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Cluster expansions at alloy surfaces: Formalism and application to segregation in Ni-Cu

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A formalism is described to calculate concentration-independent effective cluster interactions at an alloy surface in the ''unrestricted'' scheme. Although this approach is generally valid, a specific implementation is discussed in the context of the tight-binding approximation in conjunction with the direct configurational averaging method. This technique is applied to a study of segregation at the (100) surface of $\mathrm{Ni}_c\mathrm{Cu}_{1-c}$ alloys. Monte Carlo simulations show a strong tendency for Cu to enrich the surface at all temperatures and a monotonic approach of the equilibrium segregation profile to the bulk composition. The latter point has been a source of some controversy because a number of recent calculations, using widely different techniques, produce conflicting results. A critical discussion is given of the relative merits of the various methodologies. [S0163-1829(97)03521-2]

I. INTRODUCTION

It is only a slight exaggeration to say that the first-principles calculation of (binary) alloy phase diagrams has become a routine matter. This spectacular progress may be seen by consulting a recent overview of the state of the art such as can be found in Refs. 1 or 2. Only about ten years ago the first electronic-structure based diagrams were computed.[3,4] These efforts produced many valuable insights, but employed relatively unsophisticated approaches to the band structure and relied on mean-field theory. For bulk systems the tight-binding approach has been all but superseded by the more powerful first-principles methods, while mean-field theory has been complemented by large-scale Monte Carlo simulations. Some of this progress is due to improvements in the theoretical formalism, but most of it is caused by the tremendous advances in computing power. Admittedly, problems remain for a number of systems, such as those showing large lattice mismatch, a sizable amount of charge transfer, or other complications, for example due to magnetic or relativistic effects. Nevertheless, for a great many systems, first-principles calculations have not only explained the thermodynamic properties in amazing detail, they have even made predictions that are already having a direct technological impact. While much work remains, alloy design by computational means has become a reality.

In stark contrast, the related problem of predicting from first principles the segregation behavior at alloy surfaces is still in its infancy. In spite of much work, theorists cannot even agree on the segregation profile in one of the simplest of systems, the binary alloy Ni-Cu. In part, the cause of the difficulties is that electronic structure calculations for an alloy surface are considerably more complex than in the bulk: Bloch's theorem can only be applied in two dimensions, necessitating in the third the use of a slab, supercells, or some form of embedding. Charge transfer between the surface layers and into the ''vacuum'' region makes attaining electronic self-consistency much more difficult than in the bulk. Moreover, elastic effects related to size mismatch are more severe in low-dimensional geometries, giving rise to surface relaxation, reconstruction, or other local rearrangements. In addition the statistical mechanics framework underlying the thermodynamic calculations is more complex for surface problems due to the inequivalence of the sites in the various layers constituting the surface. In a remarkable parallel to the complications that beset the theorist, the experimental determination of segregation profiles is also fraught with difficulties. Effects such as preferential sputtering and sputter-induced segregation in addition to the great sensitivity of segregation behavior to the presence of even minute quantities of contaminants make it very difficult to determine the composition in the subsurface layers. Contaminants may even reverse the nature of the segregating species to the surface plane. Thus it is not surprising that conflicting reports exist, even for such a relatively simple system as Ni-Cu.

The purpose of the present paper is twofold. First, we develop the ''unrestricted'' scheme to calculate effective cluster interactions near an alloy surface. Compared to the ''restricted'' scheme used hitherto in surface calculations, this new cluster expansion of the internal energy leads to a considerable simplification of the calculations. Second, this formalism is applied in a determination of the segregation profile at the (100) surface of $\mathrm{Ni}_c\mathrm{Cu}_{1-c}$ for $c=0.25$, 0.50, and 0.75. Two of the present authors have recently studied this very problem using the tight-binding (TB) method, with direct configurational averaging (DCA) to determine interaction energies, and the Bragg-Williams method to find the segregation profile.[5] The motivation for revisiting this system is the subsequent appearance of a number of relevant papers on the same subject,[6–11] at least one of which[8] reports results that are directly at odds with those obtained in our earlier study. Since the methodologies used in these recent works differ drastically from each other it is of great interest to try to identify the source of the discrepancies in order to better understand each method's abilities and limitations. To this end calculations have been performed with the same Hamiltonian as in Ref. 5, but with a number of improvements in both the electronic and statistical treatment. Specifically, averages have been carried out over a larger number of configurations, concentration-independent interactions have

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been computed (using the unrestricted expansion), and the segregation profile has been determined by Monte Carlo simulations. The results, by and large, confirm those of Ref. 5. In particular, the equilibrium segregation profile is again found to be monotonic, and shows no evidence of the Cu depletion in subsurface layers obtained in Ref. 8.

II. MOTIVATION

Many processes of great technological importance occur at the surface of metals and metallic alloys or are initiated near the surface region. Examples include heterogeneous catalysis, adhesion of coatings, adsorption of atoms or molecules, epitaxial growth, corrosion, oxidation, friction, lubrication, magnetic domain formation, etc. A theoretical understanding of the structure and composition of the surface region, ultimately leading to the ability to control these parameters, would have great impact on a variety of industries.

In the simplest approach the phenomenon of surface segregation in a binary alloy can be understood quite easily: the element with the lower surface tension will preferentially occupy the surface plane and the approach to the bulk concentration will be monotonic or oscillatory, depending on whether the bulk alloy is an ordering or a clustering one. There are several reasons why this elementary analysis is unsatisfactory. The notion of surface tension is a macroscopic one, which should be related to microscopic parameters derived from the electronic structure of the alloy. Moreover, such a picture incorrectly assumes that the interaction parameters which govern the surface tension and the ordering or clustering tendencies remain unchanged from their bulk values. Finally, the structural rearrangements that may occur at the surface are ignored in this interpretation. For example, complications occur in the case of size mismatch since this will tend to induce surface enrichment of the minority component. Thus, while this phenomenological argument has great value in providing a physically transparent interpretation of the phenomenon, it lacks in predictive power. In keeping with the situation for bulk alloys a comprehensive treatment of surface segregation will have to be based on electronic structure information complemented by a statistical physics calculation of the thermodynamics. Both of these aspects are substantially more complicated at a surface than in the bulk.

Previous microscopic studies of surface segregation can be divided in two categories: those based on a static lattice, usually described by an Ising or lattice gas model, and those based on a continuum model in which atoms are not restricted to reside on fixed sites. The first class of models is usually treated by mean-field theory or Monte Carlo simulations, while the latter is normally studied by means of some minimization algorithm, such as (classical) molecular dynamics, Monte Carlo simulations (with particle exchanges as well as displacements), or others based on an approximation of the free energy. While the continuum approach allows for a more accurate description of displacive and substitutional disorder, it has the drawback that the full interaction potential between the various species must be known. It is a nontrivial task to do this from first principles and most treatments use a semiempirical approach, such as the embedded atom method (EAM),[12–14] or other effective medium theories.[15] The lattice models have the advantage that only a relatively small set of interaction parameters, called effective cluster interactions (ECI's), needs to be determined. For bulk systems, some major progress has recently been made towards unifying the embedded atom method and the representation through an Ising-type Hamiltonian.[14] It would be of great interest to generalize this approach to the surface problem.

