behavior is obtained more accurately by the GPT.

The organization of the remainder of the paper is as follows. Section II describes the method in detail and demonstrates the connection between the potentials obtained here and those obtained by the GPT. Section III presents results for the Al-Ni and Nb-Y systems obtained using four-atom supercells, including several treatments of relaxation effects. Section IV concludes by drawing parallels between the problem discussed here, and that of obtaining effective pair potentials for describing the geometric degrees of freedom in elemental metals.

II. METHOD OF CALCULATION

A. Derivation of EPI

The task of obtaining concentration-dependent EPI from supercell total energy calculations splits naturally

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into two parts: obtaining cluster potentials from the total-energy calculations, and resumming the cluster potentials into EPI.

1. Matching cluster potentials to total energy calculations

While this procedure has been described previously,[7] we summarize it here for clarity of presentation. The basic assumption is that the total energy of an A-B alloy, at a fixed lattice constant, may be described in terms of a fairly rapidly convergent series of concentration-*independent* cluster potentials. More precisely, we assume[9] that for any configuration of A and B atoms the total energy of the crystal is given by

$$E = \sum_{n=0}^{\infty} \sum_{C_n} V_{C_n} \xi_{C_n} .$$ (1)

Here n is the order of a cluster, and C_n is a particular cluster of order n. (The various orderings of the atoms in a cluster are not counted as new clusters.) The $n=0$ term in (1) corresponds to the part of the total energy that is independent of concentration and order. V_{C_n} is the concentration-independent potential associated with the cluster C_n and

$$\xi_{C_n} = \langle \sigma_{p_1} \times \sigma_{p_2} \times \cdots \times \sigma_{p_n} \rangle$$ (2)

is a cluster correlation function which couples to V_{C_n}. Here the p_i are sites in the cluster. The σ_{p_i} are spinlike variables associated with these sites which take on the values ± 1 according to whether the site is an A or B atom; the average value of σ_{p_i}, for example, is a measure of the concentration. The brackets in (2) denote configuration averaging.

Given (1), one can obtain the V_{C_n} from a finite number M of total energies for supercells provided one retains only M types of clusters, and assumes that the remaining cluster potentials vanish. Two clusters are considered to belong to the same type if they are related by the translational or point-group symmetry of the underlying crystal. Clusters of the same type must then obviously have the same associated cluster potentials. In Ref. 7, for example, $M=5$ was used for a fcc underlying lattice; the cluster types retained beyond the $n=0$ term in (1) were a single atom, a nearest-neighbor pair, a nearest-neighbor triangle, and a nearest-neighbor tetrahedron. The structures used in the supercell calculations were the pure A and B solids, the AB compound in the CuAu structure, and A_3B and AB_3 compounds in the Cu$_3$Au structure. The V_{C_n} are obtained as explicit linear functionals of the five supercell total energies E_m ($1 \leq m \leq M$):

$$V_{C_n} = \sum_{m=1}^{M} (\xi^{-1})_{C_n,m} E_m ,$$ (3)

with the coefficients for $M=5$ given in Ref. 7.

2. Resummation of cluster potentials into concentration-dependent EPI

While the analysis of Ref. 7 showed that valuable physical insight can be gained from the V_{C_n} themselves, it is

useful for several reasons to transform them into EPI.

(i) Ease of interpretability. The EPI are directly connected to the degree and form of order in the alloy at a particular concentration, via, for example, approximate relations[10] of the Clapp-Moss type.

(ii) Practical usefulness. The EPI are the first term in an expansion of the ordering energy which is much more rapidly convergent than the expansion based on concentration-independent potentials. For example, the convergence analysis of Ref. 3 demonstrated that even rapid oscillations in the concentration dependence of the ordering energy are obtained to an accuracy of 10–20 % by the EPI; the convergence is much slower if only concentration-independent interactions are included. The present analysis can easily be generalized to obtain higher-order concentration-dependent cluster potentials as well; we have not calculated these in the present analysis because we have access only to fairly low-order concentration-independent cluster potentials. Since the inclusion of high-order cluster potentials can lead to considerable numerical difficulties in phase diagram calculations, the improved convergence obtained by concentration dependent effective interactions is a substantial advantage.

(iii) Comparison with other approaches. EPI have by now become a standard language for describing ordering energies in alloys, and it is therefore useful to translate results for ordering properties into this language.

