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An augmented-space recursive method for the study of concentration profiles at CuNi alloy surfaces

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Abstract. We present here a method for the calculation of effective-cluster interactions for semi-infinite solid alloys required for the study of surface segregation and surface ordering on disordered surfaces. Our method is based on the augmented-space recursion coupled with the orbital-peeling method of Burke in the framework of the TB-LMTO. Our study of surface segregation in CuNi alloys demonstrates strong copper segregation and a monotonic concentration profile throughout the concentration range.

1. Introduction

In recent years, there has been considerable progress in the microscopic study of alloy phase stability, and consequently alloy phase diagrams and associated thermodynamic quantities. For such studies one needs a derivation of the lowest configurational free energy for a specified alloy system. The calculation of the configurational free energy consists of two equally important parts: (a) the setting up of models to represent the configurational internal energies in terms of effective multi-site interactions and a quantum mechanical description of the electronic structure for use in calculating these quantities from first principles, and (b) the calculation of the configuration entropy using the methods of statistical mechanics.

It has been established that, for most alloy systems, the configuration-dependent part of the internal energy can be written as a rapidly convergent sum of multi-site interatomic interactions [1]. The idea is to start with the disordered phase, set up a perturbation in the form of concentration fluctuations associated with an ordered phase, and study whether or not the alloy can sustain such a perturbation.

This approach includes the generalized perturbation method (GPM) [2], the coherent-potential-approximation- (CPA-) based embedded-cluster method [3], and the concentration wave approach [4]. Most of the work on the calculation of the electronic structure and therefore the effective multi-site interactions of disordered alloys has been based so far on the CPA. The CPA, being a single-site mean-field approximation, has its limitations. In addition, the self-consistency involved in it requires subtle convergence procedures at each energy point. Recently there have been attempts to go beyond the single-site

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approximation to calculate the effective-cluster interactions. In one of the approaches, de Fontaine and his group [5] calculated the effective-cluster interactions directly in the real space for several configurations, and the averaging was done by brute force, as it were, by summing over different configurations. The method of direct configurational averaging (DCA) [5] yielded both the concentration-dependent (canonical) and the concentration-independent (grand-canonical) effective-cluster interactions, according to the nature of the averaging procedure. Though the method did not involve any single-site approximation, the configuration-averaging scheme was restricted to a limited number of configurations. Consequently one is never certain whether sufficient configurations have been sampled or not. Nor is there any check on the relative probability weights of the configurations that are sampled.

In an alternative approach [6] we employed augmented-space recursion (ASR) coupled with the orbital-peeling method [7] to calculate the effective-cluster interactions in bulk alloys. There, analogously to the DCA, the effective-cluster interactions were evaluated in real space but the configurational averaging involved in the definition of the cluster interactions was done accurately employing the augmented-space theorem of Mookerjee [8]. The statistical part of the problem, namely the determination of the configurational entropy, was not restricted just to the mean-field Bragg–Williams approximation; indeed the latter was replaced by more accurate methods like the cluster-variation method [9] and Monte Carlo simulations. Thus the more accurate electronic structure calculations, coupled with a good statistical description, allow one to obtain accurate and reliable phase diagrams of disordered solids.

It is well known that, in thermodynamic equilibrium, an alloy surface or interface becomes enriched with one of the alloy components. This is the phenomenon of surface or interface segregation. Surface segregation has been the subject of intense study in recent years, because of the large number of technologically important phenomena that occur at or near solid surfaces and near internal interfaces such as grain boundaries. The examples include catalysis, corrosion, adsorption and many others. Most of the earlier theoretical studies of surface segregation were based on phenomenological models [10, 11]. These models were able to describe qualitatively the observed segregation in various systems in terms of a truncated Ising model with the segregating component being determined by the bond-breaking energy (or difference in surface tension) and the approach to the bulk limit (monotonic or oscillating) being determined by the sign of the ordering pair interactions. The phenomenological theories suffer from the fact that there is no *a priori* justification of the expansion of the configuration energy in terms of the truncated Ising model. Furthermore, the interaction energies entering as parameters into the Ising model are obtained from experimentally measured macroscopic quantities, without being related to the electronic structure of the disordered alloy.

Recently there have been attempts at first-principles studies of surface segregation. The segregation behaviour of CuNi has received special attention. Here the interaction energies entering in the expansion of the configurational energy of a semi-infinite disordered solid are calculated from the description of the electronic structure. Wolverton *et al* [12] employed the DCA in the framework of the empirical tight-binding formalism and Bragg–Williams approximation to determine the equilibrium free energy and the equilibrium concentration profile of CuNi and TiRh alloys for various bulk concentrations. In another approach Pasturel *et al* [13] employed the generalized perturbation method—suitably generalized to surfaces—in the framework of the tight-binding linearized muffin-tin orbital (TB-LMTO) method coupled with Monte Carlo simulations to study the surface segregation of CuNi alloys. Very recently Ruban *et al* [14] employed the Connolly–Williams method generalized

to surfaces in the framework of the TB-LMTO CPA to calculate the effective-cluster interactions defined on a surface. This was supplemented with the cluster-variation method for the configurational entropy for studying surface segregation in CuNi alloys. In addition to these first-principles methods, there are semi-empirical methods which take their inputs from first-principles calculations. One such method [15], based on the equivalent-crystal theory [16], has recently been employed to study surface segregation in CuNi alloys, in conjunction with the Monte Carlo simulations.

