PHYSICAL REVIEW B VOLUME 47, NUMBER 1 1 JANUARY 1993-I

Self-consistent ordering energies and segregation profiles at binary-alloy surfaces

H. Dreyssé
Laboratoire de Physique du Solide, Université de Nancy I, 54506 Vandoeuvre-les-Nancy, France

L. T. Wille
Department of Physics, Florida Atlantic University, Boca Raton, Florida 33431

D. de Fontaine
Department of Materials Science and Mineral Engineering, University of California, Berkeley, California 94720

(Received 5 August 1992)

We discuss the application of the direct configurational averaging method to the calculation of the thermodynamic properties of alloy surfaces. We analyze critically a number of approaches previously proposed to determine the parameters in different Ising models. We investigate the physical meaning of various interaction energies occurring in those models and compare our technique to phenomenological approaches. The formalism is applied in electronically self-consistent mean-field calculations of the segregation profile at the surface of Ni-Cu and Rh-Ti alloys at temperatures above the bulk disordering temperature.

I. INTRODUCTION

In recent years major progress has been made towards a longstanding goal in theoretical materials science: the calculation from first principles of alloy phase diagrams and the associated thermodynamic quantities.[1-3] This has necessitated important breakthroughs in *ab initio* electronic structure calculations, as well as an increased understanding of the applicable tools of statistical physics. Even so, the task is computationally very demanding and has only become feasible through improved computer hardware. Although many exciting questions remain, several groups using a range of approaches have now presented first-principles phase diagrams for a variety of systems including metals,[4-8] semiconductors,[9,10] and superconducting oxides.[11] In contrast, the determination of thermodynamic properties near surfaces or other extended defects has not yet attained the same level of sophistication. It is the purpose of the present paper to unify and review existing formalisms and to present results obtained without any adjustable parameters using the direct configurational averaging technique with the tight-binding approximation.

Alloy-phase-diagram calculations involve two computationally demanding tasks: an electronic structure calculation to determine quantum-mechanical interaction energies and a statistical physics calculation involving the minimization of a free-energy functional constructed using those energies. Both steps must be performed with very high numerical precision. The band-structure determination must be very accurate because interaction energies are formally obtained as very small differences of large cohesive energies. The statistical mechanics problem must be handled at an appropriate level of approximation, by including a sufficient number of correlation functions in a cluster variation framework[12] or by careful considerations of equilibration times and finite-size effects in a Monte Carlo simulation.[13] The same rigorous demands hold in the case of order-disorder phenomena near surfaces and interfaces, where they are exacerbated because of charge redistributions and the interplay between ordering and electronic structure.

In the last century it was recognized by Gibbs on theoretical grounds and it has been confirmed by many experiments since then, that in thermodynamic equilibrium an alloy surface (or interface) will tend to become enriched by one of the components. This is the phenomenon of surface (or interface) segregation which has been the subject of intense study over the years.[14-18] A large number of technologically important phenomena occur at or near the solid surface, or near internal interfaces such as grain boundaries.[19] Examples include catalysis, corrosion, adsorption, embrittlement, friction, deposition and growth, etc. Thus, a detailed understanding of the segregation behavior eventually leading perhaps to its control by doping or heat treatment could have many important applications. On the other hand, from a purely theoretical point of view phase transitions in reduced dimensionalities continue to be of great interest and the nature of the different types of segregation behavior has proven to be extremely rich,[20] with the possibility of segregation-induced ordering and wetting, surface sandwich formation, reconstruction, etc. Because of the great success in the description of bulk alloys, Ising models have been used extensively to model surface alloying effects as well, although care must be taken in cases where the size difference of the constituent atoms is large and elastic effects become important. Phenomenological models[21-24] 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 tensions) and the approach to the bulk limit (monotonic or oscillating) by the sign of the ordering pair interaction. While such models may have some pedagogical value it will be shown in the present paper that great care must be taken in their use and that, in fact, the point interactions (normally not considered in Ising model calculations) dominate the segregation behavior. Moreover, the phenomenological theories suffer from the fact that the interaction energies were introduced in an *ad hoc* fashion[21] or in terms of experimentally measured macroscopic quantities[22–24] and no attempt was made to relate them to the underlying electronic structure of the alloy. A great deal of work has been devoted to studying segregation in terms of the electronic structure,[25–28] but in most of those papers grave difficulties were encountered in the incorporation of temperature into a proper statistical mechanical treatment. What is needed is a method to calculate pair (and point) energies from the electronic structure and subsequently to use these energies in an appropriate statistical model. The theoretical tools to accomplish this task have only become available in the last few years.

The remainder of this paper is organized as follows. In Sec. II, the formalism is outlined with particular attention to the choice of reference medium, as this permits us to compare and contrast the present approach to others. To be specific the discussion is cast in terms appropriate for binary alloys, although the generalization to ternary alloys is straightforward. Section III presents details of the calculations for two systems: $\mathrm{Ni}_x\mathrm{Cu}_{1-x}$ which shows a miscibility gap in the bulk and $\mathrm{Rh}_x\mathrm{Ti}_{1-x}$, which is an ordering alloy. This permits us to contrast two extreme types of behavior and also facilitates comparison with bulk calculations as both systems have been studied recently. Concentration profiles are presented and compared with experimental results insofar as the latter are available. Section IV contains a more in-depth discussion of the interaction parameters and their dependence on the concentration profile. The present formalism is compared with phenomenological theories by studying the point and pair energies and relating them to macroscopic parameters. The paper closes in Sec. V with a summary of our findings and a critical discussion of the current state-of-the-art in alloy surface calculations of order-disorder phenomena.

II. FORMALISM

While much of the first-principles work on alloys and compounds in the 1980s was done with very sophisticated and time-consuming band-structure techniques based on the local-density approximation (LDA), such as the Korringa-Kohn-Rostoker (KKR) or the linear augmented-plane-wave (LAPW) methods, the last few years have seen renewed interest in the simple tight-binding model. Accurate tight-binding parameters can now be extracted from first-principles band-structure calculations, by fitting to the results of LAPW calculations[29] or by transforming the linear muffin-tin orbitals (LMTO) formalism.[30] These parameters can then be used in situations where the LDA-based techniques become unwieldy, leading to calculations that may not be strictly first principles, yet have much of the flavor of an *ab initio* method. In this spirit, in the present work the semi-infinite alloy is described within the tight-binding model in which the one-electron Hamiltonian for a given configuration σ takes the form

$$H(\sigma)=\sum_{n,\lambda}|n,\lambda\rangle\varepsilon_n^\lambda\langle n,\lambda| + \sum_{n\neq m,\lambda,\mu}|n,\lambda\rangle\beta_{nm}^{\lambda\mu}\langle m,\mu| \;, \tag{1}$$

where n and m run over lattice sites, λ and μ label the orbitals ($\lambda,\mu=1,\ldots,9$, if s, p, and d orbitals are considered). Furthermore, ε_n^λ denotes the on-site energy associated with orbital λ on site n, while $\beta_{nm}^{\lambda\mu}$ is the hopping term (overlap integral) between sites n and m and orbitals λ and μ. Except for very small clusters, it is, strictly speaking, not feasible to compute the electronic structure corresponding to the Hamiltonian (1) because the on-site energies are functions of the chemical and geometrical environment and therefore must be calculated in a self-consistent way. For bulk calculations these effects are usually neglected. In a layer geometry the computations may be simplified by assuming that on a given plane parallel to the surface the on-site energies depend only on the chemical type of the atom considered, but this approach remains to be justified *a posteriori.*

The coherent potential approximation (CPA) provides an efficient way to study the electronic structure of completely disordered alloys.[31–34] Developed in this context in the late 1960s,[35] although similar ideas date back at least to Lord Rayleigh, this approach has been extended to the semi-infinite alloy under the assumption of a different coherent potential for each plane.[36] However, this conceptually simple idea is not easy to realize and we shall discuss later how to circumvent the difficulties that this method entails. In the CPA the physical configuration is replaced by a fictitious effective medium which restores translational symmetry. This medium is determined in a self-consistent way such that an atom embedded in it produces no scattering on the average. It has been shown that of all effective medium theories the CPA provides the best single-site approximation, while attempts to go beyond the single-site approximation have been beset with great difficulties. Originally formulated within a tight-binding context (TB-CPA), the method has found its greatest successes within the framework of multiple-scattering theory[37] (KKR-CPA) and electronic structure calculations based on it have shown unsurpassed agreement with experiment for a large variety of systems. Thus, optimism grew that the CPA might also be an excellent starting point of a proper statistical mechanics theory of order-disorder phase transformations in alloys. Because of the experience gained with three-dimensional Ising model descriptions of actual systems in which parameters were fit to experiment, the need naturally arose to determine these interaction parameters from first-principles electronic structure calculations. A formalism to accomplish this was developed in the pioneering work of Ducastelle and Gautier,[38] in which it was shown that the total energy of an alloy may be obtained by a generalized perturbation method (GPM) relative to a reference medium (for example, the disordered state, treated within the CPA, although other choices could be made). The resulting expression is not a perturbation series in the usual sense since the energy is expanded in powers of $(p_n - c_n)$, where p_n is the occupation variable of site n and c_n the average occupation of that site, which are not necessarily small numbers. Nonetheless, convergence is generally rapid because the coefficients multiplying those terms are rapidly decreasing. Thus, this CPA-GPM is well suited for the study of ordering energies and has led to excellent agreement with experiment for a number of bulk systems. In the case of a semi-infinite binary alloy, N_{CPA} different coherent potentials, σ_n, must be introduced for each inequivalent plane $n = 1, \ldots, N_{\mathrm{CPA}}$. In the tight-binding framework these quantities are obtained by the self-consistency equation