There is, of course, some loss of accuracy when one translates the cluster potentials into EPI; however the results to be described later will show that most of the effects of the higher-order cluster potentials are well accounted for by the concentration dependence of the EPI.

The central step in obtaining the EPI is to approximate the higher-order correlation functions ξ_{C_n}, with $n > 2$, by truncated forms including only the pair correlation function. We choose the decoupled form

$$\begin{aligned} \xi_{C_n} &= \langle \sigma_{p_1} \times \cdots \times \sigma_{p_n} \rangle \\ &= \langle \sigma_{p_1} \sigma_{p_2} \rangle \langle \sigma \rangle^{n-2} + \langle \sigma_{p_1} \sigma_{p_3} \rangle \langle \sigma \rangle^{n-1} \\ &\quad + \cdots + \langle \sigma_{p_{n-1}} \sigma_{p_n} \rangle \langle \sigma \rangle^{n-2} - [n(n-1)-1]\langle \sigma \rangle^n . \end{aligned}$$ (4)

(The $\langle \sigma_{p_i} \rangle$ are independent of p_i, by the average translational symmetry of the alloy.) This form is readily obtained by expansion of ξ_{C_n} to second order in the concentration fluctuations $\Delta\sigma_{p_i} = \sigma_{p_i} - \langle \sigma \rangle$, and thus assumes that

$$\langle (\sigma_{p_1} - \langle \sigma \rangle) \times \cdots \times (\sigma_{p_n} - \langle \sigma \rangle) \rangle = 0, \quad n \geq 3$$ (5)

if none of the p_i are equal. It will be shown below that this particular method of truncation results in a type of EPI similar to that obtained by the GPT.

From (1), (2), and (4) it follows that in the approximation employed, E is a function only of $\langle \sigma \rangle$ and the pair probabilities $\langle \sigma_{p_i} \sigma_{p_j} \rangle$. For any two sites p_1 and p_2 we can thus define a fixed-concentration EPI

$$\phi_{p_1,p_2} = 4 \frac{\partial E}{\partial \langle \sigma_{p_1}\sigma_{p_2} \rangle} \ . \tag{6}$$

The normalization of ϕ_{p_1,p_2} is consistent with that in Ref. 1, which is such that in a model completely described by pair potentials,

$$\phi_{p_1,p_2} = (V^{AA} + V^{BB} - 2V^{AB}) \ . $$

Here V^{AA}, V^{BB}, and V^{AB} are pair potentials evaluated at the separation between the sites p_1 and p_2. Thus positive and negative values of ϕ correspond to ordering and clustering behavior, respectively.

From (1), (2), (4), and (6) we obtain the desired result

$$\phi_{p_1,p_2} = 4 \sum_{n=2}^{N_{\max}} {\sum_{C_n}}' V_{C_n} \langle \sigma \rangle^{n-2} \ . \tag{7}$$

Here $N_{\max}$ is highest cluster order included and the primed sum is restricted to clusters which contain both the sites p_1 and p_2.

Since $\langle \sigma \rangle$ is linear in the alloy concentration c we see that ϕ_{p_1,p_2} is given as a polynomial of order $(N_{\max} - 2)$ in c. Thus to obtain EPI that are rapidly varying as functions of the concentration, it is necessary to include clusters of very high orders.

B. Perturbation theoretic analysis

We now demonstrate that the method described results above in a type of EPI similar to that obtained by the GPT, provided that sufficiently high-order clusters are taking into account. In the GPT one starts with a period-

ic reference medium obtained by application of the CPA to the configuration-averaged one-electron Green's function of a completely random system. We will denote the CPA Green's function operator by $\mathbb{G}^{CPA}$. To obtain corrections due to short-range order and fluctuations, one considers[1] the scattering relative to the CPA effective medium:

$$E^{\mathrm{ord}} = -2\frac{\mathrm{Im}}{\pi} \int^{\epsilon_F} \mathrm{Tr}\langle \ln(1 - \hat{t}\mathbb{G}_{nd}^{CPA}) \rangle dE \ . \tag{8}$$