From the preceding discussion it is clear that the calculation of the effective-cluster interactions on a surface relies either on the CPA or DCA for configurational averaging. For surfaces, where the coordination of the atoms is lower than in the bulk, mean-field theories like the CPA become even less accurate than in the bulk.

The *augmented-space formalism* provides a convenient means of performing configurational averaging that is not restricted by these limitations. We have shown in our previous communications [17] that this formalism coupled with the recursion technique of Haydock *et al* [18] successfully reproduces the electronic density of states of random alloys without resorting to single-site approximations and does not require the self-consistency loops of the CPA and its generalizations. Within the augmented-space formalism, the configurational averaging is done exactly, while the approximation within the subsequent recursion on augmented space can be carried out in a controlled manner, and the estimates of the error produced have been carefully studied [19]. One works directly in real space, augmented with the space of configurations, and does away with the limitations of the k -space supercell methods. Moreover, the usual surface CPA methods which intrinsically use the surface Bloch theorem are limited to flat surfaces. They cannot, without drastic modifications, be applied to corrugations and steps which are the rule rather than the exception for real surfaces. Surface roughness is no problem for the recursive technique.

The aim of this work is to present the augmented-space recursion (ASR) as a useful and powerful method for calculation of the effective-cluster interactions that enter into the definition of the configuration energy of a semi-infinite solid. We will illustrate our method by studying the surface segregation of CuNi alloys. The main points of our methodology are:

- (i) the application of the TB-LMTO method in conjunction with the ASR to describe the electronic structure of random semi-infinite alloys;
- (ii) the application of the orbital-peeling method in augmented space for the determination of effective-cluster interactions; and
- (iii) the configurational entropy is obtained by the usual statistical techniques.

The remainder of the paper is organized as follows. In section 2 we shall present our methodology for the calculation of the equilibrium concentration profile of a semi-infinite surface. In section 3 we shall present our results, related to the study of surface segregation in CuNi alloys, together with the comparison with other methods. Finally in section 4 we shall present our conclusions.

2. Methodology

Let us consider a set of N atoms on a fixed lattice to model a binary alloy A_xB_{1-x} . This binary alloy can be mapped onto an equivalent Ising-like problem by defining *occupation* variables, n_i , which are given the values $+1$ if the i th site is occupied by an atom of type A and 0 if it is occupied by one of type B. Sanchez *et al* [20] proved that any function of the configuration may be exactly expanded in terms of quantities based on clusters of lattice

sites containing progressively greater numbers of points. These clusters of lattice sites are the fundamental building blocks of such a kind of configurational description. It has been shown by Asta *et al* [21] that the expansion of the internal energy takes the form

$$E(c) = E_0 + \sum_i E_i \delta n_i + \sum_{ii'} E_{ii'} \delta n_i \delta n_{i'} + \dots \quad (1)$$

where $\delta n_i = n_i - c$, c being the concentration $\langle n_i \rangle$. The effective-cluster interactions, namely the point E_i -interactions and the pair $E_{ii'}$ -interactions, take the forms

$$\begin{aligned} E_i &= [V_A - V_B] \\ E_{ii'} &= [V_{AA} + V_{BB} - V_{AB} - V_{BA}]. \end{aligned}$$

By definition V_I is the configuration-averaged energy with the p th site occupied by an atom of type I , and similarly V_{IJ} is the average energy of all configurations, consistent with a particular concentration, with an IJ pair at sites i and i' .

The total energy of a solid may generally be separated into two terms: a one-electron band-structure term E_{BS} and an electrostatic term E_{ES} , which includes several contributions. These are the Coulomb repulsion of the ion cores, and the correction for double counting the electron–electron interaction and the exchange and correlation in E_{BS} . Since the renormalized cluster interactions involve the difference in cluster energies, it is usually assumed that the electrostatic terms cancel out and only the band-structure contribution is important. Obviously such an assumption is not rigorously true, but it has been shown to be approximately valid for a number of alloy systems. Most of the works aimed at calculating the effective-cluster interactions which start from the disordered side are based on the band-structure contribution alone. Our work also makes this assumption.