For bulk systems, four main techniques have been proposed to calculate the ECI's from first principles. These are the generalized perturbation method (GPM),[16] the embedded cluster method (ECM),[17,18] the Connolly-Williams method,[19] and the method of direct configurational averaging (DCA).[20,21] The underlying paradigm of these approaches is the Ising model, whose connection with the electronic structure was put on a rigorous footing in the formalism developed by Sanchez, Ducastelle, and Gratias.[22] These authors showed that the total energy of a disordered or partially ordered alloy may be expanded in a complete set of orthonormal cluster functions, whose expansion coefficients are the ECI's. This expansion may be performed in the space of all possible configurations of the alloy (as in the original paper of Sanchez *et al.*) or it may be restricted to a subspace that only includes those configurations with fixed concentration. The distinction is an important one as the first approach leads to concentration-independent ECI's while in the second case these interactions depend explicitly on concentration. The essential equivalence of these two approaches for bulk systems was established by Asta *et al.* in a formal analysis,[23] and numerically confirmed by Wolverton *et al.*[24] As pointed out by Sanchez[25] the main difference between the two schemes is that they are based on distinct choices of basis. Originally the terms ''grand canonical'' and ''canonical'' scheme were used to distinguish these two approaches, although now the terms ''unrestricted'' and ''restricted'' sum are preferred, since the choice of ECI's does not enforce a statistical mechanics treatment in either the canonical or grand canonical ensemble.

In the past most microscopic determinations of ECI's near an alloy surface have employed the restricted scheme since it was assumed that the segregation profile needs to be determined simultaneously with the interaction parameters in a self-consistent manner. Only recently has it been realized that the problem may be solved in the unrestricted approach which allows the quantum mechanical problem to become decoupled from the statistical physics problem.[26] In the present paper, therefore, the Ni-Cu system, previously studied in the restricted summation scheme,[5] is reanalyzed in the unrestricted scheme, all other parameters remaining the same. Moreover, the opportunity is taken to compare and contrast this approach to various others that have recently been proposed in the literature.

We will not attempt a full overview of the experimental and theoretical situation with regards to surface segregation in the Ni-Cu system, but refer the reader instead to the recent papers that form the basis for the present work and the references therein.[5–11] In short, there is general consensus that Cu segregates strongly at all temperatures and for all bulk concentrations, with the outer layer being almost pure Cu at low temperatures. There is considerably more debate about the approach to the bulk concentration. Some authors obtain a monotonic profile, while others find a depletion in Cu in the subsurface layer(s). There is disagreement on this point both amongst experimentalists as amongst theorists. Electronic structure calculations indicate that the dominant terms in the ECI's are the so-called point energies (akin to a chemical potential) which are considerably larger than the effective pair interactions (EPI's), other cluster interactions being negligible. Whether the concentration profile will be monotonic or not depends on the sign of the point energies. It is this variable about which disagreement exists, while there is also considerable scatter in the numerical values of point and pair energies. However, the concentration profile is not very sensitive to the absolute values of these interactions, although other observables (such as surface core-level shifts) are.

In Ref. 5 tight-binding calculations were performed for the Ni-Cu system from which point and pair energies were extracted by means of the DCA in the restricted scheme, i.e., the ECI's and the concentration profile had to be iterated to self-consistency simultaneously. Only temperatures above the bulk critical temperature were considered so that the Bragg-Williams method could be used with confidence. In this temperature range and within the restricted scheme the segregation is completely dominated by the point energies. The segregation profile was found to be monotonic. Pasturel *et al.*[6] determined (concentration-dependent) interaction parameters in this alloy using the GPM in the context of a tight-binding formulation of the linear-muffin-tin-orbital method (TB-LMTO) with the coherent potential approximation (CPA) to treat the disorder. Segregation profiles were calculated by means of the Monte Carlo method. For the (100) surface of $\mathrm{Ni}_{0.75}\mathrm{Cu}_{0.25}$ and $\mathrm{Ni}_{0.50}\mathrm{Cu}_{0.50}$ all point energies were found to be positive, although inclusion of the pair interactions produced a segregation profile that showed a small Cu depletion in the third layer below the surface. For $\mathrm{Ni}_{0.25}\mathrm{Cu}_{0.75}$ the point energies oscillated in sign but the segregation profile turned out to be monotonic. Good *et al.*[7] employed a semiempirical method based on the equivalent crystal theory (ECT) using as experimental input the heats of solution in the dilute limits. Monte Carlo simulations were performed to determine segregation profiles, which were found to be monotonic. Ruban *et al.*[8] performed a large number of LMTO-CPA calculations from which they extracted (concentration-independent) ECI's for clusters up to the tetrahedron by means of the Connolly-Williams method. The ensuing concentration profiles were calculated by the cluster variation method (CVM) and showed an oscillatory behavior. This pattern was established, independent of any specific Ising model to which the interactions were subsequently fitted, by calculating the surface energy for various compositions. Moreover, it was consistent with the point energies which were also oscillating in sign as a function of the layer index. The authors speculate that the reason for the discrepancy concerning the nature of the segregation profile may be related to the use of one-electron energies in some of the earlier papers rather than total energies as in their work. Rittner *et al.*[9] used EAM potentials to calculate segregation free energies for a large number of systems, by means of the free-energy minimization method (FEM). This technique minimizes the free energy directly and includes approximations to the configurational and vibrational entropy. Moreover, it allows one to include structural relaxations in the formalism by performing the minimization with respect to the atomic coordinates. For Ni-Cu the effects of relaxation and vibrational entropy were only slight, but in other cases they were shown to have pronounced consequences. The FEM had previously been used to investigate segregation in Ni-Cu, using the EAM, in an extensive study by Wang *et al.*[27] These authors had obtained segregation profiles that showed Cu depletion in the subsurface layers. The same conclusion had been reached in a prior EAM study of Ni-Cu using Monte Carlo simulations with particle interchanges, as well as lattice relaxation.[13] Schulthess *et al.*[10] applied the GPM within the context of a layer version of the Korringa-Kohn-Rostoker (KKR) method with the single-site CPA to treat disorder. Although the main subject of the paper is the Ni-Al system, a short discussion of some results for Ni-Cu is given since the authors wished to study the effects of electronic self-consistency in a system with negligible charge transfer and elastic effects. The non-self-consistent point energies all had the same sign, leading to a monotonic segregation profile, while the self-consistent energies showed a sign reversal. The authors found that there was a partial cancellation of errors by not going to self-consistency and neglecting double-counting terms. They stressed that there is no argument ''à la Friedel'' to justify this and concluded that good agreement with experimentally determined surface concentrations must be considered accidental. Very recently, Drchal *et al.*[11] performed a very careful study of the effects of self-consistency in surface segregation calculations. These authors continued their earlier work,[6] in which non-self-consistent calculations were performed, and analyzed the effects of going electronically self-consistent. In addition to the band-energy contribution to the total energy, contributions from core states, double counting, and the Madelung term were incorporated. The changes in point energies and ECI's due to these effects were found to be quite large. In particular, in the self-consistent scheme point energies were reduced and converged faster compared to the non-self-consistent calculations. Also the surface EPI was found to be considerably larger in the self-consistent method. The magnitude of the second-neighbor interaction in the bulk and in the top layer now turned out to be smaller than that of the first-neighbor EPI. The concentration profiles were found to be monotonic, except at low concentrations where Cu enrichment in the first and second layers was obtained, but with a depletion in the third layer. Thus, these findings are at odds with those of Ruban *et al.*[8] although the methodology is essentially equivalent. Also, they highlight the importance of charge transfer in the surface region.