Here E^{ord} is the configuration-dependent part of the one-electron energy, $\hat{t} = \sum_i t_i$, where t_i is the scattering operator associated with the atom at site i relative to the CPA reference medium, and $\mathbb{G}_{nd}^{CPA}$ contains only the intersite contributions to $\mathbb{G}^{CPA}$. The site scattering operator can be written in the form

$$t_i = \frac{(1+\sigma_i)}{2}t_i^A + \frac{(1-\sigma_i)}{2}t_i^B \ , \tag{9}$$

where $t_i^{A(B)}$ is the scattering operator associated with an $A(B)$ atom on site i. Since the CPA effective medium is defined by

$$\langle t_i \rangle = \frac{1 + \langle \sigma_i \rangle}{2}t_i^A + \frac{(1 - \langle \sigma_i \rangle)}{2}t_i^B = 0 \ , \tag{10}$$

we have

$$t_i = (\sigma_i - \langle \sigma_i \rangle)(t_i^A - t_i^B) = (\sigma_i - \langle \sigma_i \rangle)\Delta t_i \ ,$$

defining Δt_i. Thus, expanding (8) in powers of $\hat{t}$, one obtains

$$E^{\mathrm{ord}} = -2\frac{\mathrm{Im}}{\pi} \int^{\epsilon_F} dE \sum_{n=2}^{\infty} \frac{(-1)^n}{n} \sum_{p_1 \neq p_2 \neq p_3 \cdots} \langle (\sigma_{p_1} - \langle \sigma \rangle) \times \cdots \times (\sigma_{p_n} - \langle \sigma \rangle) \rangle \mathrm{Tr}(\Delta t_{p_1} \mathbb{G}_{p_1 p_2}^{CPA} \Delta t_{p_2} \cdots \Delta t_{p_n} \mathbb{G}_{p_n p_1}^{CPA}) \ . \tag{11}$$

EPI can be obtained from Eq. (11) in two ways. The simplest way is to truncate the series at $n=2$, in which case E^{ord} is manifestly given entirely in terms of pair contributions. This is the method that has been most commonly used in physical applications. By (10), this approximation would provide exact results for a hypothetical system which satisfies Eq. (5), for all possible $(p_1, \ldots, p_n)$, including even those consisting entirely of repetitions of two sites. A more accurate type of EPI is obtained if one retains all terms in (11) containing only two sites. Then (5) is assumed to hold only for $(p_1, \ldots, p_n)$ containing three or more sites, while the higher-order correlation functions involving only two sites are treated exactly. However, neither of these approximations is physically realizable, since, for example, no term involving only squares of the $(\sigma_{p_i} - \langle \sigma \rangle)$ can vanish.

In the present approach, the energy is given entirely in terms of correlation functions involving only distinct sites. Thus (5) is assumed only for nonrepeating terms with $p_1, \ldots, p_n$ all distinct. Since

$$\sigma^n = 1 \quad n \text{ even} \ ,$$
$$\sigma^n = \sigma \quad n \text{ odd} \ , \tag{12}$$

the configuration averages of the remaining terms are already completely determined by the nonrepeating terms. For example, using (5) and (12) we obtain

$$\langle (\sigma_1 - \langle \sigma \rangle)(\sigma_2 - \langle \sigma \rangle)(\sigma_1 - \langle \sigma \rangle)(\sigma_3 - \langle \sigma \rangle) \rangle$$

$$= (1 - \langle \sigma \rangle^2)\langle (\sigma_2 - \langle \sigma \rangle)(\sigma_3 - \langle \sigma \rangle) \rangle - 2\langle \sigma \rangle \langle (\sigma_1 - \langle \sigma \rangle)(\sigma_2 - \langle \sigma \rangle)(\sigma_3 - \langle \sigma \rangle) \rangle$$

$$= (1 - \langle \sigma \rangle^2)\langle (\sigma_2 - \langle \sigma \rangle)(\sigma_3 - \langle \sigma \rangle) \rangle \ . \tag{13}$$

Furthermore, the approximations (4) and (5) are physically realizable in this case; it is straightforwardly shown that they correspond to the first term in a high-temperature expansion of the correlation functions, provided the Hamiltonian generating them contains only pair contributions. Thus the present approximation obtains exactly the ordering energy in this limit, provided sufficiently high-order clusters are included. The terms with repeated indices are therefore implicitly assigned the values which are rigorously determined by the values of the nonrepeating terms. It follows that the present approximation for the EPI includes in an approximate fashion many of the three-atom and higher-order terms in the GPT expansion.

III. RESULTS FOR SPECIFIC SYSTEMS

Before presenting our results, we briefly describe our treatment of lattice strain effects. We use the following distinct approaches.