The calculation of the effective-pair interactions may be most accurately carried out by the *orbital-peeling method* of Burke (see [18]). The mathematical details of this method have been extensively described in [18]. We shall quote the final results:

$$\begin{aligned} E_i &= \sum_I \xi_I \sum_{\alpha=1}^9 \left[\sum_{k=1}^{P-1} z_k^{\alpha,I} - \sum_{k=1}^P p_k^{\alpha,I} + (N_p^{\alpha,I} - N_z^{\alpha,I}) E_F \right] \\ E_{ii'} &= \sum_{(IJ)} \sum_{\alpha=1}^9 \xi_{IJ} \left[\sum_{k=1}^{P-1} z_k^{\alpha,(IJ)} - \sum_{k=1}^P p_k^{\alpha,(IJ)} + (N_p^{\alpha,(IJ)} - N_z^{\alpha,(IJ)}) E_F \right]. \end{aligned} \quad (2)$$

Here $z_k^{\alpha,I}$ and $p_k^{\alpha,I}$ are the zeros and poles of the resolvent $\langle G_\alpha^I \rangle$, and $\xi^I = 1$ if $I = A$; otherwise it is -1 . $N_p^{\alpha,I}$ and $N_z^{\alpha,I}$ are respectively the numbers of zeros and poles below E_F . Similarly, the corresponding quantities with superscript (IJ) are similar quantities for the *peeled* Green function $\langle G_{ii'}^{IJ} \rangle$.

At this point it is worth mentioning that our scheme of calculation of the renormalized effective-cluster interactions is similar to other methods based on embedding clusters in an effective medium. The calculation involves the determination of the electronic structure as well as averaging over different configurations. It is precisely this averaging procedure which makes our approach distinct from the methods based on the CPA and DCA.

The expression for the configurational energy in terms of the effective-cluster interactions holds good for the semi-infinite alloy system also. For a semi-infinite alloy or alloy surfaces, since there is no translational symmetry, all the sites are inequivalent as in the bulk alloy. The configurational internal energy for a semi-infinite alloy with inequivalent sites may be obtained by averaging the configuration energy defined by equation (2). Furthermore, we assume that the concentration varies normally to our flat surface only. This assumption is reasonable for a semi-infinite system with a flat surface. Since the

environments of the points on the same layer parallel to the surface are equivalent, there is no reason for the composition to vary along a layer. With this assumption the intrinsic internal energy may be written as

$$U = E/N = E^0/N + \sum_{\lambda} (N^{\lambda}/N) E_{\lambda} (c_{\lambda} - c) + \sum_{\lambda} (N^{\lambda}/N) \sum_{\mu} z^{\lambda\mu} E_{\lambda\mu} (c_{\lambda} - c)(c_{\mu} - c). \quad (3)$$

c_{λ} is the concentration of a particular plane λ and $z^{\lambda\mu}$ are the nearest neighbours lying in the plane μ for a site in the plane λ . So the calculation of the configurational internal energy reduces to the evaluation of the effective-cluster interactions defined on a surface.

For the purpose of recursion we shall consider the most localized, sparse tight-binding Hamiltonian derived systematically from the LMTO [24] and generalized to random alloy surfaces.

The setting up of the augmented-space Hamiltonian and the running of the recursion on the augmented space has already been discussed in great detail in our previous communications [7, 16]; we shall restrict ourselves to the main results. Readers are referred to these references for details.

These values of the point and pair interactions yield the configurational internal energy. We only need to compute the configurational entropy to obtain the configurational free energy. This free energy when minimized yields the equilibrium concentration profile, near the surface of a disordered alloy.

In order to estimate the configurational entropy, in this communication we shall employ the Bragg–Williams approximation, where only the point correlation functions are retained in the expression for entropy. The Bragg–Williams approximation is known to produce quite accurate results for the fully disordered alloy at temperature T above the bulk order–disorder temperature T_c . For the study of surface segregation we will consider the temperature T to be greater than T_c . The expression for entropy is then given by

$$S = - \sum_{\lambda} (N_{\lambda}/N) k_B [c_{\lambda} \ln c_{\lambda} + (1 - c_{\lambda}) \ln(1 - c_{\lambda})] \quad (4)$$

where k_B is the Boltzmann constant. In addition, we have an external constraint fixing the bulk concentration:

$$\sum_{\lambda} c_{\lambda} N_{\lambda}/N = \text{constant}. \quad (5)$$

So the expression for the free energy becomes

$$F = \sum_{\lambda} \frac{N_{\lambda}}{N} \left\{ \left[E_{\lambda} + \sum_{\lambda'} z^{\lambda\lambda'} \delta c_{\lambda'} \right] \delta c_{\lambda} + k_B T \sum_{\lambda} [c_{\lambda} \ln c_{\lambda} + (1 - c_{\lambda}) \ln(1 - c_{\lambda})] - \mu c_{\lambda} \right\} \quad (6)$$

where μ is the chemical potential. Minimizing F with respect to concentrations c_{λ} we have

$$\frac{c_{\lambda}}{1 - c_{\lambda}} = \exp \left[- \left(E_{\lambda} + \sum_{\lambda'} z^{\lambda\lambda'} E_{\lambda\lambda'} \delta c_{\lambda'} - \mu \right) / k_B T \right]. \quad (7)$$