III. METHODOLOGY

The formalism that is at the basis of the present work is the tight-binding Ising model (TBIM) pioneered by Tréglia, Legrand, and Ducastelle.[28–30] These authors have shown that the total energy of a binary alloy system, A_cB_{1-c}, with N sites may be written as

$$E(p_n^I)=E_0+\frac{1}{N}\sum_{n,I} p_n^I V_n^I+\frac{1}{2N}\sum_{n,m,I,J} p_n^I p_m^J V_{nm}^{IJ}+\cdots, \tag{3.1}$$

where the p_n^I are occupation numbers, equal to 1 if site n is occupied by an atom of species I (A or B) and equal to 0 otherwise. In this representation the statistical physics resembles that of a lattice gas model rather than an Ising model, but it is easy in the case of a binary alloy to make the transformation to an Ising model through the introduction of the pseudospin variables σ_n equal to $+1$ for an A atom, and -1 for a B atom, by substituting $\sigma_n = 2p_n^A - 1$. In Eq. (3.1), V_n^I are the point energies for each species, V_{nm}^{IJ} are the pair interactions, etc. These quantities may be calculated using the GPM as shown by Tréglia *et al.*[28–30] or they may be computed by means of the DCA.[5,31,32] In studies of bulk systems the point energies can usually be ignored, unless there are inequivalent sites in the system, but at a surface, due to the symmetry breaking, they must be included. In fact, it turns out that in most cases these quantities are the dominant ones to determine the segregating species and the concentration profile.

As was mentioned before, Sanchez, Ducastelle, and Gratias[23] have formalized the Ising model approach. These authors showed that (in the unrestricted scheme) the internal energy of an alloy may be written as

$$E = V_0 + \sum_\alpha m_\alpha V_\alpha \xi_\alpha . \tag{3.2}$$

Here the V_α are the ECI's, for the cluster α which contains n_α sites and has multiplicity m_α, and the ξ_α are cluster correlation functions (or cumulants) defined as

$$\xi_\alpha = \langle \sigma_1 \sigma_2 \cdots \sigma_{n_\alpha} \rangle , \tag{3.3}$$

where the angular brackets denote a configurational average. These correlation functions form a complete orthonormal set in the space of all 2^N possible configurations and provide a natural setting for the CVM. Comparing the TBIM expression [Eq. (3.1), after transformation to spin variables] and the unrestricted summation [Eq. (3.2)] one notes that a formal identity has been established between the electronic structure and the statistical physics. The explicit expression for the point energies reads

$$V_p = \tfrac{1}{2}[E_p^A - E_p^B], \tag{3.4}$$

and for the EPI's

$$V_{pq} = \tfrac{1}{4}[E_{pq}^{AA} + E_{pq}^{BB} - E_{pq}^{AB} - E_{pq}^{BA}]. \tag{3.5}$$

Here p and q denote lattice sites and E_p^I (E_{pq}^{IJ}) is the total energy of a system consisting of an atom of type I on site p (and one of type J at site q) embedded in a completely disordered medium. Similar expressions hold for the other ECI's. It is clear that all of these interactions are concentration independent. However, it is possible to find other expansions similar to Eq. (3.2) based on a different set of basis functions. In particular, a natural way to proceed is to consider the restricted scheme in which the system is kept at a constant concentration c. In that case the expansion for the internal energy reads

$$E(c) = \tilde{V}_0(c) + \sum_\alpha m_\alpha \tilde{V}_\alpha \delta\tilde{\xi}_\alpha , \tag{3.6}$$

with correlation functions defined as

$$\delta\tilde{\xi}_\alpha = \langle (\sigma_1 - \overline{\sigma_1})(\sigma_2 - \overline{\sigma_2}) \cdots (\sigma_{n_\alpha} - \overline{\sigma_{n_\alpha}}) \rangle , \tag{3.7}$$

where $\overline{\sigma_i} = 2c_i - 1$ is the average spin on site i. The concentration-dependent ECI's (indicated by the tilde) have formal definitions similar to Eqs. (3.4) and (3.5), but with the added constraint of fixed concentration. In Eq. (3.7) we have allowed for the possibility that inequivalent sites may be present so that the c_i may take on different values on different sites. For a bulk system in which all sites are equivalent, one has of course $c_i = c$, for all i.

The fact that, depending on the approach used, one could obtain ECI's that either depend on concentration or do not, remained a puzzling and somewhat controversial issue for a number of years. For bulk systems, a major clarification was provided in a paper by Asta *et al.*[23] in which the equivalence of the two approaches was formally established and transformation formulas between the restricted and unrestricted ECI's were given. Specifically, the authors demonstrated that the unrestricted ECI's can be recovered from the restricted ones through a renormalization procedure. Moreover, it was shown that (in a bulk system with all sites equivalent) the restricted ECI's at fixed overall concentration $c = 0.50$ are identical to the unrestricted ones:

$$V_\alpha = \tilde{V}_\alpha (c = 0.50). \tag{3.8}$$

This powerful result allows one to obtain unrestricted ECI's by performing all calculations for an equiatomic composition.

For alloy surface problems the distinction between the two schemes becomes particularly poignant. In the restricted scheme one needs to determine the ECI's corresponding to the equilibrium segregation profile parallel to the surface at a given temperature. Since this profile in turn depends on the values of the ECI, this requirement leads to a time consuming self-consistency procedure in which ECI's and layer concentrations need to be iterated to convergence simultaneously. This process may be accelerated somewhat by taking advantage of the nearly linear dependence of the point energies on concentration,[5] but it nevertheless makes the computations awkward and involved. In particular, new ECI's need to be determined for each bulk concentration or temperature. In contrast, as we will see, the proper implementation of the unrestricted scheme is to perform all averages over configurations that have an equiatomic composition in each layer parallel to the surface. Thus, for a given alloy system the ECI's can be computed once and for all, independent of bulk concentration or temperature.

In the present work it will be assumed that we deal with surfaces of systems that have all sites in the bulk equivalent, although the generalization to other cases is straightforward. Thus, the system may be taken as made up of layers parallel to the surface and the inequivalent sites may be labeled simply by the index p of the layer in which they are located, $p = 1$ being the surface layer. The average spins $\overline{\sigma_i}$ in Eq. (3.7) in general take on different values depending on the layer index. If $\overline{\sigma_p}$ is taken to be zero for all p, i.e., $c_p = 0.50$ for all p, one notes that the $\delta\tilde{\xi}_\alpha$ reduce to ξ_α. Comparing Eqs. (3.2) and (3.6) and taking into account that the correlation functions form a complete orthonormal set, we find that the restricted and unrestricted ECI's are identical under this condition. This generalizes, to the case of structures with inequivalent sites, Eq. (3.8). It shows that the proper procedure to calculate ECI's in the unrestricted scheme is to demand that the average concentration on each inequivalent site is kept at 50%. In the case of a surface this leads one to impose this condition layer by layer.

Furthermore, it is possible to establish a relationship between the point energies in plane p relative to the bulk values ($p=\infty$) and the difference in p-plane tensions of the pure elements.[26] A generalization of the notion of surface tension, the p-plane tension τ_p^I of the pure element I is defined as the difference in binding energy of an atom when it is located in plane p relative to its value in the bulk. For $p=1$ this reduces to the definition of surface tension. In the Appendix it is shown that

$$V_p - V_\infty = \frac{1}{2}(\tau_p^A - \tau_p^B) + \sum_{n_\alpha \text{odd}, \geqslant 3} \cdots . \tag{3.9}$$

The correction terms run only over clusters with an odd number of sites larger than two (triplet, quintuplet, etc.) and in many cases are negligible. Thus, to a very good approximation twice the point energy difference $V_p - V_\infty$ should equal the difference in p-plane tensions, a result first observed by Tréglia *et al.*[28] for $p=1$ and here generalized and rigorously demonstrated. This is a remarkable finding, since it relates alloy parameters (V_p) to pure-element quantities (τ_p^I). However, it only holds if ECI's for triplets and higher order clusters are indeed negligible compared to the other terms.