$$c_n^A t_n^A + c_n^B t_n^B = 0 \ , \tag{2}$$

where t_n^i $(i = A, B)$ is the scattering t matrix given by

$$t_n^i = \frac{\varepsilon_n^i - \sigma_n}{1 - (\varepsilon_n^i - \sigma_n) F_n} \tag{3}$$

with

$$F_n = \frac{1}{9} \sum_{\lambda} F_n^{\lambda} \ , \tag{4}$$

where F_n^{λ} is the diagonal matrix element $\hat{G}_{nn}^{\lambda\lambda}(E)$ of the CPA Green's function operator $\hat{G}$ defined through

$$\hat{G}(z) = (z - H_{\mathrm{CPA}})^{-1} \ , \tag{5}$$

where H_{CPA} is the CPA Hamiltonian, similar to (1) but with the on-site energy replaced by the coherent potential σ_n (taken here to be orbital independent):

$$\begin{aligned} H_{\mathrm{CPA}} = {} & \sum_{n,\lambda} |n,\lambda\rangle \sigma_n \langle n,\lambda| \\ & + \sum_{n \neq m, \lambda, \mu} |n,\lambda\rangle \beta_{nm}^{\lambda\mu} \langle m,\mu| \ . \end{aligned} \tag{6}$$

Thus, the actual Hamiltonian may be broken up into a CPA contribution and a configuration-dependent perturbation term:

$$H(\sigma) = H_{\mathrm{CPA}} + H \ , \tag{7}$$

where

$$H = \sum_{n,\lambda} |n,\lambda\rangle (\varepsilon_n^{\lambda} - \sigma_n) \langle n,\lambda| \tag{8}$$

is the perturbation term which gives the method its name.

Introducing the occupation numbers p_n^i, equal to 1 if site n is occupied by an atom of type i and equal to 0 otherwise, the total energy of the binary alloy with N sites for a configuration $\{p_n^i\}$ can be written as[38]

$$E(\{p_n^i\}) = E_0 + \frac{1}{N} \sum_{n,i} p_n^i V_n^i + \frac{1}{2N} \sum_{n \neq m, i, j} p_n^i p_m^j V_{nm}^{ij} + \cdots \ , \tag{9}$$

where V_n^i is the point energy,

$$V_n^i = \frac{1}{9\pi} \mathrm{Im} \int^{E_F} dE \sum_{\lambda} \ln[1 - (\varepsilon_n^{\lambda} - \sigma_n) F_n^{\lambda}] \ , \tag{10}$$

and V_{nm}^{ij} is a pair energy,

$$V_{nm}^{ij} = -\frac{1}{9\pi} \mathrm{Im} \int^{E_F} dE \sum_{\lambda,\mu} (\hat{G}_{nm}^{\lambda\mu})^2 t_n^i t_m^j \ . \tag{11}$$

Higher-order contributions may be derived in a similar manner and temperature may be included by multiplying the integrand by a Fermi function. It is important to note that these expressions are exact for a given configuration $\{p_n^i\}$. As Eqs. (10) and (11) show, the quantities V_n^i and V_{nm}^{ij} must be obtained through an electronic structure calculation, clearly illustrating that ordering phenomena in alloys are driven by variations in the electron states. Note that in the above derivation it has been assumed, as is customary, that only the one-electron band-structure term contributes to the energetics.[39] While the derivation in terms of the GPM is the most transparent, a number of alternative techniques have been proposed to calculate the ordering interactions. These methods include the embedded cluster method (ECM) of Gonis and collaborators[40] which has been shown to be equivalent to the GPM,[41] the method of concentration waves proposed by Gyorffy and Stocks,[42] the Connolly-Williams method,[43] and the closely related ε-G approach of Zunger and collaborators.[6] There are minor differences between these various procedures, depending mainly on the level of truncation of the series (9), but all have been successfully used to describe bulk alloys in a first-principles setting.

In order to better understand the physical meaning of the point and pair energies (10) and (11) and to make the connection with the Ising model calculations it is instructive to look at their interpretation in a statistical physics context. To this end we can use an elegant expression for the internal energy first given by Sanchez, Ducastelle, and Gratias.[44] Introducing pseudospin variables σ_n (not to be confused with the CPA potentials; these variables are equal to $+1$ if site i is occupied by an A atom, and to -1 otherwise, i.e., $\sigma_n = 2p_n^A - 1$), these authors have shown that the internal energy can be written as a sum over all clusters α in the given system

$$E = V_0 + \sum_{\alpha} V_{\alpha} \xi_{\alpha} \ , \tag{12}$$

where ξ_{α} is the correlation function for cluster α defined by

$$\xi_{\alpha} = \langle \sigma_1 \sigma_2 \cdots \sigma_{n_{\alpha}} \rangle \ , \tag{13}$$

if there are n_{α} sites in the cluster considered. Here and in the remainder of this paper the angular brackets denote an ensemble average. Within this formalism the V_{α} are called effective cluster interactions (ECI). For a pair of atoms, one at site n, the other at site m, the ECI reduces to an effective pair interaction (EPI) which reads

$$V_{nm} = \tfrac{1}{4} (W_{nm}^{AA} + W_{nm}^{BB} - W_{nm}^{AB} - W_{nm}^{BA}) \ , \tag{14}$$

where W_{nm}^{ij} is the total energy of the system consisting of an atom of type i at site n and an atom of type j at site m

in the fully disordered medium.[45] After transformation of the correlation functions to occupation numbers, a formal identification can be realized between the two expressions (9) and (12) leading to the conclusion that V_n^i, the point energy defined in (10), is equal to the total energy of the system containing one atom of type i at site n in the completely disordered medium, while V_{nm}^{ij}, the pair energy defined in (11), is equal to $W_{nm}^{ij}-(V_n^i+V_m^j)$.

In addition, a reference level for the energies can be chosen, since it is always possible to add a constant term to the free energy. Although this is an arbitrary choice it must be a reasonable one on physical grounds and for the bulk alloy it has been shown that the CPA medium is the best one. For an alloy surface, however, the situation is more complex and the following two cases can be considered. In situation A examined in the remainder of this paper the temperature is higher than T_c, the critical order-disorder temperature for the bulk at the concentration being studied. In that case it is very reasonable to take as the reference medium the completely disordered state described by the CPA. At temperatures below T_c (situation B) ordering occurs and consequently the disordered state is not a good reference point and no reference level is explicitly considered. This case has been studied extensively by Tréglia, Legrand, and collaborators[46–52] and we refer the reader to these papers for further details.

For a binary AB alloy and using the CPA medium as the reference level, Eq. (9) can be rewritten as follows. If p_n equals p_n^A, then $p_n^B=1-p_n$, and using the CPA self-consistency equation the total energy is

$$E(\{p_n^i\})=V_0+\frac{1}{N}\sum_n (p_n-c_n)(V_n^A-V_n^B)+\frac{1}{2N}\sum_{n,m}(p_n-c_n)(p_m-c_m)V_{nm}+\cdots\ , \quad (15)$$

where c_n is the concentration on plane n and V_{nm} equals

$$V_{nm}=V_{nm}^{AA}+V_{nm}^{BB}-V_{nm}^{AB}-V_{nm}^{BA}\ . \quad (16)$$

This gives the connection between the EPI defined in the statistical physics context (14) and the pair energies defined in (11) in terms of the electronic structure. In practice it has been found[53] that in many cases nearest-neighbor pairs for the fcc structure and nearest- and next-nearest-neighbor pairs for the bcc structure provide an accurate description of the corresponding phase diagram. However, for certain alloys higher-order clusters and further-neighbor interactions may be needed, such as in the case of PdV.[54,55]