For a semi-infinite system it is expected that $c_{\lambda} \rightarrow c_{bulk}$ in the bulk fairly rapidly. The Lagrangian multiplier can then be deduced from equation (7) by setting $c_{\lambda} = c_{bulk} = c$, and equation (7) reduces to

$$\frac{c_{\lambda}}{1 - c_{\lambda}} = \left(\frac{c}{1 - c} \right) \exp \left\{ - \left[(E_{\lambda} - E_{bulk}) + \sum_{\lambda'} z^{\lambda\lambda'} E_{\lambda\lambda'} \delta c_{\lambda'} \right] / k_B T \right\}. \quad (8)$$

We will employ equation (8) to determine the equilibrium concentration profile.

3. Results and discussion

The formalism developed in the previous section has been employed to calculate the point and pair interactions, and therefore to obtain the uniform concentration profile of the $\text{Cu}_c\text{Ni}_{1-c}(001)$ surface at three different concentrations (namely $c = 0.25, 0.50$ and 0.75) at a temperature of 800 K, much higher than the bulk order–disorder temperatures of the alloys.

The surface segregation in $\text{Cu}_c\text{Ni}_{1-c}$ has been the subject of many experimental and theoretical investigations. Even though it is a relatively simple alloy, whose bulk phase diagram is well understood, its surface behaviour has been the source of controversy. A large number of experiments using a diversity of surface-sensitive probes (catalytic activity measurements [26], Auger electron spectroscopy [27], x-ray and ultraviolet photoemission spectroscopy [28], time-of-flight atom probing [29], low-energy ion scattering [30]) have provided strong evidence that Cu segregates strongly at the surface for all compositions. In contrast [31] reported evidence for a reversal in segregating species with Ni segregating for compositions with c greater than 0.84, and Cu segregating for concentrations less than this value.

A second debated observation for the CuNi system concerns the composition of the sub-surface layers, with some experiments claiming that the approach to the bulk limit is monotonic, while others find evidence for Cu depletion in the layer immediately below the surface. Theoretical analysis of the system has also provided mixed results [14].

This set of studies motivated us to look for the surface segregation in CuNi alloys by a different methodology. Furthermore, our choice of the CuNi system is also motivated by the following features of this alloy system:

- (a) the elastic contributions are small;
- (b) the relativistic effects are negligible for the valence band structures;
- (c) there are no magnetic interactions since at 800 K the alloy is non-magnetic over the whole range of concentrations; and
- (d) the charge-transfer effects are small as the two elements are adjacent to each other in the periodic table.

We now mention some details concerning the numerical part of the problem. In the present calculation we have used the self-consistent bulk potential parameters for Cu and Ni evaluated at their equilibrium Wigner–Seitz (WS) radii by the scalar relativistic TB-LMTO method. The basis set was composed of $\ell = 0, 1, 2$ orbitals. So the matrices occurring are of order nine. The potential parameters Δ_ℓ^I and γ_ℓ^I of the constituent I were scaled by the factors $(\text{WS}^I/\text{WS}^{\text{alloy}})^{2\ell+1}$ to account for the fact that the Wigner–Seitz radius of the constituent I , WS^I , is different from that of the alloy, WS^{alloy} . The choice of the different Wigner–Seitz radii for Cu and Ni allowed us to take into account charge self-consistency approximately, yet accurately and consistently as emphasized by [25]. For surface problems this constitutes a reasonable choice for illustrating our method. However, as argued by [32], potential parameters derived from charge self-consistent film or super-cell calculations provide a better choice, since such calculations not only provide layer-dependent potential parameters, but also a more realistic description of the boundary conditions at the surface. In the present calculation we have assumed hard-wall-like boundary conditions for the vacuum–solid interface.

For the augmented-space recursion, a four-shell augmented-space map was generated from a cluster of 400 sites with the starting atom chosen in the layer of interest. The point and pair interactions were computed by the augmented-space recursion coupled with

the orbital-peeling method. The recursion coefficients were computed with both the first- and second-order Hamiltonians up to eight levels exactly and appended with an analytic terminator of Luchini and Nex [33]. We found that as the point and pair interactions are differences of integrated quantities, there seemed to be little benefit in doing the calculation with the second-order Hamiltonian. In principle for the calculation of the point and pair interactions one should start from the homogeneous reference medium with different concentrations in each layer, and vary the concentrations until a self-consistent set is obtained. Here, to illustrate the applicability of our method, we limit ourselves to the simple but plausible case where ‘reference medium’ refers to the homogeneous bulk alloy determined from the ASR calculations as described earlier. This description was the basis of the calculation for the GPM ([13] as well as other work based on the tight-binding Ising model developed by Treglia and co-workers [34]).