Once the parameters in the Hamiltonian have been determined the statistical mechanics problem of minimizing the associated free energy must be solved. The simplest way of doing so is by means of the Bragg-Williams method in which the entropy is taken to have the very simple form given by regular solution theory. The resulting system of coupled equations, discussed below, is well known and must be solved numerically for the concentration in each layer.[5] Its analytical properties may be understood in terms of the theory of area preserving maps.[29] This approach is known to work well at elevated temperatures above the bulk order-disorder transition temperature. One may then assume that the segregated layers are disordered. The Bragg-Williams approximation is but the lowest order one in a sequence of mean-field theories known as the cluster variation method (CVM). Higher order approximations within the CVM have also been used to solve segregation problems, notably in a formulation based on the tetrahedron as the basic cluster.[8] This procedure also leads to a set of coupled equations for the occupancies in the various layers. It has the advantage that correlation functions may be determined and that it is applicable at all temperatures. Monte Carlo simulations are also a natural way to simulate the kinetics and equilibrium properties at an alloy surface and, with the advent of fast workstations, may very well become the technique of choice for accurate work.[33]

In the Bragg-Williams approximation, assuming only nearest-neighbor EPI's, one finds a system of coupled equations for the concentrations in the various layers, which may be written in the form

$$\frac{c_p}{1-c_p} = \frac{c_\infty}{1-c_\infty}\exp(-E_{\text{seg}}^p / k_B T), \tag{3.10}$$

where k_B is Boltzmann's constant and E_{seg}^p is the segregation energy for the pth plane. In the restricted scheme one has

$$E_{\text{seg}}^p = 2(\widetilde{V}_p - \widetilde{V}_\infty), \tag{3.11}$$

while in the unrestricted scheme the general expression is much more complicated and also depends on the concentrations c_{p-1}, c_p, and c_{p+1}:

$$\begin{aligned} E_{\text{seg}}^p = {} & 2(V_p - V_\infty) + 2[Z_1 V_{pp}(2c_p - 1) \\ & + Z_2 V_{p,p-1}(2c_{p-1} - 1) + Z_2 V_{p,p+1}(2c_{p+1} - 1)] \\ & - 2(Z_1 + 2Z_2) V_{\infty,\infty}(2c - 1). \end{aligned} \tag{3.12}$$

Here Z_1 denotes the number of nearest neighbors in the plane, and Z_2 the number of out-of-plane nearest neighbors. In order for this expression to be valid for all p values, one must take V_{10} to be zero. If the EPI's were negligible the concentration dependence would disappear and one would get

$$E_{\text{seg}}^p \approx 2(V_p - V_\infty), \tag{3.13}$$

but in general the full expressions [Eq. (3.12)] must be used. In view of Eqs. (3.9)–(3.12) one notes that the component with the lowest surface tension will enrich the surface. The approach to the bulk concentration (monotonic or oscillatory) will depend on the behavior of the p-plane tensions and/or the sign of the EPI's. It may seem that Eq. (3.11) is the simpler expression, but one must keep in mind that the point energies in that case are concentration dependent, so that the system of equations (3.10) must be iterated to self-consistency simultaneously with the point energies. On the other hand, Eq. (3.12) contains concentration-independent interactions, which need not be adjusted during the self-consistency cycle on Eq. (3.10). One also notes that in the case $c_p = 0.50$, for all p, the expression (3.12) reduces to Eq. (3.11), i.e., under the constraint of equiatomic composition on all planes the restricted and unrestricted scheme become equivalent, as was established before. However, the present observation is based on the Bragg-Williams approximation, while the result holds completely generally.

IV. RESULTS

The TB parameters used in the present work were obtained by a fit to first-principles calculations for the pure elements[34] and include s, p, and d orbitals. These are identical to the values on which our previous work[5] was based and are used here again to permit a direct comparison of the restricted and unrestricted schemes. The applicability of these types of parameters to ECI calculations has been questioned[35] and it is likely that better parameter sets could currently be calculated, e.g., by the TB-LMTO method. Nevertheless, to compare the two averaging schemes in a consistent way, the use of the same parameters is indicated. Off-diagonal disorder is treated by Shiba's prescription. The ECI's are computed directly by orbital peeling, using the recursion method in combination with the DCA.[21] Local charge neutrality was imposed by a rigid shift of the ener-

TABLE I. Comparison of point energies (in eV, relative to bulk values) obtained by various authors. Note that the values from Refs. 5, 6, and 11 were obtained in the restricted scheme (and consequently are concentration dependent), while those from Ref. 8 and the present work are calculated in the unrestricted scheme.

Plane	Ref. 5	Ref. 6	Ref. 8	Ref. 11	Present work
1	0.39–0.67	0.15–0.17	0.189	0.147	0.69
2	0.04–0.13	-0.007–0.014	-0.036	-0.0004	0.0052
3	–	0.001–0.002	0.0023	-0.007	0.0011

gies. Further details can be found in Ref. 5. In contrast to that work, the present study calculates averages over 50 configurations generated in the unrestricted scheme, i.e., an average composition of 50% in all the layers was enforced as discussed in the previous section.

The resulting parameters, valid at all concentrations, are listed in Table I (point energies, relative to the bulk values) and Table II (EPI's). Also listed in Table I are the point energies found in our previous work and by other authors. These have been adjusted to agree with the sign convention and spin representation used in the present paper. Interactions due to further neighbor and higher order clusters were found to be negligible. This is in contrast to the work of Pasturel *et al.*[6] and Ruban *et al.*[8] who find quite large second-neighbor interactions. The former authors obtained concentration-dependent interactions and found that for 50 and 75 % Cu content the second-neighbor interaction dominated the first-neighbor interaction in magnitude. These authors found higher cluster interactions (triplets, etc.) to be negligible. On the other hand, in the work of Ruban *et al.*[8] a very large contribution was obtained for the four-point cluster. However, this is an artefact of the Connolly-Williams method which is not based on a rigorous expansion such as Eq. (3.2), but will tend to have all sorts of effects lumped together in the last term of the truncated expansion. Also, the results of Pasturel *et al.*[6] were somewhat modified by going to self-consistency[11] with the second-neighbor interaction no longer dominating, although still sizable.

As can be seen in Table I, in the present work the point energies are monotonic and positive, leading to Cu segregation in all layers. This is in conflict with the result of Ruban *et al.*[8] where an oscillation was obtained, an issue that will be addressed below. One also notes that in the present work the point energy in the surface layer is considerably larger than that obtained by other authors. However, care must be taken in comparing these values since the present results were obtained in the unrestricted scheme and a renormalization of parameters occurs. Nevertheless, it appears that the point energies obtained with the Papaconstantopoulos parameters are anomalously high. This may be seen by using Eq. (3.9) (for $p=1$) and subsituting the calculated or measured surface energies. Two groups have recently computed surface energies for Cu(100) and Ni(100), Abrikosov and Skriver[36] using the TB-LMTO-CPA method and Alden *et al.*[37] using a spin-polarized Green's function technique also based on the TB-LMTO method within the atomic sphere approximation (ASA). Surprisingly enough, the two methods yield quite large deviations. For the surface energy of Cu(100), Abrikosov and Skriver find 0.71 eV, while Alden *et al.* obtain 0.85 eV. For the paramagnetic Ni(100) fcc surface Abrikosov and Skriver get 0.95 eV and Alden *et al.* 1.03 eV. The source of the differences is not clear from the published results. We also note that Abrikosov and Skriver[36] obtained a deviation from linear behavior of the alloy surface energy that has the opposite sign from that found experimentally. This disagreement was attributed to the effects of segregation in experiment, since the calculation was performed for an unsegregated surface. Using the Abrikosov and Skriver surface energies in Eq. (3.9) one finds a point energy difference $(V_1 - V_\infty)$ of 0.12 eV while the Alden *et al.* results yield a point energy difference of 0.09 eV. These values are noticeably smaller than all computed values in Table I. This discrepancy is not due to magnetic effects, since the surface energy for Ni(100) in the ferromagnetic state only increases to 1.07 eV (Ref. 37) which shifts the point energy up to 0.11 eV, still a good deal below the computed values. The cause of this disagreement between the rigorous relation Eq. (3.9) and the computations is not clear at present, but it illustrates the difficulties that face an accurate determination of the ECI's at an alloy surface. We note that in other systems, such as MoW (Ref. 38) Eq. (3.9) was found to hold to within 10%.