In the same manner we can identify in (15) the effective point interaction Δ_n given by

$$\Delta_n=V_n^A-V_n^B\ . \quad (17)$$

This quantity gives the variation of the total energy of the disordered alloy when at site n a B atom is replaced by an A atom. For equivalent sites in the bulk, Δ_n is unique (i.e., independent of n) but for an alloy with a surface different values must be computed according to the plane considered. Moreover, when all sites are equivalent (as in the bulk of the fcc lattice) the single-site interaction does not contribute to the ordering energy and thus there is no need to calculate it explicitly in a thermodynamic study. Finally, it is important to note that although the total energy of a transition metal cannot be written as a sum of pair potentials, the ordering energy can be written as a rapidly convergent series of point and pair interactions.[2]

For an alloy in which successive layers are completely disordered the p_n's are uncorrelated so that in such a case we can write

$$\langle (p_n-c_n)(p_m-c_m)\rangle=\langle p_n-c_n\rangle\langle p_m-c_m\rangle=0\ , \quad (18)$$

and thus only the point energies V_n give a nonzero contribution in Eq. (15). In this case the segregation phenomena, for the electronic part at least, are only driven by the values of the point energies. However, when ordered structures are present (corresponding to situation B above) the EPI's give an explicit contribution.[46–52]

Expression (15) for the internal energy may be used in a Monte Carlo simulation or in a mean-field calculation based on the cluster variation method (CVM).[12,56] In the latter case, in addition to the internal energy one needs to know an approximate expression for the entropy in order to perform a phase diagram calculation. Depending on the temperature under study one may have to include clusters up to a certain maximum size in the formalism. For temperatures above T_c the point-approximation or Bragg-Williams method is known to give adequate results,[57] but in other cases larger clusters may be needed.[56] In either case, the self-consistent equilibrium profile is obtained by minimizing the resulting free energy relative to the concentrations in the various planes. A complication arises because, for a semi-infinite binary alloy, all the quantities V_n^i and V_{nm}^{ij} are functions of the concentration profile as can be seen from Eqs. (10) and (11) while they also determine the concentration profile. Thus, a fully self-consistent calculation must be performed: starting from an initial guess for the concentrations one iterates until the interactions and concentration profile are consistent. This approach corresponds to the canonical ensemble and details of computations based on it will be given further in this paper. We remind the reader that the present derivation assumes that the CPA is a good reference medium and thus it is expected to be valid for temperatures above T_c (situation A defined above). In that case, the segregation is driven by the sign of the variation of the effective *point* interaction $\Delta_1=V_1^A-V_1^B$ between the surface and the bulk (as long as no elastic contribution to the free energy is considered) and an electronically self-consistent calculation of the Δ's is essential. To simplify this calculation it is tempting to speculate about alternative approaches. It has previously been demonstrated that for bulk alloys a grand canonical approach can be used with success.[54] In the case of a semi-infinite alloy this would correspond to a system with the same concentration of A and B atoms on all the planes. By analogy to the bulk case the convergence of expression (9) may be expected to be slower in the grand canonical case than in the canonical case. The viability of this formalism remains to be established and is currently under study. The calculations presented here have been performed for the canonical case.

For alloys with a surface, translational symmetry perpendicular to the surface of the disordered medium is lost, while parallel to the surface it has been restored by the CPA condition. Thus, for a given separation between sites n and m, not only one EPI, as in the bulk, must be considered, but different values according to the position of n and m. For example, if only nearest neighbors on a fcc lattice are considered, terms such as $V_{n,n}$ and $V_{n,n+1}$ must be retained (n labels planes parallel to the surface, $n=1$ is the top layer). In order to have a systematic notation, one can extend a convention introduced previously[54] according to which $V^{m_1 m_2 \cdots m_{n1}}_{n_1 n_2}$ is the ECI with n_1 atoms that are neighbors of order n_2, and in which $m_1, m_2, \ldots$ label the planes parallel to the surface. For example, V^{12}_{21} denotes the effective pair (subscript 2) interaction between nearest (subscript 1) neighbors with one atom in the surface plane (superscript 1) and the other one in the plane immediately below the surface (superscript 2). For point energies the index n_1 is equal to 1, for pair energies n_1 equals 2, etc. For higher-order clusters a graphical representation must be given.[54]

The main problem is now to compute the point energies and in a general manner the effective cluster interactions. As mentioned before, various approaches for bulk binary alloys have been proposed,[6,38,40–43] but for a semi-infinite medium a supplementary difficulty arises due to the lack of translational symmetry in the direction perpendicular to the surface or interface, which makes use of the CPA cumbersome. Recently we proposed a conceptually simple method based on taking an average over a small number of random configurations to obtain the effective cluster interactions.[45,58] In principle, the ECI are differences of total energies of large systems, but since only localized perturbing potentials are considered the effective cluster interaction can be obtained directly as a global expression, using the generalized phase-shift approach.[59] Following Friedel, the generalized phase shift may be defined as

$$\eta(z)=\ln\frac{\det G^{\sigma}_{AA}\det G^{\sigma}_{BB}}{\det G^{\sigma}_{AB}\det G^{\sigma}_{BA}} , \tag{19}$$

where G^{σ}_{ij} is the Green's function corresponding to the Hamiltonian (1) but with atoms i and j at sites n and m. (This quantity is not to be confused with the CPA Green's function.) We have shown elsewhere[58] that the EPI may be written as

$$V_{nm}=\left\langle -\frac{1}{4\pi}\mathrm{Im}\int_{-\infty}^{E_F}\eta(z)dz\right\rangle . \tag{20}$$

The recursion method, introduced in solid-state physics by Haydock,[60] permits a calculation of the Green's functions G^{σ}_{ij} in real space and, by using the "orbital peeling trick" proposed by Burke[61] following the ideas of Einstein and Schrieffer,[62] the determination of the effective pair interaction needs the computation of only 4×9 diagonal elements of the Green's function, while the point interaction needs only 2×9 terms.

In this paper we will focus on the simple but physically interesting case of the fully disordered alloy at temperatures T above the bulk order-disorder temperature T_c. In that case the Bragg-Williams method is known to produce quite accurate results.[57] Thus, only the point correlation functions need to be considered and the entropy reduces to

$$S=\sum_n c_n \ln c_n+(1-c_n)\ln(1-c_n) . \tag{21}$$

The equilibrium concentration profile is obtained by minimizing the free energy with respect to the correlation functions (i.e., concentrations) and, denoting by c_B the bulk concentration, we find in a straightforward manner

$$\frac{c_n}{1-c_n}=\frac{c_B}{1-c_B}\exp[-(V^A_n-V^B_n)/k_BT] \tag{22}$$

(where k_B is Boltzmann's constant), a result remarkably similar to that obtained in phenomenological theories[21] but with point energies, rather than EPI's, in the exponential. If elastic contributions to the free energy are considered, they appear in the exponential of Eq. (22). This is essential when the atomic sizes are very different. *A priori* the point energies are functions of the concentration profile and to a good approximation they turn out to depend only on the plane considered.

In more complex situations and below T_c ordering may occur and the contribution of the EPI's to the free energy can no longer be neglected. In that case a set of coupled transcendental equations for the concentrations in the layers is obtained which must be solved numerically. These equations are similar to those in Ref. 21, but with concentration-dependent EPI's and point interactions, for example, if only nearest-neighbor EPI's are included for the (100) surface on the fcc lattice they read

$$\overline{\sigma_n}=\tanh\{[4V_{nn}\overline{\sigma_n}+4V_{n,n-1}\overline{\sigma_{n-1}}+4V_{n,n+1}\overline{\sigma_{n+1}}-\Delta_n]/k_BT\}, \quad n=1,2,\ldots, \tag{23}$$

where $\overline{\sigma_n}=2c_n-1$, is the average value of the pseudospin variable in the nth plane and $\overline{\sigma_0}\equiv 0$. In simple situations the numerical solution of the system (23) may be accomplished by straightforward iteration to the fixed point of the equations, but this approach has the drawback that it cannot detect whether multiple solutions are present. The same holds for the more rapidly convergent Newton-Raphson scheme. To avoid this shortcoming an elegant method was proposed by Tréglia *et al.*[46–52] following earlier work by Pandit and Wortis[63] based on the properties of flow under area-preserving maps. This mathematical approach to solving coupled equations allows the numerical algorithm to detect multiple solutions and to describe discontinuous and layering transitions, although the method is intrinsically unstable and numerically not very accurate. A complete study should use the area-preserving map approach to describe the transitions and then utilize a more stable algorithm to compute the precise location of the phase boundaries. In the following we shall consider only cases where the solutions are unique and these complications do not arise.

In this paper we study two alloys which present different behavior in the bulk: the Ni_xCu_{1-x} system, which is well known to possess a large miscibility gap,[64] and the Rh_xTi_{1-x} alloy, which exhibits various ordered phases.[65] Bulk calculations for both systems have been reported recently.[66,7,58] The choice of these systems was guided by the fact that magnetic effects are negligible (except perhaps at the Ni-rich end of the Ni-Cu system), relativistic effects may be safely ignored, and atomic size differences are small so that elasticity must not be included in the calculations. Preliminary results using the direct configurational averaging approach were briefly presented elsewhere.[67,68] After the determination of the equilibrium profile we shall concentrate on the properties of the ECI, with particular emphasis on the point interactions and the EPI.