(i) Complete neglect of lattice relaxations. All the supercell total energies E_m in (3) are calculated at a fixed lattice constant, which is taken to be independent of concentration. Thus from M total-energy calculations we obtain $\phi_{p_1p_2}$ for all c.

(ii) Inclusion of global relaxations. For each concentration the E_m are obtained at a fixed lattice constant. However, for each concentration a new lattice constant is used. The concentration-dependent lattice constant is obtained by linear interpolation between the A and B lattice constants calculated in the fcc structure. Here the assumption is that at a given concentration, the A and B atoms reside on a perfect undistorted lattice. The number of total-energy calculations required is $M \times$ (number of concentrations treated).

(iii) Inclusion of local relaxations. Here we artificially ignore the constraints on the cluster bond lengths imposed by the rest of the lattice. Each supercell total energy E_m is obtained at the lattice constant at which E_m is minimized. It is thus assumed that each cluster in the alloy is able to relax to its preferred lattice constant. This is not an accurate approximation for the closely packed alloys mentioned under (ii), but is likely to be a better approximation for liquid alloys. Furthermore, extended x-ray absorption fine structure data[11] show that in alloys having very open structures such as the zinc-blende structure, bond lengths can be closer to the constituent bond lengths than to the average alloy bond length.

In our calculations we use $M = 5$ and include only nearest-neighbor clusters of up to four atoms on a fcc lattice, with the cluster interactions obtained from A, A_3B, AB, AB_3, and B total-energy calculations as described in Ref. 7 (cf. Sec. II). $\phi_{p_1p_2}$ is then a quadratic function of c and is obtained only for p_1 and p_2 nearest neighbors. We thus drop the subscripts on ϕ. We feel that truncation of the cluster expansion at the $M = 5$ level is a reasonable approximation for systems (such as those under consideration here) in which the ordering energy is large in comparison with the expected contributions from Fermi surface effects, such as those seen[5] in Cu-Pd alloys. This belief is confirmed by comparison of the magnitudes of the

four-atom interaction V_4 and the pair interaction V_2 in the two systems to be studied here, as well as in our preliminary results for eight other Al transition-metal alloys. In these systems the average strength of V_4 relative to V_2 is 6–7 %. Although the relative contribution from V_4 to ϕ is enhanced by a combinatoric factor (this can be as large as 6 for concentrations close to zero or unity, but is only $\frac{3}{2}$ at 25% and 75% concentrations), this indicates a reasonable degree of convergence already at the four-atom supercell level. While the resulting potentials cannot quantitatively treat the competition between different ordered phases such as the Cu_3Au and Al_3Ti structures, they should provide a good description of the overall concentration dependence of the ordering tendency. This type of understanding is essential in a variety of metallurgical problems.

We now display results for an ordering alloy system and a clustering one. The total energies are calculated with the augmented-spherical-wave method[12] using a local exchange-correlation functional of the Hedin-Lundquist form.[13] Relativistic effects are neglected.

A. Ni-Al

We have neglected the magnetic effects associated with the Ni atoms for simplicity. This should lead to no significant errors since the energy associated with spin polarization is small (< 0.1 eV per atom) even in pure Ni, and the spin polarization is expected to vanish over most of the phase diagram. Furthermore, neglect of the spin polarization energy, which drops with increasing temperature, is in the spirit of our high-temperature approximation for the higher-order interatomic correlation functions.
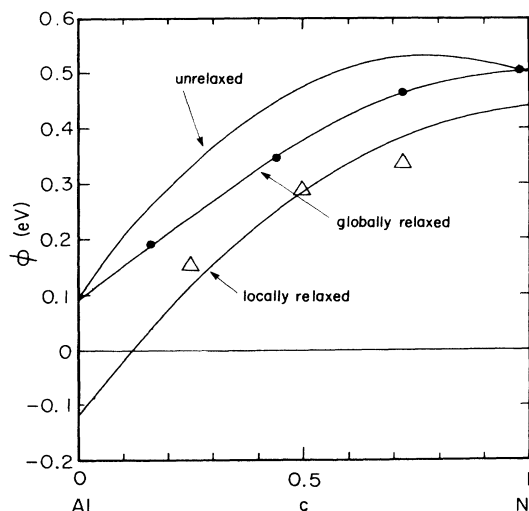

FIG. 1. Effective pair interactions for Ni-Al system. Treatments of relaxation described in Sec. III. Triangles denote values of interaction obtained by matching to calculated heats of formation for ordered supercell compounds. Circles denote calculated points for locally relaxed potential. (Additional points are calculated outside the range of lattice constants shown, so that no extrapolation is performed.)