TABLE II. EPI's V_{pq} (in meV/pair), for sites in planes p and q, obtained in the present work. Bulk sites are denoted by ∞.

p	q	V_{pq}
1	1	-8.46
1	2	-6.82
2	2	-9.89
2	3	-12.79
3	3	-14.82
3	4	-14.41
4	4	-13.70
∞	∞	-14.01

The (nearest-neighbor) EPI's listed in Table II are all negative, which is consistent with the clustering tendency of the Ni-Cu system. In the surface region the EPI is considerably reduced compared to that in the bulk. Simple moment arguments[28] would predict an increase in magnitude at the surface, but in a full (self-consistent) calculation this does not necessarily hold, as can also be seen in Fig. 3 of Ref. 5. Moreover, the present calculations are performed in the unrestricted scheme, which means that the interactions are renormalized with higher order terms compared to results obtained in the restricted scheme. This must also be kept in mind when comparing the present results with those from Refs. 5 and 6. We note that Drchal *et al.*[11] found the reverse trend for the surface EPI: it was found to be almost three times as large as that in the bulk. The bulk EPI in the present work is very close to concentration-dependent ones obtained in Ref. 5 in which the restricted scheme was used. The concentration dependence of those EPI's was rather mild, so that the good agreement between the two schemes for this parameter is not unexpected. From the bulk EPI one can estimate (using the tetrahedron-octahedron approximation of the CVM) a bulk order-disorder temperature at $c=0.50$ of $T_c=850$ K, in fair agreement with the experimental value for the top of the miscibility gap at 628 K for a concentration of $c=0.67$.[39] As mentioned before and as observed by others,[35] the Papaconstantopoulos TB parameters[34] do not form an optimal starting point for the purpose of determining ECI's. Therefore a shift of 30% of a phase boundary is not unreasonable (see also Table I in Ref. 35). In this regard for bulk systems the TB method is certainly not able to compete with more accurate first-principles calculations, notably those based on density functional theory (DFT). This does not exclude that it generally gives quite adequate qualitative trends. Moreover, as discussed in the Introduction, the surface problem is considerably more complicated, even for those first-principles methods. Part of the discrepancy between the calculated and experimental phase boundary must be attributed to relaxation effects as discussed recently by Asta and Foiles.[14]

For completeness we also mention that Vaks *et al.*[40] have used neutron scattering data to calculate the EPI's over a range of concentrations in the bulk for the Cu-Ni system. These authors find fairly large second-neighbor interactions (opposite in sign to the first-neighbor interactions). This overall tendency is in agreement with the results from DFT calculations for the surface problem.[8,11] The source of the discrepancy with the present results, which find the second-neighbor interactions to be negligible, is not clear. We do note that Sluiter and Turchi,[41] who also used a TB model, found only weak second-neighbor interactions in bulk Cu-Ni. Thus, it is possible that this deviation is due to shortcomings of the TB approach, a matter that deserves further study. However, we note that Vaks *et al.*[40] also find sizable fourth-neighbor interactions especially in the Ni-rich end of the composition range, a rather unexpected result. Further experiments would be welcome.

In the present work, the Monte Carlo method is used to determine the segregation profile. This technique has the advantage over the Bragg-Williams method of being applicable at all temperatures and of permitting the determination of the state of order in the layers parallel to the surface. Moreover, it also allows one to obtain information about the kinetics of segregation. There are a number of options in the way the simulation cell is set up in a Monte Carlo study of surface segregation. Clearly, to minimize finite-size effects it is advantageous to have periodic boundary conditions in the two directions parallel to the surface. The main question is what to do with the modeling of the ''bulk.'' One possibility is to terminate the system by a layer that is periodically supplied with atoms so as to maintain the desired bulk concentration. This is the approach favored by Eymery and Joud[33] and also used by Pasturel *et al.*[6,11] The slight disadvantage of this scheme is that it violates the condition of detailed balance each time that atoms are supplied to the system. Another possibility, employed in the present work, is to treat all layers, except the last one, in the canonical ensemble, and to fix the chemical potential in the last layer to the bulk value and consider it in the grand canonical ensemble. The disadvantage of this approach is that it is more difficult to fix the bulk concentration to a specific value. In both approaches, the ''bulk'' layer also has fewer neighbors than the other layers (except for the surface). This will tend to produce minor artefacts (depletion in one of the species) in the last two layers. One could work around this by artificially increasing the EPI in the last layer, or by increasing the number of neighbors in some fashion. We have preferred not to resort to such measures, but we will report all segregation profiles truncated just before the last two layers. In order to speed up convergence towards the equilibrium profile it is advantageous to start the calculations with a configuration consistent with an estimated profile, obtained for example by the Bragg-Williams method or from a Monte Carlo simulation on a small sample.

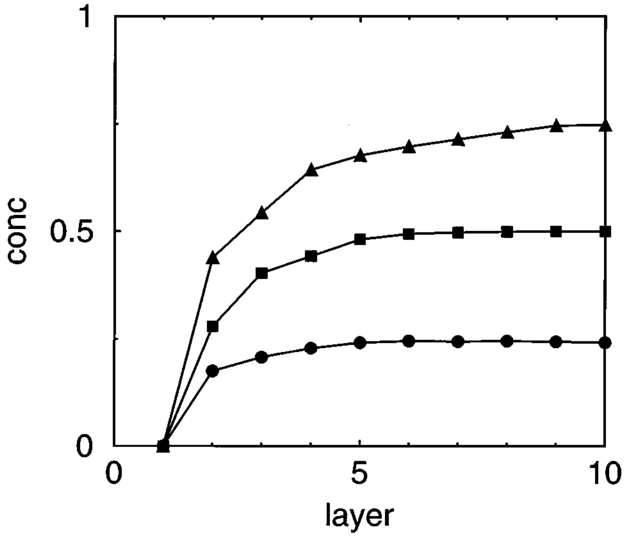

FIG. 1. Concentration profiles for various layers at $T=1000$ K and bulk concentrations $c=0.25$ (circles), 0.50 (squares), and 0.75 (triangles).