III. RESULTS

Some of the advantages of the direct configurational averaging (DCA) method are that it avoids the CPA approximation, that it permits a calculation in real space, and that it allows the possibility to take into account *s*, *p*, and *d* orbitals on the same footing. In addition the recursion method also supports a straightforward treatment of the off-diagonal disorder, which in the CPA framework introduces complications.[69] Three different sets of hopping integrals were used: β^{AA} and β^{BB} are generally taken to be the same as for the pure elements and may therefore be computed with a good level of accuracy,[29,45] a reasonable and widely adopted assumption[70] is to take β^{AB} as the geometric mean of β^{AA} and β^{BB} (i.e., $\beta^{AB}=\sqrt{\beta^{AA}\beta^{BB}}$, the so-called Shiba prescription). Alternatively, if calculations for the ordered AB compound are available they might be used to determine the hopping integral β^{AB}. In the Slater-Koster scheme,[71] $\beta_{IJ}^{\lambda\mu}$ are related to the three- and two-center integrals. Electronic self-consistency is ensured as customary by imposing local charge neutrality through a rigid shift of the on-site energies. In practice, it is found that perturbing potentials are only needed for the surface plane and the two following planes. Effective cluster (point, pair, etc.) interactions are obtained after a two-level self-consistency loop. First, for a given concentration profile, the perturbing potentials on the planes in the surface region are determined. Next the concentration profile is adjusted in order to obey Eq. (22) or (23). A careful investigation of the variation of the point and pair interactions has shown that in the cases studied here these quantities are sensitive only to the immediate neighbors leading to a reasonable computation time.

Formally, the method developed for alloy surfaces by Tréglia *et al.*[46–52] is similar to our approach. As discussed before, apart from the source of the tight-binding parameters and other technical details, the main difference lies in the choice of the reference medium. A semi-infinite medium with the same concentration and the same coherent potential (corresponding to the bulk value) on every plane was chosen by Tréglia *et al.* As a consequence these authors must explicitly consider effective pair interactions in addition to the effective point interactions at all temperatures. As already discussed[72] the choice of the reference medium is arbitrary, but it is intuitively clear and borne out by our calculations that our approach, for temperatures above T_c (situation A), gives better convergence. In other cases one must consider renormalized effective cluster interactions[48,54] and the problem is again to determine those cluster interactions that give significant contributions. From previous studies,[54] one may expect that in certain cases triplet interactions may be of the same order of magnitude as some pair interactions.

In this work we report results obtained for two semi-infinite alloys: Ni_xCu_{1-x} (all x) which presents a clustering trend in the bulk and Rh_xTi_{1-x} (near $x=0.75$) which exhibits various ordered structures. For the compositions considered both alloys are based on a fcc lattice of which, unless otherwise specified, the (001) surface will be considered. Preliminary results were briefly presented elsewhere.[67,68] All calculations were performed for temperatures above the bulk critical temperature, corresponding to a completely disordered system in the bulk, but this does, of course, not exclude ordering in the surface region. In this temperature regime the Bragg-Williams approximation is known to work quite satisfactorily.[57] Let us note that for temperatures below T_c the physical processes are more complex because the average concentration defined on each plane may differ strongly from the average concentration in the bulk. As a simple example, consider an AB_3 alloy in the LI_2 structure. At low temperatures, parallel to the (001) surface, the lattice is a succession of planes with compositions close to 100% B and 50% B, although at the surface and in the immediate subsurface layers the concentration may differ from these values due to segregation effects. In any case, apart from the problems of a proper reference medium discussed above, a simple Bragg-Williams approach, which neglects correlations, is inconsistent and a generalization of the cluster variation method appropriate for surfaces must be used.[56]

In the present work *s*, *p*, and *d* orbitals are considered. If only *d* orbitals were included the factor 9 in Eqs. (4), (10), and (11) would be replaced by 5. The hopping integrals for the pure elements are taken from Papaconstantopoulos's book[29] and were obtained by this author through a fit to very accurate first-principles LAPW calculations for the pure elements. The recursion method was applied using the algorithms developed by Nex and collaborators.[73] As usual, local charge neutrality was imposed on each atom through a rigid shift of the on-site energies.[45,58] Seven levels of the continued fraction for the Green's function diagonal elements have been computed, with the Beer-Pettifor[74] prescription for the termination of the continued fraction. In order to obtain satisfactory convergence it was found for the point energies to be necessary to average over 20 configurations while for the pair energies 15 configurations were needed. Higher-order and further-neighbor cluster interactions were found to be negligible in all cases studied here. These findings are consistent with our earlier studies using the DCA for the bulk.

The Ni_xCu_{1-x} system has been the subject of many experimental[75-88] and theoretical[81,89-96] investigations. Even though it is a relatively simple alloy, whose bulk phase diagram is well understood, its surface behavior has been the source of some controversy. A large number of experiments using a diversity of surface-sensitive probes (catalytic activity measurements,[75] Auger electron spectroscopy,[76] x-ray and ultraviolet photoemission spectroscopy,[77,80,81,88] time-of-flight atom probe,[78,83,86] low-energy ion scattering,[79,82,84,85,87] photoemission of adsorbed xenon,[87] low-energy electron diffraction, etc.) have provided incontrovertible evidence that Cu segregates strongly to the surface for all compositions, with the surface concentration increasing monotonically as a function of the bulk concentration, x. It came therefore as a great surprise when Sakurai *et al.*[83] reported evidence for a reversal in segregating species with Ni segregating for compositions less than $x=0.16$ and Cu segregating for concentrations larger than this value. While there was originally some theoretical evidence that such a phenomenon might be understood in terms of surface magnetism[90] or charge transfer,[91] more careful studies[93] did not support this notion. Moreover, subsequent experiments did not confirm Ni segregation for small x and several suggestions were made to explain the experimental observations. It was pointed out,[84] for example, that a small concentration of contaminants (specifically, sulfur or oxygen) might lead to precisely the type of effects that were observed by Sakurai *et al.*[83] This illustrates clearly how sensitively the surface concentration may depend on the overall composition and, in particular, the local electronic structure. A second debated observation for the Ni-Cu system concerns the composition of the subsurface layers, with some experimentalists claiming that the approach to the bulk limit is monotonic, while others find evidence for Cu depletion in the layer immediately below the surface.[78] Theoretical analyses of this system have also given mixed results. Because the determination of the equilibrium subsurface concentration is a notoriously difficult problem reasonable doubt may still be cast on either observation.

In Fig. 1, we display the concentration profile near a Ni_xCu_{1-x} (001) alloy surface with the bulk Ni concentration kept at $x=0.75$ and 0.25, at a temperature $T=1.1T_c$ [corresponding to approximately 225 and 425 °C, respectively]. As observed experimentally, very strong Cu segregation occurs towards the surface plane with the composition in the subsurface layers very rapidly approaching the bulk concentration. This was found to be the case over the entire concentration range and, in particular, no reversal in segregating species was observed. It is to be noted that our calculations properly account for charge-transfer effects and therefore do not support an earlier suggestion that charge transfer might be responsible for a segregation reversal. As can be seen in Fig. 1, the concentration profile is monotonic reflecting the clustering tendency of the Ni-Cu system, as would also be predicted by the phenomenological theories. In all cases studied we found the approach to the bulk value to be monotonic, with no evidence for Ni enrichment just below the surface. Thus, we disagree with other experimental[78] and theoretical[96] works in which a Cu deficiency was observed. While it is clear from the sign of the point interactions calculated here that such an effect is not expected on the basis of electronic interactions alone, it may be due to contributions that were neglected here, most likely of elastic or magnetic origin. However, it is also possible that the experimental observations were based on nonequilibrium phenomena, for example, due to sputter-induced subsurface segregation.[79] Thus, the issue deserves further study.

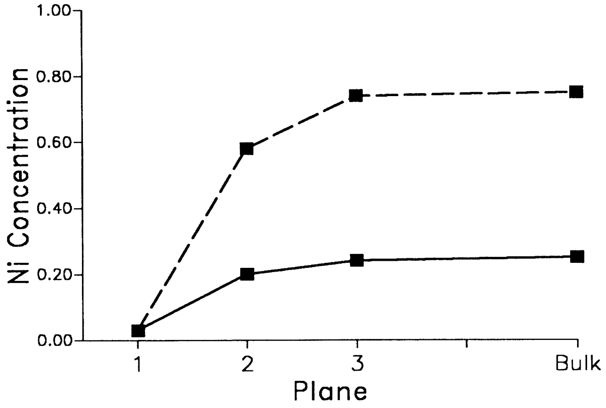

FIG. 1. Self-consistent equilibrium concentration profiles at (001) surface of Ni_xCu_{1-x} alloy ($T=1.1T_c$): the solid line corresponds to $x=0.25$; the dashed line to $x=0.75$.