Although the lattice constant in this system does not vary linearly with concentration, as is assumed in obtaining the globally relaxed potential, the resulting corrections to the EPI are small and are neglected here.

The globally relaxed EPI, shown in Fig. 1, displays a strong concentration dependence. Its large positive value at the Ni-rich end is consistent with the very strong ordering tendency in Ni_3Al, which remains ordered up to its melting point[14] of 1658 K. At the Al-rich end the value of ϕ drops rapidly. The unrelaxed curve is obtained at a fcc lattice constant of $6.64a_0$, which is close to that of Ni. This curve shows that even if concentration-induced lattice constant changes are neglected, the concentration dependence of ϕ is strong. However, the large discrepancy between this EPI and the globally relaxed EPI at 50% concentration indicates that the lattice constant changes must be included to obtain a satisfactory description of the EPI.

The locally relaxed curve lies below the other two for all concentrations. This type of behavior is expected if one naively associates ϕ with the heat of formation at a particular concentration. Then, the value of the *globally* relaxed EPI at 50% concentration, for example, corresponds to the energy required to separate the $Al_{0.5}Ni_{0.5}$ into constituent elemental Al and Ni, which are constrained to have the lattice constant of $Al_{0.5}Ni_{0.5}$. The *locally* relaxed EPI, on the other hand, corresponds to the elemental Al and Ni having their preferred lattice constants. The latter clearly requires less energy than the former, so that globally relaxed EPI must be more positive than the locally relaxed EPI. Of the three calculated EPI, this is the most closely related to solid solubilities. Although our restriction to four-atom clusters prevents a definite conclusion about whether ϕ changes sign at the Al-rich end, we note that a negative value of ϕ is consistent with the very low solid solubility[14] (0.023% at 640 °C) of Ni in Al; in contrast the solubility[14] of Al in Ni is 10% at 640 °C.

The triangles in Fig. 1 denote the values of ϕ obtained by matching to the calculated heats of formation of Al_3Ni, NiAl, and Ni_3Al, with all total energies evaluated at equilibrium lattice constants. Since the compounds are forced to occupy a fcc lattice, the Al_3Ni and NiAl compounds are hypothetical. The discrepancy between these points and the locally relaxed EPI is a measure of the error induced by the high-temperature approximation (4) for the higher-order correlation functions. Even in this case, where the cluster potentials are evidently large in magnitude and the assumed temperature is zero, the discrepancies are quite small. By contrast, comparison of this curve with the globally relaxed curve shows that in this system obtaining in EPI from the heat of formation results in 30% discrepancies.

It is instructive to compare the EPI values obtained here to those obtained[15] from a fit to the Ni-rich part of the Ni-Al phase diagram based on empirical Lennard-Jones potentials. We expect that the EPI describing the solid part of the phase diagram should be intermediate between the globally relaxed and the locally relaxed EPI. The EPI values obtained from the empirical fit are 0.31 eV at 75% Ni and 0.40 eV at pure Ni. By comparison,

our globally relaxed values are 0.47 and 0.50 eV, and the locally relaxed values 0.39 and 0.44 eV. Thus the calculated EPI display semiquantitative agreement with the empirical ones and the sign of the concentration dependence is obtained correctly. Calculations with larger supercells will be required in order to obtain more quantitative accuracy.

B. Nb-Y

Since this system does not form a solid solution, we focus on the liquid part of the phase diagram. Because of the greater freedom of motion in the liquid relative to the solid, it is probably modeled best by the locally relaxed EPI (cf. Fig. 2). This EPI is negative for all concentrations, consisting with the observed miscibility gap in the liquid. The concentration dependence of the EPI is strong, the magnitude at the Nb end exceeding that at the Y end by a factor of 3. The miscibility gap in this system is shifted substantially toward the Nb-rich end,[16] indicating that the interaction favoring phase separation is stronger at this end. While to our knowledge no detailed calculations of the effect on the liquid phase diagram of the concentration dependence of the EPI have been performed, this behavior appears to be consistent with that of the calculated EPI.