Monte Carlo simulations were performed as described for a simulation cell consisting of 12 layers each containing a 32×32 mesh (with two atoms per unit cell) parallel to the surface, corresponding to the (100) surface of a fcc structure. Simulations for systems containing more layers or more sites per layer produced no noticeable difference. The sample was first equilibrated over 1000 Monte Carlo steps per particle (MCSP), starting from an estimated segregation pofile, and averages were calculated over the next 2000 MCSP. Figure 1 shows the concentration profiles thus obtained at a temperature of 1000 K, well above the bulk critical temperature, for three bulk concentrations ($c=0.25$, 0.50, 0.75). One notes that the top layer is pure Cu for all bulk concentrations, a consequence of the large point energy in the surface layer. Also the approach to the bulk concentration is monotonic and fairly rapid, although not as fast as predicted by the Bragg-Williams approximation or Eq. (3.10). We have also compared the results calculated by the Bragg-Williams method and those obtained by Monte Carlo simulation at temperatures above and below T_c. If only point interactions were present, i.e., if the EPI's were negligible, the Bragg-Williams approximation would become exact and yield identical results to the Monte Carlo method. Our results showed that the differences between the two for temperatures above T_c were rather small, while strong deviations occurred below T_c. This reflects the increasing effect of the clustering tendency between like atoms below T_c. However, inspection of snapshots showed that even at temperatures above the bulk order-disorder temperature T_c clustering in the layers near the surface occurred. Thus the statement that the Bragg-

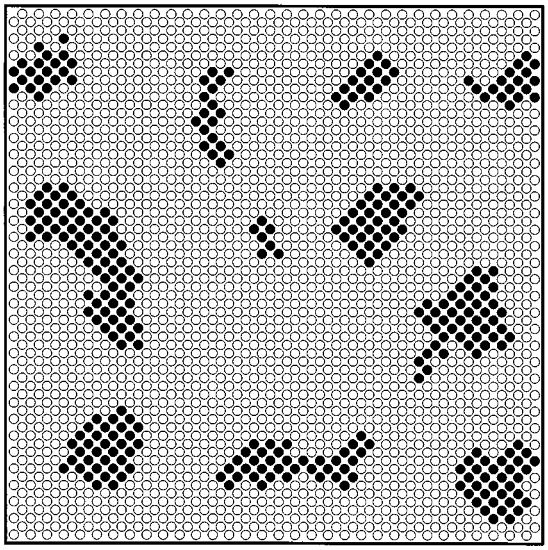

FIG. 2. Snapshot of the first layer below the surface in Ni-Cu for bulk concentration $c=0.50$ at $T=500$ K. Filled circles denote Ni atoms and open circles represent Cu atoms.

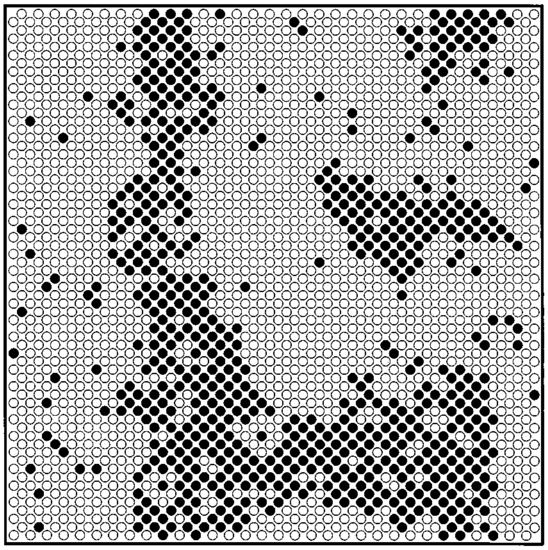

FIG. 3. Snapshot of the first layer below the surface in Ni-Cu for bulk concentration $c=0.50$ at $T=1000$ K. Filled circles denote Ni atoms and open circles represent Cu atoms. Even though the system is above the bulk order-disorder temperature there is still a strong tendency towards clustering.

Williams method is appropriate for temperatures above T_c must be interpreted with some care.

We also note that a Cu depletion of the subsurface layers was observed in the early stages of the simulation following a quench of a completely disordered system. Starting from a configuration with equal composition in all layers, Cu diffusion to the surface (and corresponding Ni diffusion into the bulk) was so strong that a Cu-depleted (Ni-enriched) zone remained in layers 2 and 3. However, this was merely a kinetic effect and the expected monotonic profile was obtained as the simulation proceeded. Care was taken to ensure that thermal equilibrium was reached in the simulation (by calculating staggered averages and monitoring the layer concentrations). However, at low temperatures a kinetically arrested oscillating profile may well exist as a long-lived state. Such nonequilibrium effects may also be at the root of experimental reports of Ni enrichment in the subsurface region.

Representative snapshots of the first layer below the surface (i.e., $p=2$) for a bulk concentration $c=0.50$ are shown in Figs. 2 and 3. These were obtained at $T=500$ K (Fig. 2) and 1000 K (Fig. 3). One notes at $T=500$ K the presence of a number of Ni domains (filled circles) embedded in a Cu matrix, consistent with the attractive in-plane EPI and as expected for a clustering alloy. More interestingly, at $T=1000$ K one observes that there is still considerable short-range order and that, in spite of numerous ''point defects,'' Ni atoms tend to be surrounded predominantly by Ni atoms. This layer can certainly not be considered as completely disordered, even though the system is well above the bulk order-disorder transition temperature. One also notes that the total Ni concentration in the second layer is larger at 1000 K than at 500 K, consistent with the greater influence of entropy effects which begin to overcome the point energies, as can also be seen qualitatively from Eq. (3.10).

The intra- and interlayer nearest-neighbor correlation functions expressed as the fraction of Cu-Cu and Cu-Ni first-neighbor pairs for these two cases are shown in Figs. 4 and 5 in which the strong clustering tendency of like atoms (owing to the negative nearest-neighbor EPI) is evident. The open box represents the fraction of Cu-Cu nearest-neighbor bonds in each layer or between layers. Since the first layer is pure Cu in both cases, its correlation function is unity and sets the scale in Figs. 4 and 5. The shaded box indicates the fraction of unlike (i.e., Cu-Ni) bonds. For a phase separating alloy at low temperatures this quantity should go to zero in the thermodynamic limit as a circumference to area ratio. In the present case the minimum number of unlike pairs possible is

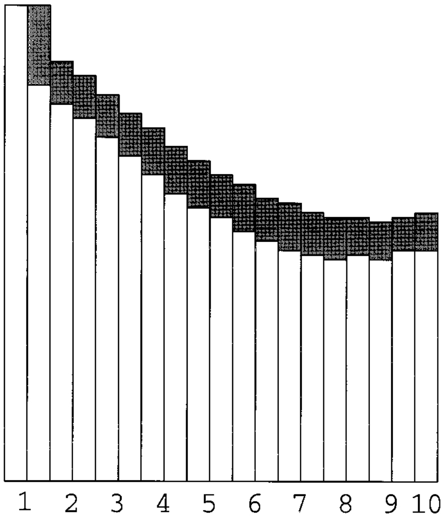

FIG. 4. Fractions of nearest-neighbor pairs of various types within layers and between adjacent layers for $c=0.50$ and $T=500$ K. The open box denotes Cu-Cu bonds and the shaded box represents Ni-Cu bonds. The abscissa indicates the layer index p, with the histogram to the left corresponding to the intralayer occupancy and that to the right corresponding to the nearest-neighbor bonds between planes p and $p+1$.

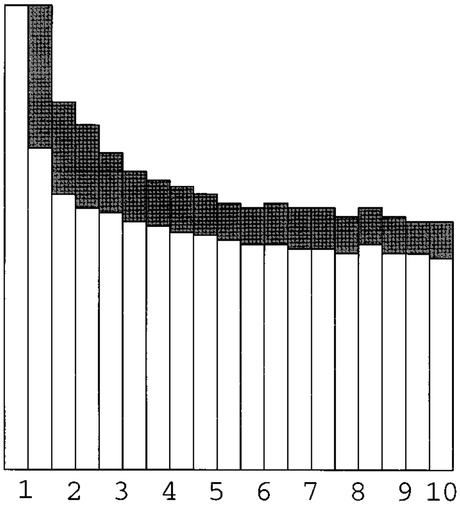

FIG. 5. Fractions of nearest-neighbor pairs of various types within layers and between adjacent layers for $c=0.50$ and $T=1000$ K. (See Fig. 4 for symbols.)