In Fig. 2, we show the equilibrium profile at a temperature $T=1.1T_c$ (approximately 1925 °C) near the (001) face of a Rh_xTi_{1-x} system with a fixed Rh bulk concentration $x=0.75$. The segregation profile is oscillatory, as expected for an ordering alloy, with a very rapid ap-

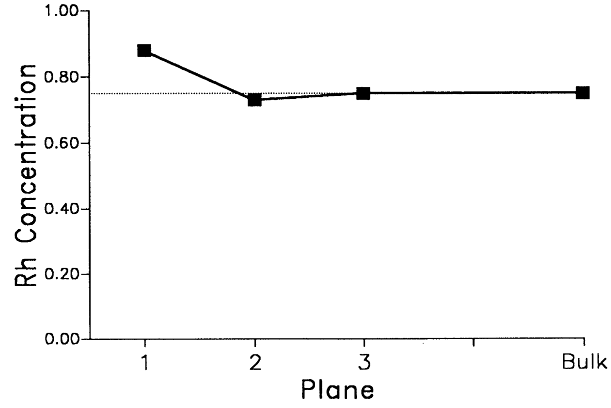

FIG. 2. Self-consistent equilibrium concentration profile at (001) surface of Rh_xTi_{1-x} with a bulk Rh concentration $x=0.75$ at temperature $T=1.1T_c$.

proach of the bulk limit. Our calculations predict moderate Rh (solvent) enrichment. Unfortunately no experimental results seem to be available for this system. It is suggested that this would be a good system for further study, as the Miedema theory[23,24] predicts no segregation, while the current work and a model based on surface enthalpies[24] predict Rh segregation. It is interesting to note that the surface enthalpies are directly proportional to the point energies included in our model.

IV. DISCUSSION

Because they are key quantities in the formalism and also because their determination is the computational bottleneck, we now turn to a more detailed discussion of the interaction parameters, specifically the pair and point interactions as higher-order terms turned out to be negligible in the system studied here. In order to better understand the effects of electronic and atomic self-consistency various "artificial" (i.e., non-self-consistent) configurations will be considered. While the motivation is mainly pedagogical, nonequilibrium profiles may be realized experimentally by rapid quenching or ion bombardment and thus the nature of the interactions under those conditions may have some independent interest. Also adsorbed monolayers may alter the equilibrium segregation profile and lead to concentration gradients similar to those introduced here.

A. Effective pair interactions

The EPI's play a major role in the ordering processes in bulk binary alloys. These quantities can be measured experimentally through diffuse scattering intensities[97] and can be computed by techniques such as the inverse Monte Carlo method.[98] They also have a simple physical interpretation: $V_{nm} > 0$ (<0) indicates an ordering (clustering) trend between sites n and m. Of course, the interplay between the ordering tendencies of various sites may lead to complicated ordered structures, even when only short-range interactions are considered, one famous example being the axial next-nearest-neighbor Ising (ANNNI) model[99] which supports a whole range of modulated states. A knowledge of the EPI's is also necessary to perform a zero-temperature ground-state analysis,[100] the first step in a full phase diagram calculation. In the case of a semi-infinite alloy below the bulk T_c, the variations of the EPI are essential to study segregation and ordering phenomena and they are also key ingredients in phenomenological theories.[21] As was discussed before, only for completely disordered systems are the segregation phenomena driven exclusively by the variation of the point energies.

First we investigate the variation of the EPI as a function of the concentration profile. Brown and Carlsson[101] performed a model study of the influence of defects (localized or extended) on the EPI. The results obtained by those authors showed an increase of the EPI with decreasing coordination number. However, the calculations were made under very restrictive assumptions: neither off-diagonal disorder nor electronic self-consistency were considered and the concentration profile was taken to be flat (uniform concentration on all the planes). Under these conditions, Brown and Carlsson[101] showed that the EPI are proportional to $Z^{-3/2}$, where Z is the coordination number. However, binary alloys are well known to present strong segregation effects on the surface plane. In addition, since the EPI in the bulk may vary strongly as a function of concentration[45] *a priori* no general rule for the value of the EPI on the surface plane can be expected and a complete study must be made.

In Fig. 3 we present the variation of the EPI for two nearest neighbors located in various layers in a semi-infinite $\mathrm{Ni}_x\mathrm{Cu}_{1-x}$ host for the equilibrium profiles (shown in Fig. 1) corresponding to bulk concentrations $x = 0.75$ and 0.25. It is to be kept in mind that in both cases the concentration of Ni on the surface plane is very small as was found throughout the entire concentration range. Calculations for bulk Ni-Cu (Refs. 66 and 102) show a decrease of the nearest-neighbor and next-nearest-neighbor EPI's with decreasing Ni concentration. These results combined with Fig. 3 thus point to a competition between the values in the bulk and those at the surface. For a bulk concentration $x = 0.75$ we also observe a large variation of the EPI for a point in the surface plane and the other point in the plane immediately below it. The strong changes of the EPI in this case are a consequence of the large variations in composition near the surface. The variations in the concentration profile are relatively smaller for a Ni bulk concentration $x = 0.25$ and the variations of the EPI in that case are consequently also much smaller.

In $\mathrm{Rh}_x\mathrm{Ti}_{1-x}$ the EPI have been found to be very sensitive to the concentration in the bulk.[45] In Fig. 4 are reported the nearest-neighbor EPI's of a $\mathrm{Rh}_x\mathrm{Ti}_{1-x}$ alloy with a Rh bulk concentration $x = 0.75$. Two electroni-

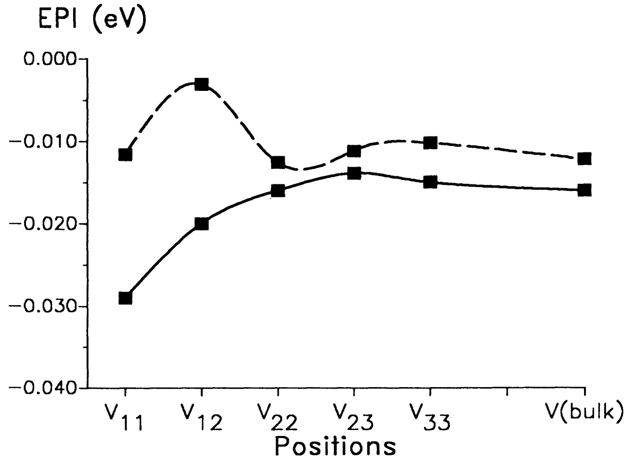

FIG. 3. Nearest-neighbor effective pair interactions, V_{21}^{nm} (in eV), at the (001) surface of a $\mathrm{Ni}_x\mathrm{Cu}_{1-x}$ alloy with a bulk concentration $x = 0.25$ (solid line) and $x = 0.75$ (dashed line) for the equilibrium profile given in Fig. 1. For ease of notation V_{21}^{nm} is denoted as V_{nm} where the index 1 denotes the surface plane. These curves are obtained through a fully self-consistent calculation.

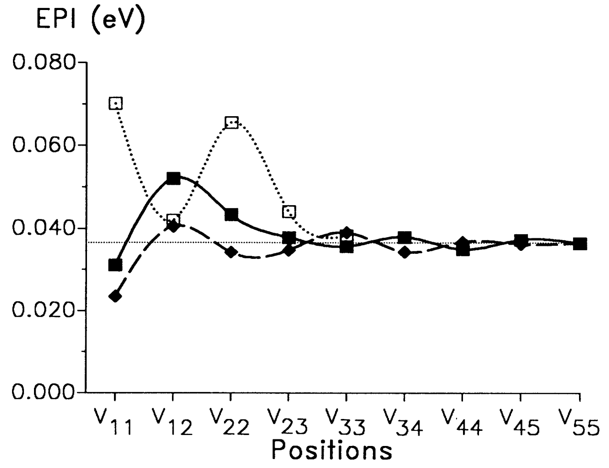

FIG. 4. Nearest-neighbor intralayer (V_{nn}) and interlayer ($V_{n,n+1}$) effective pair interactions (in eV) at the (001) surface of a Rh_xTi_{1-x} alloy with a Rh bulk concentration $x=0.75$ for various concentration profiles (solid line: equilibrium profile from Fig. 2; dashed line: $c_1=0.52$, $c_2=0.78$, $c_3=0.74$, $c_n=0.75$, $n>3$; dotted line: $c_n=0.75$ for all n). The curves in the solid and dashed lines were calculated with full electronic self-consistency imposed. The dotted curve corresponding to the uniform profile was obtained without any electronic self-consistency.