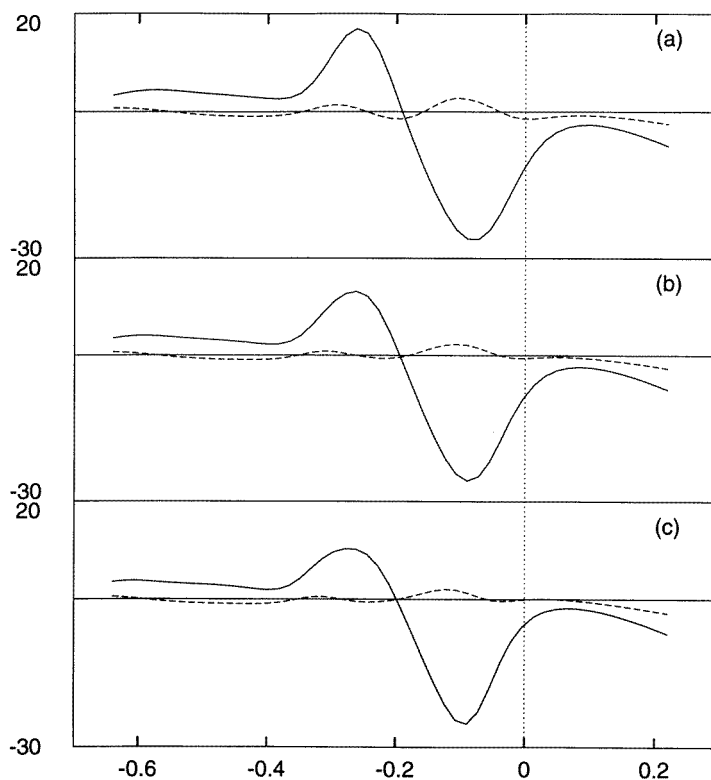


Figure 1. The difference ($E_p - E_{bulk}$) of the point cluster energies between the p th atomic layer (index 1 refers to the surface) and the bulk layer b for fcc (001) Cu–Ni alloys versus energy (solid curves: $p = 1$, dotted curves: $p = 2$). (a) $\text{Cu}_{0.75}\text{Ni}_{0.25}$, (b) $\text{Cu}_{0.50}\text{Ni}_{0.50}$, (c) $\text{Cu}_{0.25}\text{Ni}_{0.75}$. All energies are measured from the respective Fermi levels.

The values of the point cluster energies are very important, and play a decisive role for the ordering and segregation phenomena in inhomogeneous systems like alloy surfaces. In figure 1 we show for the first top layers ($p = 1, 2$) the point cluster energies $E_p - E_{bulk}$ between the energy resolved on site terms and the value corresponding to the bulk at three different concentrations 0.75, 0.50 and 0.25 (top to bottom).

As demonstrated by [34], this difference is roughly proportional to the difference in the surface tensions of the pure constituents. We find a quick convergence of the point cluster energies to their bulk value. This differences may vary dramatically and even change sign. This may be quite important for the segregation process, because the alloy can gain or lose energy when atoms in the top layer are interchanged mutually.