$2L/L^2$ ($L=32$), i.e., about 6%. The fraction of unlike bonds in Fig. 4 ($T=500$ K) levels off at about 7–8 %, reflecting the presence of a few domains, similar to those shown in Fig. 2. At 1000 K (Fig. 5) the unlike-pair probability fluctuates between 9 and 10 % consistent with the higher degree of disorder, but considerably smaller than 50% as expected for a completely disordered system. This signals again that the surface region retains a high degree of short-range order even above the bulk order-disorder temperature. Of particular interest is the pair correlation function between the first and second layers: it gives 16% unlike pairs at 500 K and 32% unlike pairs at 1000 K, reflecting the higher Ni content at higher temperature. Also, for $p=10$ we find 49% Cu-Cu pairs and 43% Ni-Ni pairs at 500 K, while both fractions equal 45% at 1000 K. The stronger clustering tendency for Cu compared to Ni at low temperatures is a consequence of the strong Cu enrichment to the surface plane. These sites act as ‘‘nuclei’’ for ordered domains that percolate deep into the system. Thus the surface point energy makes its effect felt ten layers deep, although the actual point energy for $p=10$ has long reached its bulk value. Such correlation effects are outside the scope of the Bragg-Williams method, but dominate the thermodynamic behavior at low temperatures.

V. DISCUSSION AND CONCLUSIONS

We have presented the unrestricted averaging scheme to calculate ECI’s near an alloy surface. As demonstrated here, both mathematically and numerically, this method is equivalent to the restricted scheme, but leads to a considerable savings in computer time since the concentration-independent ECI’s need to be determined only once. This approach was used in a study of Ni-Cu alloys, using TB parameters identical to those of earlier work.[5] The numerical results obtained in the two schemes are very similar, demonstrating the utility of the unrestricted scheme. Quantitatively, differences for bulk transition temperatures are on the order of 30%, consistent with earlier observations.[35] The difference with experiment is partly due to the limitations of the Papaconstantopoulos TB parameters and partly to relaxation effects.[14] The segregating species is found to be Cu, due to the large point energy in the top layer in agreement with all other theoretical treatments, as well as experiment. This is consistent with the fact that Cu has a lower surface tension than Ni. To analyze such trends a rigorous relation between point energies and p-plane tensions has been established. The segregation profile is found to be monotonic in agreement with several previous theories, but in conflict with the most accurate electronic structure treatment to date by Ruban *et al.*[9] It is therefore worthwhile to critically analyze the approximations inherent in the various treatments.

Schulthess *et al.*[10] and Drchal *et al.*[11] have stressed the importance of charge self-consistency in surface calculations. The present results use a primitive form of charge self-consistency through the simple expedient of imposing local charge neutrality via a rigid shift for all the bands for each inequivalent atom. More sophisticated forms may be envisioned, for example by shifting different levels by different amounts according to the symmetry of the orbitals. In view of the DFT-based calculations which point to the importance of a proper treatment of this effect in the surface region, this possibility deserves further study.

A number of studies of surface segregation, including that of Ruban *et al.*,[8] employ the Connolly-Williams method[19] in which a *truncated* expression of the form (3.2) or (3.6) is postulated to hold and the expansion coefficients exactly fitted to a series of total-energy calculations for ordered structures. For bulk systems the method has been widely used and has led to mixed results. A critique has been presented by Sluiter and Turchi[42] and by Mikalopas and collaborators.[43] The main drawback of the method is that it is not based on a full (infinite) expansion in which the parameters may be given a precise physical meaning. Rather, the fitting parameters contain all sorts of effects convoluted together in an attempt to precisely mimic the ordered structures. Frequently one finds that changing the number of clusters in the expansion drastically alters the values of the parameters. Also the decreasing magnitude of the ECI’s with the number of sites which is often found to hold in practice can no longer be ascertained. In particular, it may be that the last term retained in the expansion is artificially large. This may be seen in the parameters of Ruban *et al.* where one finds a very large quadruplet interaction.

Ruban *et al.* tried to circumvent the limitations of the Connolly-Williams method by performing a direct calculation of the surface energy of various segregated systems. They fixed the concentration of all layers except the top one at 50% and found that the minimum surface energy occurred for 100% Cu in the top layer. Next, they fixed the top layer at 100% Cu and that of all other layers, except the second one, at 50% and minimized the surface energy with respect to the concentration in the second layer. The minimum was now found to occur at 0% Cu concentration for $p=2$. From this they concluded that Cu depletion of the layer immediately below the surface is energetically favorable. This is a very powerful argument indeed for an oscillatory profile. Nevertheless, the condition of 50% concentration from the third layer onwards is an artificial constraint that is not expected to hold in actuality. Moreover, the surface energy is a multidimensional function of the various layer concentrations and fixing all variables except one may very well lead to spurious minima. One cannot rule out that the actual global minimum of this function resides in a region of parameter space that was left unexplored. Still, this direct calculation is very compelling and it would be interesting to ascertain that these results continue to hold for other concentration profiles.

Ruban *et al.* argue that methods based on a sum of one-electron energies (such as that used here) all give monotonic profiles, while those based on minimizing the total energy yield oscillatory profiles. This seems to indicate that electron exchange and correlation effects are responsible for the Cu depletion in the second layer an issue that deserves further study. We note in passing that the EAM calculations quoted in Ref. 8 as being based on a total energy could hardly be considered equivalent to full electronic structure calculations. The EAM is based on a classical many-body potential with empirically determined parameters. Although it continues to be a very useful technique, it does not have the same level of predictability as the DFT-based electronic structure calculations. Thus, the evidence for oscillatory profiles is less compelling than may appear from Table I in Ref. 8. Moreover, the recent study of Drchal *et al.*[11] includes a very careful analysis of the effects of electronic self-consistency and leads to monotonic profiles, further undermining the argument that the nature of the segregation profile (monotonic vs oscillatory) is a consequence of going electronically self-consistent.

Elastic effects, due to size mismatch or structural rearrangements at the surface (relaxation, reconstruction, etc.) are not normally included in the TBIM, but may have to be for certain systems. The simplest approximation to account for differences in atomic size is through the use of continuum elasticity theory.[30] The net effect is to add an elastic term to the segregation energies (3.11) and (3.12). As a result, the energetics of the problem is modified, but the atoms may still be taken to reside on a rigid lattice. More complex is the situation in which atomic displacements are to be considered. To describe the internal energy in those cases one needs to know interatomic potentials. It is well established that for transition and noble metals (and their alloys), pair potentials alone are not sufficient to describe these systems' cohesive properties. The determination of the necessary many-body potentials from first principles is a very complex problem in its own right to which much effort has been devoted.[44] The thermodynamics for such situations is also more involved and is typically treated by molecular dynamics or Monte Carlo simulations with displacive and interchange excitations.[13,15] Recently, the EAM has been used in conjunction with a second-order expansion of the energy with respect to displacements to yield a Hamiltonian that is still formally that of a lattice gas and may be treated by mean-field or Monte Carlo techniques.[14] This is a very interesting development and a generalization to the surface problem could produce great progress. We note that it is possible to perform molecular dynamics simulations based on a TB Hamiltonian (with a repulsive term added to it),[45,46] but one must then keep in mind that the hopping integrals, etc., depend on interatomic distance so that the electronic structure treatment becomes quite involved. DFT-based first-principles calculations also become more complicated when atomic displacements are allowed. As shown by Tersoff[47] new surface phases may occur due to these effects. A further complication, not yet included in any of the first-principles calculations of surface segregation, is the presence of a vibrational entropy term. The importance of phonon effects on bulk phase diagrams has only recently been realized (see Ref. 14 and references therein) and it seems very likely that such effects will also play an important role at and near a free surface. For bulk Ni-Cu vibrational entropy only leads to relatively small corrections[14] but in other systems the effects may be more pronounced.