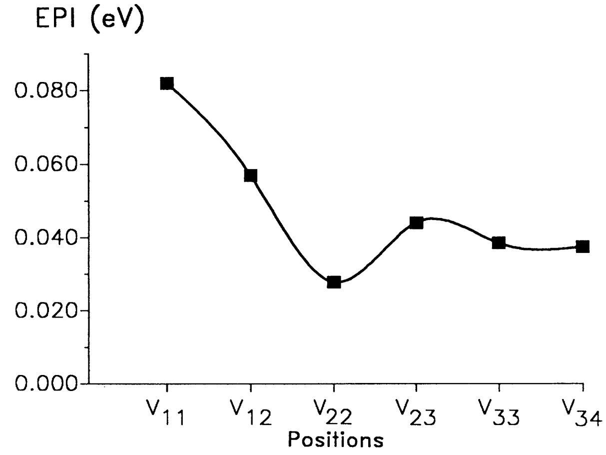

FIG. 5. Nearest-neighbor intralayer (V_{nn}) and interlayer ($V_{n,n+1}$) effective pair interactions (in eV) at the (001) surface of a Rh_xTi_{1-x} alloy with a Rh bulk concentration of 0.50 for a uniform concentration profile. This curve was obtained with full electronic self-consistency imposed and the alloy assumed to be in a hypothetical fcc structure.

cally self-consistent concentration profiles were considered: one (solid line) corresponding to the equilibrium profile given in Fig. 2, the other one (dashed line) artificially corresponding to a strong depletion of Rh in the surface plane ($c_1=0.52$) with an oscillating profile ($c_2=0.78$, $c_3=0.74$, $c_n=c_B=0.75$ for $n>3$). We observe in both cases a small decrease in surface intralayer EPI relative to the bulk value and a mild increase for the surface-subsurface interlayer EPI. Let us recall that the bulk EPI of the fcc Rh_xTi_{1-x} alloy is an increasing function of the Rh concentration.[45] The differences between these two self-consistent profiles can, as in the previous case of Ni_xCu_{1-x}, be understood as a competition near the surface between the EPI bulk values and the local surface concentration. Of course, this is only a qualitative argument that must be backed up by a full calculation. In Fig. 4, we also report by a dotted line the EPI corresponding to an alloy with a $c_n=0.75$ for all planes and no electronic self-consistency. We notice a sharp increase of the EPI near the surface, especially the intralayer interactions, in agreement with the calculations of Tréglia *et al.*[46-52] and Brown and Carlsson[101] who also did not consider electronic self-consistency.

The relative influence of the concentration profile and coordination number can be deduced from Fig. 5, which shows self-consistent EPI for the (001) surface of Rh_xTi_{1-x} (assumed to be in the fcc structure) with a Rh bulk concentration $x=0.50$. A uniform segregation profile with $c_n=0.50$ on each plane is assumed and the calculations have been driven to full electronic self-consistency. We observe a sharp increase of the intralayer surface EPI, V_{11}, and the surface-subsurface EPI, V_{12}, a result that is to be expected according to the arguments of Brown and Carlsson.[101] In this particular case it turns out that the effects are amplified by the surface charge redistribution, although this is by no means a general trend.

We can conclude that similarly as in the bulk the EPI are functions of the concentration profile. This points out the importance of the compositional and electronic self-consistency. Let us note that in the present work the point energies and the effective pair interactions have been computed directly from the electronic structure and that the former dominate the segregation behavior (at least for temperatures above T_c). Simple models[21] predict that a positive (negative) EPI in the bulk will drive a nonmonotonic (monotonic) concentration profile. In our case the EPI for the systems considered here have the same sign and this simple relation appears to be satisfied.

B. Point energies

For $T>T_c$, in the Bragg-Williams approximation, the segregation is completely driven by the variation of the point energies relative to the bulk values. Special care must therefore be taken in their computation. As already pointed out, the point energies are functions of the concentration and a full calculation must be performed. However, it would be interesting to obtain general trends. In Ref. 68 we have reported the point energies for a surface atom of a Rh_xTi_{1-x} (001) alloy with a bulk Rh concentration $x=0.75$ for varying surface concentrations. The concentration profiles were scaled to present a similar oscillatory behavior. The main results were that for the non-self-consistent calculations, Δ_1^1 exhibits a decreasing, nearly linear behavior versus the surface concentration, the extremal values being around 0.55 to -0.20 eV, indicating a very important variation with a possible segregation-type change, while for the self-consistent calculations, a similar decreasing behavior was found but with a much smaller slope: the extremal values were around 0.29 and 0.18 eV (see Fig. 3 in Ref. 68).

In order to establish if this is a general type of behavior, we have investigated the point energies for the Ni_xCu_{1-x} alloy with $x=0.25$, 0.50, and 0.75 in the bulk and for various surface concentrations, for which the results are shown in Fig. 6. For $x=0.75$ calculations were performed with and without electronic self-consistency, while for $x=0.25$ and 0.50 only the non-self-consistent results are reported. These calculations were performed under the assumption of a monotonic concentration profile and the values for the concentration on the planes following the surface were scaled to be consistent with the equilibrium concentration profile (Fig. 1). First, it must be noted that in all cases the point energies versus the surface plane concentration present a nearly uniform monotonic behavior. As can be seen the effect of an electronically self-consistent treatment is to decrease the point energies. For a bulk Ni concentration $x=0.75$ the reduction is between about 0.10 eV for a Cu-rich surface and 0.20 eV for a Ni-rich surface. It is to be noted that, as in the Rh-Ti case,[68] the point energies in the self-consistent calculations vary less than if no self-consistency is considered. This makes compositionally self-consistent calculations feasible because an interpolation scheme on the point energies may be used to accelerate the iterative solution towards a self-consistent concentration profile. Another interesting result is that, in the non-self-consistent calculations, the point energies for various bulk Ni concentrations have roughly the same slope, the values increasing with an increase of the bulk Ni concentration.

As is known from phenomenological theories,[21] the surface crystallographic orientation plays an important role in determining the segregation profile. In Fig. 7 are reported the point energies for a Ni_xCu_{1-x} alloy with a bulk Ni concentration $x=0.75$ for the low-index surface orientations. Scaled monotonic concentration profiles were assumed and no electronic self-consistency was imposed. Again a nearly linear behavior was found with similar trends for the three curves. The magnitudes of the point energies decrease in going from the (110), to the (001), and finally (111) orientation: this corresponds exactly to going from the most open surface to the most closely packed one and is in agreement with simpler models.[21] It has been shown already that the Ni_xCu_{1-x} alloy is the prototype of an alloy where this simple phenomenological law applies.[27] As pointed out by Tréglia *et al.*,[49] these point energies are of the same order of magnitude as the difference of the surface tensions.

C. On the validity of the pair-interaction models

For transition metals it is well established that the total energy cannot be written as a sum of pair energies.[2] However, for the ordering energy in the bulk it has now amply been demonstrated that an expansion in effective pair interactions is feasible and rapidly convergent, although this argument does not necessarily hold in the case of inequivalent sites such as in the *A*15 compounds[72] or near a surface. However, the pair model in view of its simplicity is very attractive. The Ising model with only pair interactions has been studied in great detail and its properties are well understood. Therefore, it is very interesting to see under what conditions it is possible to utilize a pair energy expansion. We must insist that such an expansion has no formal justification but we would like to understand its success and limits of applicability. In a pair model, in the absence of elastic contributions, the segregation is driven by the variation of the quantity[21]

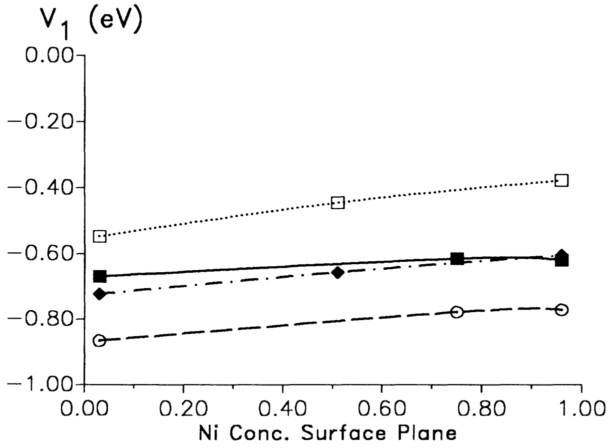

FIG. 6. Point energies at the (001) surface of a Ni_xCu_{1-x} alloy, for various Ni bulk concentrations: $x=0.25$ (dotted line), $x=0.50$ (dash-dotted line), and $x=0.75$ (dashed line). These three curves were obtained without electronic self-consistency. Also reported are the values obtained for a Ni bulk concentration $x=0.75$ with full electronic self-consistency (solid line). The concentration profiles were taken by appropriate scaling of the equilibrium profile (Fig. 1).