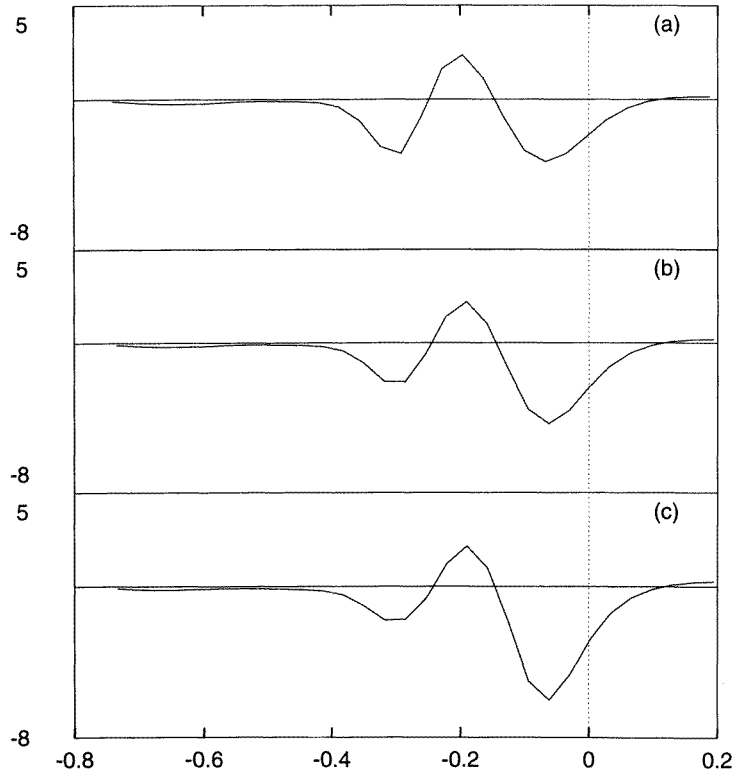


Figure 2. The nearest-neighbour pair potential V_1 versus energy for bulk CuNi alloys: (a) $\text{Cu}_{0.75}\text{Ni}_{0.25}$, (b) $\text{Cu}_{0.50}\text{Ni}_{0.50}$, (c) $\text{Cu}_{0.25}\text{Ni}_{0.75}$. All energies are measured from the respective Fermi levels.

In figure 2 we have plotted the nearest-neighbour renormalized effective-pair interactions as a function of energy at three different concentrations for the bulk CuNi alloys. The shape of the curves is in agreement with those obtained by other methodologies, with a phase-separating region at the band edge (characterized by a negative value of the pair potential) and an ordering region near the band centre (characterized by a positive value of the pair potential). However, at the Fermi energies the negative value of the pair potential suggests that the alloy tends to phase separate in the bulk even for high Ni concentrations, in agreement with other theories and experiment.

In figure 3 we present the energy-resolved nearest-neighbour renormalized effective-pair interactions $V_{R_p R_q}$ for the fcc (001) CuNi random alloy at three different concentrations. The full, dashed and dotted lines denote the surface ($p = q = 1$), interlayer ($p = 1, q = 2$) and the bulk ($p = q = 3$) respectively.

Again the pair potentials preserve all of the features observed for the bulk, and the

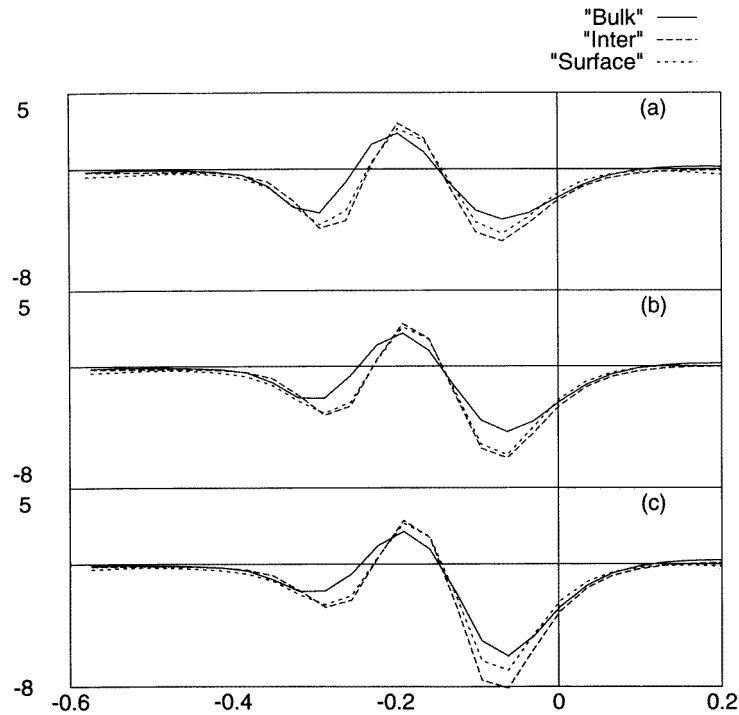


Figure 3. The nearest-neighbour pair interactions V_{R_p, R'_q} for the fcc (001) CuNi random alloy. The dashed, dotted and solid lines denote the surface ($p = q = 1$), interlayer ($p = 1, q = 2$) and bulk ($p = q = 3$) respectively versus energy for CuNi alloys: (a) $\text{Cu}_{0.75}\text{Ni}_{0.25}$, (b) $\text{Cu}_{0.50}\text{Ni}_{0.50}$, (c) $\text{Cu}_{0.25}\text{Ni}_{0.75}$. All energies are measured from the respective Fermi levels.

negative values of the pair potential indicate that it has a phase-separating tendency at $T = 0$. A comparison of figure 1 with figure 3 shows that the point interactions dominate the pair interactions and play a decisive role in the segregation process. The calculations of the pair potentials made to determine the uniform concentration profile are restricted to the nearest-neighbour interactions.

Once we have obtained the pair and the point interactions, equation (20) can be solved to yield the equilibrium concentration profile. This equilibrium concentration profile is presented in figure 4 and indicates strong Cu segregation at the surface for all bulk concentrations of Cu. Furthermore, the concentration profile is monotonic in agreement with some recent work [13, 12, 15].

Before we compare our results with other earlier work, in particular studies based on the GPM and the DCA, it is worthwhile to examine these methods in some detail. The DCA shares some of the features of our ASR:

- (i) in both methods the calculation is carried out in real space without resorting to any single-site approximation; and
- (ii) both of the methods use orbital peeling to obtain the effective-renormalized-pair interactions.