In summary, this paper has presented three main contributions: a new formalism for surface segregation calculations based on the unrestricted ensemble, new results for the segregation of Ni-Cu alloys, and a critical discussion of the state-of-the-art in first-principles calculations of surface segregation. The formal development of a methodology based on the unrestricted averaging scheme promises to be very useful. It will permit future studies to determine point energies and ECI's in a single calculation, rather than necessitating a self-consistency loop for each new bulk concentration and temperature. It also permits surface studies to proceed on an equal footing with bulk studies. As an added bonus, we have established an exact relation between the p-plane tensions and the point energies and ECI's. This finding explains earlier observations that the difference in point energies is very close to the difference in p-plane tensions, since the correction terms are usually very small. Our numerical results for Ni-Cu continue the debate about the nature of the segregation profile, notably whether the subsurface layers show a Cu depletion or not. Our results show unambiguously that, within the approximations made, no Cu depletion can be found. This finding is at variance with some, but not all, calculations that treat the electronic structure problem in a more sophisticated manner (based on DFT). The discrepancy may be due to the tight-binding parameters used, the approximate treatment of charge transfer, or the inherent inapplicability of the tight-binding method to this type of problem. Of these, the electronic self-consistency is the most troublesome and its treatment may have to be improved upon in future studies. We have analyzed the approximations typically made in DFT-based studies of the segregation problem and conclude that there are potentially sources of error that outweigh the gains made by going to a more accurate electronic structure method. We also note that the DFT-based methods show considerable disagreement as to the sign and magnitude of various point energies and ECI's indicating that these parameters are very sensitive to the details of the calculation. In particular, the rigorous relation between the point energy difference and the pure element surface tensions, was found to be violated for all calculations considered here. We also observed that previous calculations[36,37] of the pure element surface energies differed from each other by a substantial amount. Both of these issues deserve further study and point to the complexity of the alloy surface problem even for DFT-based methods. Moreover, all techniques to date neglect vibrational entropy effects and either do not treat size mismatch or do so only in a very crude manner. These two effects can be very pronounced at surfaces and may have to be taken into account in future studies. Experimental investigation of the Ni-Cu system should be able to guide theory, although the determination of the equilibrium subsurface composition is a very daunting task. Kinetic effects and the presence of contaminants may easily lead to faulty conclusions. Further theoretical and experimental work would be most welcome.

ACKNOWLEDGMENTS

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APPENDIX: RELATION BETWEEN POINT ENERGIES AND p-PLANE TENSIONS

In a study of bulk alloy systems Wolverton *et al.*[35] derived a relation between the point energies and the cohesive energy of the pure elements. Here this approach is generalized to the case of a semi-infinite alloy, which will permit us to establish a relation between point energies and p-plane tensions,[26] thereby demonstrating rigorously a pattern first observed by Tréglia *et al.*[28] For completeness, we note that the present derivation is only strictly valid in the tight-binding model. For the DFT-based methods the layer decomposition of the energies used here is no longer valid, although it may hold approximately.

We consider a semi-infinite binary alloy in the unrestricted scheme. Following Eq. (3.2) its internal energy may be expressed as

$$E=V_0+\sum_p \overline{\sigma_p}V_p+\sum_p \sum_{\alpha\supset p,n_\alpha\geqslant 2} m_\alpha V_\alpha \xi_\alpha , \tag{A1}$$

where the sum over p is carried out over the planes parallel to the surface and the sum over α runs over those clusters which contain at least one site in plane p. In the completely disordered state the cumulant (3.3) reduces to a product of point correlation functions and Eq. (A1) simplifies to

$$E_{\mathrm{dis}}=V_0+\sum_p \overline{\sigma_p}V_p+\sum_p \sum_{\alpha\supset p,n_\alpha\geqslant 2} m_\alpha V_\alpha \prod_{i=1}^{n_\alpha} \overline{\sigma_{p_i}}. \tag{A2}$$

Differentiating this expression with respect to $\overline{\sigma_p}$ one derives easily

$$V_p=\left(\frac{\partial E_{\mathrm{dis}}}{\partial \overline{\sigma_p}}\right)_{\{\overline{\sigma_p}\}=0}. \tag{A3}$$

In addition, the formation energy (E_{form}) of the disordered system is defined as the difference between the cohesive energy of this alloy (E_{dis}) and the weighted sum of the cohesive energies $E_A^0(p)$ and $E_B^0(p)$, for each plane p, of the pure semi-infinite metals A and B, i.e.:

$$E_{\mathrm{form}}=E_{\mathrm{dis}}-\sum_p \{c_pE_A^0(p)+(1-c_p)E_B^0(p)\}. \tag{A4}$$

We emphasize that this relation only holds exactly within the TB model. Combining the two equations (A2) and (A4), taking into account Eq. (A1) for the pure elements, one finds for the formation energy

$$E_{\mathrm{form}}=\sum_p \sum_{\alpha\supset p,n_\alpha\geqslant 2} m_\alpha V_\alpha\left(\prod_{i=1}^{n_\alpha}\overline{\sigma_{p_i}}-\frac{1+\overline{\sigma_p}}{2}-\frac{1-\overline{\sigma_p}}{2}(-1)^{n_\alpha}\right). \tag{A5}$$

Next, differentiating this expression with respect to $\overline{\sigma_p}$ one obtains

$$\left(\frac{\partial E_{\mathrm{form}}}{\partial \overline{\sigma_p}}\right)_{\{\overline{\sigma_p}\}=0}=\sum_{\alpha\supset p,n_\alpha\geqslant 3} m_\alpha V_\alpha\left(\frac{-1+(-1)^{n_\alpha}}{2}\right). \tag{A6}$$

Finally, differentiating Eq. (A4) with respect to $\overline{\sigma_p}$ and combining the result with Eqs. (A3) and (A6) leads to

$$V_p=\frac{1}{2}\{E_A^0(p)-E_B^0(p)\}+\sum_{\alpha\supset p,n_\alpha\geqslant 3} m_\alpha V_\alpha\left(\frac{-1+(-1)^{n_\alpha}}{2}\right). \tag{A7}$$

This expression for the point energies is the analogue of Eq. (23) in Ref. 35. It can now be simplified by recalling the notion of the p-plane tension τ_p^I (surface tension for $p=1$), defined as the difference in energy when one interchanges, in the pure metal I, an atom in the bulk ($p=\infty$) with an atom in plane p:

$$\tau_p^I=E_I^0(p)-E_I^0(\infty). \tag{A8}$$

Substituting this result into Eq. (A7), and using Eq. (A1) for the pure elements, one finds the following relation between point energies and p-plane tensions:

$$V_p-V_\infty=\frac{1}{2}\{\tau_p^A-\tau_p^B\}+\sum_{\alpha\supset p,n_\alpha\geqslant 3} m_\alpha V_\alpha\left(\frac{-1+(-1)^{n_\alpha}}{2}\right)-\sum_{\beta,n_\beta\geqslant 3} m_\beta V_\beta\left(\frac{-1+(-1)^{n_\beta}}{2}\right), \tag{A9}$$

where the V_β are the effective cluster interactions in the bulk. One notices, as was mentioned in the text, that only the ECI's for clusters with an odd number of sites contribute in Eq. (A9).

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