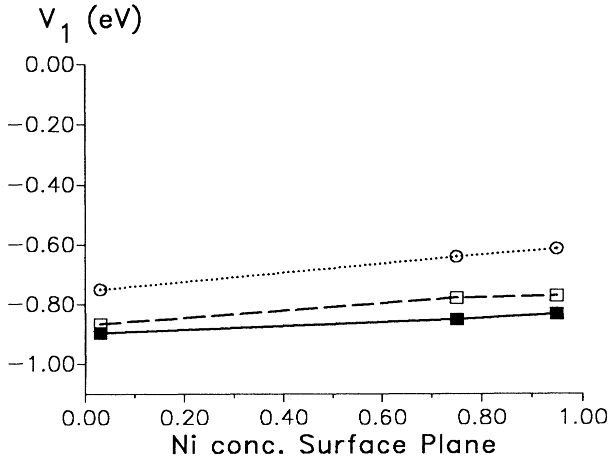

FIG. 7. Point energies at the surface of a Ni_xCu_{1-x} alloy with a Ni bulk concentration $x=0.75$ for various surface orientations: (110), solid line; (001), dashed line; and (111), dotted line. Electronic self-consistency has not been imposed. The concentration profiles were obtained by appropriate scaling of the equilibrium profile (Fig. 1).

TABLE I. Variation of the bond-breaking term Δ_{ij} and the point energy Δ_i (both in eV) relative to the bulk values near the (001) surface of a semi-infinite $Ni_{0.25}Cu_{0.75}$ and $Ni_{0.75}Cu_{0.25}$ alloy. All quantities have been calculated for the equilibrium concentration profile at $T=1.1T_c$ shown in Fig. 1. The index 1 or 2 denotes, respectively, a site on the surface plane or on the plane immediately below, while ∞ denotes a bulk site.

Ni bulk concentration	$x=0.25$	$x=0.75$
$\Delta_{11}-\Delta_{\infty\infty}$	-0.65	-1.29
$\Delta_{12}-\Delta_{\infty\infty}$	-0.15	-0.72
$\Delta_{22}-\Delta_{\infty\infty}$	-0.13	-0.14
$\Delta_{1}-\Delta_{\infty}$	-0.39	-0.67
$\Delta_{2}-\Delta_{\infty}$	-0.04	-0.13

$$\Delta_{nm}=\tfrac{1}{2}(V_{nm}^{AA}-V_{nm}^{BB}) \tag{24}$$

between the surface and the bulk (the "bond-breaking" term). In earlier works these quantities were considered as parameters and were fit to some macroscopic property often leading to quite good agreement with experiment. In the present work the bond-breaking terms were computed for the Ni_xCu_{1-x} system, within the DCA method, for two equilibrium profiles (Fig. 1) corresponding to a Ni bulk concentration $x=0.25$ and 0.75 (Table I). One can notice, especially for the $x=0.75$ bulk Ni concentration, that $(\Delta_{ij}-\Delta_{\infty\infty})$ is approximately equal to $(\Delta_i+\Delta_j-2\Delta_\infty)$. These bond-breaking terms are also functions of the concentration profile. Therefore, using a bond-breaking term computed from the electronic structure will lead to very similar results as using the exact expressions with the point energies. This result is not completely surprising, if we keep in mind the definition of the point and pair energies given in Eqs. (10) and (11). In fact, between say, V_{nn}^{AA} and V_n^A, the only difference is that for the first term one forces a given neighbor of a first A atom to be an A atom whereas for the second term this site has only a probability x to be occupied by an A atom. However, let us recall that it is this subtle difference which determines the value of the EPI. In a bulk alloy usually all the sites are equivalent and thus the phase diagram is computed from these EPI and if necessary higher-order cluster interactions. At the surface this no longer holds, but quite frequently the approximate relation mentioned above is satisfied, and thus a pair-interaction model with fitting parameters can provide an accurate description. However, it must be pointed out that an examination of other alloys shows that usually this relation is not as closely satisfied as for Ni_xCu_{1-x} with a Ni bulk concentration $x=0.75$ and consequently the predictions of the pair-interaction model are not as accurate. Nevertheless, in all cases studied the sign of the bond-breaking term was the same as that of the segregation energy given by the point terms, and thus no qualitatively incorrect predictions would result.

V. CONCLUSIONS

We have presented a detailed analysis of the Ising-model approach to surface ordering phenomena in terms of the electronic structure. The proper choice of a reference medium has been discussed and the role of the interaction parameters entering the formalism has been clarified. Self-consistent concentration profiles calculated without any adjustable parameters were obtained for the Ni_xCu_{1-x} and Rh_xTi_{1-x} systems. In the former case we find strong Cu enrichment at all surfaces and throughout the concentration range with no evidence for subsurface Cu depletion, which has been suggested by time-of-flight experiments and confirmed in a number of theoretical studies. However, there is no universal agreement on this behavior and further work needs to be done to settle this issue. For the Rh-Ti system we predict moderate Rh enrichment in agreement with one previous theoretical study, although other theories find no segregation. Clearly this would be a good system for experimental scrutiny and further first-principles work.

Our results indicate that for temperatures above T_c and in the absence of elastic effects the segregation is driven by the variation of the point energies which is the microscopic analogue of the difference of the surface tensions. Analogous effects were found in the Ni_xCu_{1-x} system by Tréglia *et al.*[49] using an approach similar to ours in the Bragg-Williams method and in a recent Monte Carlo study based on the same parameters.[95] Let us note that previous phenomenological models[21] have attributed to the sign of the EPI the character of the concentration profile: oscillatory or monotonic. In our exact derivation based on the underlying electronic structure, all the information is contained in the point energies. Clearly, the accurate determination of the point energies to calculate the equilibrium concentration profile is of the utmost importance. However, we find that the parameters used in phenomenological theories very frequently have the same sign and are approximately of the same magnitude as those entering our formalism, thus leading to predictions for the segregation behavior that are qualitatively remarkably accurate.

Future applications of our formalism for systems with atomic size disparities will incorporate a microscopic theory of the elastic contributions to the free energy. As discussed by Tréglia *et al.*[46–52] this may be accomplished through a second moment expansion, while it is also possible to treat these effects in Monte Carlo simulations.[94,96] Other lines of inquiry include the feasibility of a grand-canonical description discussed above, and a further analysis of the problem of an appropriate choice of reference medium which is extremely important in the case that ordered structures are present. The present formalism may be expanded to include magnetism which would permit us to study the interplay of magnetic and compositional ordering near surfaces and interfaces. Our computer programs may also be easily modified to handle segregation at internal interfaces for which exciting experimental results have been reported recently.[103]

One of the main motivations of the present study was to relate surface segregation to the electronic band structure without introducing any adjustable parameters. This was accomplished by using the recursion method with tight-binding parameters obtained through a fit to first-principles LAPW calculations.[29] While it would be preposterous to call this a true first-principles calculation, it is an important step towards such a scheme. In this regard it is of interest to mention some other recent methods that are based on a similar philosophy. The tight-binding LMTO method proposed by Andersen, Jepsen, and Sob[30] was recently extended to treat semi-infinite ordered[104] and disordered[105] systems. For alloys the method uses layer Green's functions techniques and imposes the CPA condition. No segregation profiles were calculated, but the relative magnitudes of the EPI's were studied. In agreement with our work it was found that the EPI depend strongly on the position and that in certain cases further-neighbor EPI's may dominate over the first-neighbor interactions. Applications so far have used self-consistent bulk potential parameters, but extension to appropriate surface potentials determined from slab or supercell calculations are envisioned. At present the method is restricted to the use of the atomic sphere approximation. Another approach based on density functional theory uses a generalization of the embedded atom method[106] (EAM) to the case of alloy surfaces.[94,96] As originally implemented[94] the method uses Monte Carlo simulations including atomic displacements in the grand-canonical ensemble keeping volume, total number of atoms, and chemical potential difference fixed. Because this is a very time consuming procedure, a recent implementation[96] has employed a free-energy minimization technique in the point approximation (similar to the present Bragg-Williams method) but with atomic vibrations included in the local harmonic model. Both implementations have been quite successful, but as they are based on the EAM potentials which are not unique and include fitting parameters they are somewhat less first principles then the present method and that based on the TB-LMTO scheme.[105]

In keeping with a similar trend for bulk phase stability calculations it may be questioned to what extent an LDA-based first-principles calculation of surface point and pair interactions may be accomplished without transforming to a tight-binding Hamiltonian. While the formalism to perform KKR-CPA calculations in a layer geometry has been around for a while,[107] it is only recently that the implementation of charge-self-consistent calculations has been accomplished.[108] Because such calculations are very time consuming, it seems impossible at present to perform the compositional self-consistency loop discussed in the present paper, to ensure that the interaction energies are calculated for the equilibrium concentration profile. This would be true irrespective of whether the GPM or the ECM are used to compute the energies. The only way out of this impasse would be to determine concentration-independent interactions in the grand-canonical approach alluded to before, but the viability of this scheme remains to be established and is currently under study. Because slab and supercell calculations have now reached the same level of accuracy as bulk calculations, one might alternatively want to start from first-principles calculations for the ordered compounds and extract ordering energies from those by application of the Connolly-Williams method. Although the number of interactions to be determined may be rather large, and some doubts will remain as to which interactions to include and which not, this might be a practical alternative. In particular, a judicious choice of the structures in the basis set might be possible, perhaps by a generalization to surface structures of the special quasirandom structures proposed by Zunger *et al.*[109] for bulk systems.