The main point of difference between the two lies in the method of carrying out the configurational averaging involved in the definition of point and pair interactions. In the

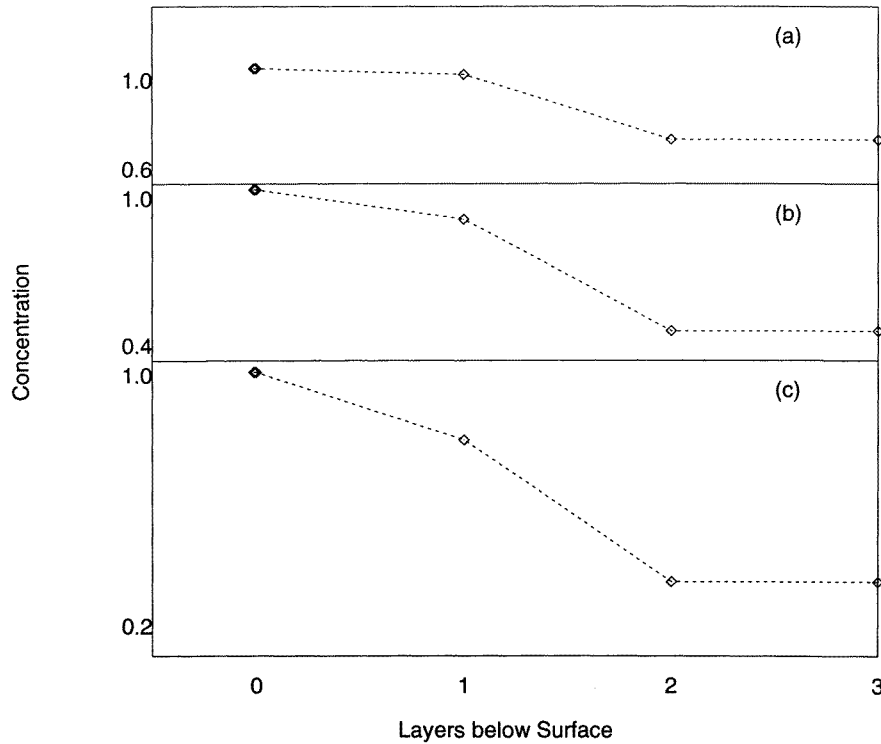


Figure 4. The concentration of Cu versus the number of layers below the surface for (001) CuNi binary alloys: (a) $\text{Cu}_{0.75}\text{Ni}_{0.25}$, (b) $\text{Cu}_{0.50}\text{Ni}_{0.50}$, (c) $\text{Cu}_{0.25}\text{Ni}_{0.75}$.

canonical version (i.e. in the case where the point and pair interactions are concentration dependent), they are obtained for several distinct randomly generated configurations (consistent with concentration) and the averaging is done, by brute force, directly as a weighted sum. Because the point and the pair interactions are integrated quantities, they are expected to converge quickly with the number of configurations sampled. However, in principle, such a method cannot sample all possible realizations, or, in other words, there is no certainty that the thermodynamic limit has been achieved. In contrast, in the ASR, the configuration averaging is done using the augmented-space theorem. The subsequent termination of the recursive generation of the continued fraction of the configuration-averaged Green function can be carefully controlled. Furthermore, we have employed TB-LMTO potential parameters to parametrize our alloy Hamiltonian, but in the DCA the tight-binding parameters were obtained from [35] where the values were obtained by fitting the results to a very accurate first-principles linearized augmented-plane-wave calculation for the pure elements.

The GPM method is distinct from the other methods. The main features of the method are

- (i) it uses the TB-LMTO in the orthogonal γ -representation for the description of the electronic structure;
- (ii) the single-site CPA is used for the configuration averaging; the effective-cluster interactions are therefore concentration dependent;

- (iii) the calculation is carried out in reciprocal space; and
- (iv) the effective-pair interactions in this scheme are renormalized.

The point interactions are the most crucial for the purpose of surface segregation, so in table 1 we have presented the results for the point interactions, for the first two layers, obtained by three different methods, namely the DCA, GPM and ASR methods at three different concentrations.

Table 1. Effective point interactions in mRyd/atom for various concentrations for CuNi alloys. The values are taken from [11] for the TB-DCA and from [12] for the GPM.