Comparison of the globally and locally relaxed EPI's shows that the lattice strain effects are very large as is expected from the large mismatch in the atomic volumes. (The atomic volume of Y exceeds that of Nb by over 80%.) As for Al-Ni, these effects favor ordering. In this case, they are large enough to change the sign of the EPI. Thus if the two constituents were artificially forced to have the same lattice constant, ordering would actually be favored over phase separation.

IV. CONCLUSION

In this paper we have shown that using a resummation scheme, one can generate EPI similar in character to those obtained by the GPT, starting from the supercell
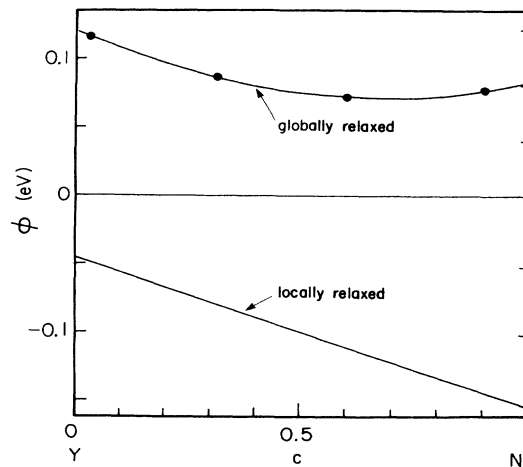

FIG. 2. Effective pair interactions for Nb-Y system.

TABLE I. Analogy between resummation schemes for potentials describing atomic rearrangements in elemental metals and those describing alloy ordering energies. On the right-hand side, $n(\mathbf{r})$ denotes density of atoms.

	Alloy EPI	Elemental pair potentials
Source of cluster potentials	Supercell total energy calculations	Moments of one-electron density of states
Truncation scheme	$\langle \sigma_1 \sigma_2 \times \cdots \times \sigma_n \rangle = \cdots$ $\langle \sigma_1 \sigma_2 \rangle \langle \sigma \rangle^{n-2} + \cdots$	$\langle n(\mathbf{r}_1) \times \cdots \times n(\mathbf{r}_n) \rangle =$ $\langle n(\mathbf{r}_1) n(\mathbf{r}_2) \rangle \langle n \rangle^{n-2} + \cdots$
Type of potential obtained by resummation	Constant concentration	Constant volume

method described in Ref. 7. The concentration dependence of the EPI thus obtained has direct manifestations in alloy phase diagrams. It is instructive to compare the resummation scheme described here to one analyzed earlier[17] for "bond-breaking" and "constant-volume" interatomic potentials in elemental metals. The analogy between the two schemes is illustrated in Table I. Through analysis of the moments of the electronic density of states, one can generate[18] a series of cluster potentials which describe fairly accurately energies associated with a large variety of atomic rearrangements in elemental metals (at least within the tight-binding approximation). For example, the pair potential derived from the second moment describes broken-bond energies. The moment-derived cluster potentials are analogous to the V_{C_n} in Eq. (3). As in the alloy case, the cluster potentials are somewhat unwieldy and it is desirable to resum them into an effective pair potential valid for a small range of atomic rearrangements. In the elemental case this is accomplished through a second-order expansion in the nonuniform part of the density of atoms, which is directly analogous to our second-order expansion in the alloy concentration fluctuations. The resulting potentials are of the same type as those obtained from pseudopotential expansions[19] about a uniform electron gas. The elemental potentials are valid at constant volume, while the alloy potentials described here are valid at constant concentration. Unlike the present case, however, the higher-order correlation functions obtained by expansion in the density fluc-

tuations are not physically realizable, since they are missing, for example, the $\mathbf{r}_1 = \mathbf{r}_2$ δ-function terms. Thus there is no class of statistical behaviors, such as the high-temperature limit for the EPI, in which they ar rigorously exact. They do, of course, provide fairly accurate results for a variety of simple metal systems. The neglect of the δ-function terms is closely analogous to the neglect of terms with repeated indices in the simplest version of the GPT.

As suggested in Ref. 17, new types of resummation schemes may lead to potentials which have a different range of validity or are more accurate than those described here. There are, for example, a number of truncation schemes for the higher-order correlation functions which are more sophisticated than that given by (4). Since the present scheme corresponds to a high-temperature expansion, the more sophisticated schemes may be more useful for lower temperatures at which the short-range order is substantial. These schemes may be included in the present formalism with essentially no extra effort.

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