Point interaction	Concentration	DCA	GPM	ASR
$E_1 - E_{bulk}$	0.25	-49.3	-22.5	-22.4
	0.50	—	-24.0	-18.8
	0.75	-28.7	-23.5	-11.9
$E_2 - E_{bulk}$	0.25	-9.6	-2.0	-2.9
	0.50	—	-0.5	-1.2
	0.75	2.0	-2.9	-0.22

It is clear from table 1 that the agreement on the values of $E_1 - E_{bulk}$ and $E_2 - E_{bulk}$ is better between the GPM and our work. This may be attributed to the fact that TB-LMTO-GPM and TB-LMTO-ASR employ the same method for the description for the electronic structure. The point interactions are very small energy differences (of the order of a few tens of Ryd per atom spin) and are very sensitive to the particular description of the electronic structure. This feature of the effective-cluster interactions is also observed with our bulk calculations. Moreover the effective-cluster interactions, namely the point and pair interactions obtained in [13] by the GPM, are renormalized, in contrast to the usual GPM calculations. As a consequence the agreement is better with the ASR method, which is based on the embedded-cluster approach and always yields renormalized cluster interactions. The crucial point of difference between the two approaches lies in the methods of configuration averaging. The GPM employs the CPA while the ASR method employs the augmented-space formalism. This may be the reason for the observed differences in the computed values for the pair and the point interactions.

Although the schemes of calculation for the DCA and ASR methods are similar as discussed earlier, the observed differences may be attributed to the following.

(i) The DCA employs the tight-binding parameters derived from first-principles LAPW calculations of the elements to parametrize the Hamiltonian.

(ii) It uses the prescription of Shiba to obtain the off-diagonal matrix elements connecting the unlike atoms. In our work in the augmented space, it is not necessary to use this prescription, and we have built up the off-diagonal matrix elements from the potential parameters Δ_i^α and Δ_j^α and the structure matrix S_{ij}^β .

(iii) The configuration-averaging procedure is quite different as discussed earlier.

(iv) In the DCA the charge neutrality is achieved by shifting the on-site energy of one constituent with respect to the other, such that the configurationally averaged atom is charge neutral. In our scheme, as explained earlier, we have used the prescription of [25] and used unequal WS radii for the constituents, with charge neutrality in each of the spheres. The position of the Fermi energy depends sensitively on charge neutrality, and may lead to appreciable change in the pair potentials.

Finally in table 2 we have compared our concentration profile with that obtained by

other methods, namely the DCA [12] using the Bragg–Williams approximation for the configurational entropy, and the GPM [13] using more accurate Monte Carlo simulations and semi-empirical equivalent-crystal theory [15] in the framework of Monte Carlo simulations. We have employed the ASR coupled with the Bragg–Williams approximation.

Table 2. A comparison of concentrations in different layers for three different bulk concentrations of Cu–Ni alloys obtained by various methods. The values are taken from [12] for the GPM, [11] for the DCA and [14] for the effective-cluster theory (ECT).

Method	Bulk	First layer	Second layer	Third layer
GPM	0.25	0.90	0.25	0.15
	0.50	0.96	0.62	0.50
	0.75	0.98	0.80	0.75
DCA	0.25	0.98	0.45	0.25
	0.75	0.98	0.80	0.75
ECT	0.22	0.90	0.50	0.25
	0.47	0.90	0.65	0.47
	0.75	0.98	0.82	0.75
ASR	0.25	0.96	0.73	0.25
	0.50	0.94	0.65	0.50
	0.75	0.99	0.97	0.75

In all cases we find strong Cu segregation in the first surface layer, and the concentration profile is monotonic and rapidly assumes the bulk value. These results do not agree with the oscillatory concentration profile obtained in [14] by using the Connolly–Williams method in conjunction with the cluster-variation method adapted to surfaces. In [14] it was argued that the methods which are based on the one-electron contribution of the total energy predict monotonic concentration profiles whereas calculations based on the minimization of the total energy of the system lead to oscillatory segregation profiles for the (001) surfaces of Cu–Ni alloys. The calculations of the effective-cluster interactions, starting from the disordered side, are all based on the band-structure contribution and are yet to be generalized to the total energy contributions. A recent study based on the equivalent-crystal theory and Monte Carlo simulations uses the experimental heat of solution and also predicts monotonic concentration profiles. Furthermore, one cannot rule out the approximations involved in the concentration wave method, and its application to the transition metals is still debated. It appears that, to settle this question, one cannot at present appeal to experiments, since they are at variance with each other as discussed earlier. It is understood that Cu segregates strongly at the surface, but more careful analysis is required to predict the concentration profile of the CuNi alloys.

4. Conclusions

In conclusion, our results demonstrate that the augmented-space recursion and orbital peeling in conjunction with the TB-LMTO formalism constitute a viable and computationally feasible approach for the calculation of the effective-cluster interactions in the binary substitutionally disordered semi-infinite alloys, and consequently for the study of surface segregation and surface ordering in disordered surfaces. Since the method does not involve a single-site approximation it is particularly accurate for surfaces and lower-dimensional geometries. Nowhere is the flatness of the surface required; the recursion merely needs

information about the neighbouring coordination. We shall present calculations on the effect of surface roughness in a future communication.

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