ACKNOWLEDGMENTS

We would like to thank the scientific committee of NATO and NSF-CNRS grants for partial financial support. L.T.W. is supported by Grant No. DE-FG05-89ER-45392 from the U.S. Department of Energy. D.d.F. is supported by the Director, Office of Energy Research, Materials Science Division, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

---

[1] D. de Fontaine, in *Electronic Band Structure and its Applications*, edited by M. Yussouf (Springer, Berlin, 1987), p. 410.

[2] A. E. Carlsson, Solid State Phys. **43**, 1 (1990).

[3] *Statics and Dynamics of Alloy Phase Transformations*, edited by P. E. A. Turchi and A. Gonis, 1992 (Kluwer, Dordrecht, in press).

[4] C. Sigli, M. Kosugi, and J. M. Sanchez, Phys. Rev. Lett. **57**, 253 (1986).

[5] K. Terakura, T. Oguchi, T. Mohri, and K. Watanabe, Phys. Rev. B **35**, 2169 (1987); T. Mohri, K. Terakura, T. Oguchi, and K. Watanabe, Acta Metall. **36**, 547 (1988).

[6] A. A. Mbaye, L. G. Ferreira, and A. Zunger, Phys. Rev. Lett. **58**, 49 (1987); S. H. Wei, A. A. Mbaye, L. G. Ferreira, and A. Zunger, Phys. Rev. B **36**, 4163 (1987); A. Zunger, S. H. Wei, A. A. Mbaye, and L. G. Ferreira, Acta Metall. **36**, 2239 (1988).

[7] M. Sluiter, P. Turchi, F. Zezhong, and D. de Fontaine, Phys. Rev. Lett. **60**, 716 (1988).

[8] M. Sluiter, D. de Fontaine, X. Q. Guo, R. Podloucky, and A. J. Freeman, Phys. Rev. B **42**, 10460 (1990).

[9] A. Qteish and R. Resta, Phys. Rev. B **37**, 6483 (1988).

[10] L. G. Ferreira, S. H. Wei, and A. Zunger, Phys. Rev. B **40**, 3197 (1989); J. E. Bernard, R. G. Dandrea, L. G. Ferreira, S. Froyen, S. H. Wei, and A. Zunger, Appl. Phys. Lett. **56**, 731 (1990); S. H. Wei, L. G. Ferreira, and A. Zunger, Phys. Rev. B **41**, 8240 (1990); K. C. Hass, L. C. Davis, and A. Zunger, *ibid.* **42**, 3757 (1990).

[11] P. A. Sterne and L. T. Wille, Physica C **162-164**, 223 (1989); in *Atomic Scale Calculations of Structure in Materials*, edited by M. S. Daw and M. A. Schluter, MRS Symposia Proceedings No. 193 (Materials Research Society, Pittsburgh, 1990); G. Ceder, M. Asta, W. C. Carter, M. Kraitchman, D. de Fontaine, M. E. Mann, and M. Sluiter, Phys. Rev. B **41**, 8698 (1990); L. Szunyogh and P. Weinberger, *ibid.* **43**, 3768 (1991).

[12] R. Kikuchi, Phys. Rev. **81**, 998 (1951); D. de Fontaine, Solid State Phys. **34**, 73 (1979).

[13] *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, Berlin, 1979).

[14] *Interfacial Segregation*, edited by W. C. Johnson and J. M. Blakely (American Society for Metals, Cleveland, 1979).

[15] W. M. H. Sachtler and R. A. Van Santen, Appl. Surf. Sci. **3**, 121 (1979).

[16] F. F. Abraham and C. R. Brundle, J. Vac. Sci. Technol. **18**, 506 (1981).

[17] P. M. Ossi, Surf. Sci. **201**, L519 (1988).

[18] *Surface Segregation Phenomena*, edited by P. A. Dowben and A. Miller (CRC, Boca Raton, 1990).

[19] D. McLean, *Grain Boundaries in Metals* (Clarendon, Oxford, 1957); M. P. Seah, J. Phys. F **10**, 1043 (1980).

[20] R. Lipowsky, Phys. Rev. Lett. **49**, 1575 (1982); R. Lipowsky and W. Speth, Phys. Rev. B **28**, 3983 (1983); D. M. Kroll and G. Gompper, *ibid.* **36**, 7078 (1987); G. Gompper and D. M. Kroll, *ibid.* **38**, 459 (1988).

[21] F. L. Williams and D. Nason, Surf. Sci. **45**, 377 (1974); D. Kumar, A. Mookerjee, and V. Kumar, J. Phys. F **6**, 725 (1976).

[22] F. F. Abraham, Phys. Rev. Lett. **46**, 546 (1981).

[23] A. R. Miedema, Z. Metallk. **69**, 455 (1978).

[24] J. R. Chelikowsky, Surf. Sci. **139**, L197 (1984).

[25] G. Kerker, J. L. Moran-Lopez, and K. H. Bennemann, Phys. Rev. B **15**, 638 (1977); S. Mukherjee, J. L. Moran-Lopez, V. Kumar, and K. H. Bennemann, *ibid.* **25**, 730 (1982).

[26] P. Lambin and J. P. Gaspard, J. Phys. F **10**, 2413 (1980); J. P. Muscat, J. Phys. C **15**, 867 (1982).

[27] R. Riedinger and H. Dreyssé, Phys. Rev. B **27**, 2073 (1983); H. Dreyssé and R. Riedinger, *ibid.* **28**, 5669 (1983); M. C. Desjonquères and D. Spanjaard, *ibid.* **35**, 952 (1987).

[28] S. Mukherjee and J. L. Moran-Lopez, Surf. Sci. **189/190**, 1135 (1987).

[29] D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[30] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984); O. K. Anderen, O. Jepsen, and M. Sob, in *Electronic Band Structure and its Applications*, edited by M. Yussouf (Springer, Berlin, 1987), p. 1; J. Kudrnovsky, V. Drchal, and J. Masek, Phys. Rev. B **35**, 2487 (1987); J. Kudrnovsky and V. Drchal, *ibid.* **41**, 7515 (1990).

[31] J. S. Faulkner, Prog. Mater. Sci. **27**, 1 (1982).

[32] F. Ducastelle, in *Alloy Phase Stability*, edited by G. M. Stocks and A. Gonis (Kluwer, Dordrecht, 1989), p. 293.

[33] F. Ducastelle, *Order and Phase Stability in Alloys* (North-Holland, Amsterdam, 1992).

[34] A. Gonis, *Green Functions for Ordered and Disordered Systems* (North-Holland, Amsterdam, 1992).

[35] P. Soven, Phys. Rev. **156**, 809 (1967); B. Velicky, S. Kirkpatrick, and H. Ehrenreich, *ibid.* **175**, 747 (1968); R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. **46**, 465 (1974).

[36] N. F. Berk, Surf. Sci. **48**, 289 (1975).

[37] P. Weinberger, *Electron Scattering Theory for Ordered and Disordered Matter* (Clarendon, Oxford, 1990).

[38] F. Ducastelle and F. Gautier, J. Phys. F **6**, 2039 (1976); G. Tréglia, F. Ducastelle, and F. Gautier, *ibid.* **8**, 1437 (1978); F. Ducastelle and G. Tréglia, *ibid.* **10**, 2137 (1980); A. Bieber, F. Ducastelle, F. Gautier, G. Tréglia, and P. Turchi, Solid State Commun. **45**, 585 (1983). The preceding papers describe applications of the GPM within the TB-CPA formalism. For an extension to the KKR-CPA see P. Turchi, G. M. Stocks, W. H. Butler, D. M. Nicholson, and A. Gonis, Phys. Rev. B **37**, 5982 (1988).

[39] M. O. Robbins and L. M. Falicov, Phys. Rev. B **29**, 1333 (1984).

[40] A. Gonis and J. W. Garland, Phys. Rev. B **16**, 2424 (1977); A. Gonis, W. H. Butler, and G. M. Stocks, Phys. Rev. Lett. **50**, 1482 (1982).

[41] A. Gonis, X. G. Zhang, A. J. Freeman, P. Turchi, G. M. Stocks, and D. M. Nicholson, Phys. Rev. B **36**, 4630 (1987).

[42] B. L. Gyorffy and G. M. Stocks, Phys. Rev. Lett. **50**, 374 (1983).

[43] J. W. D. Connolly and A. R. Williams, Phys. Rev. B **27**, 5169 (1983); A. E. Carlsson, *ibid.* **35**, 4858 (1987); M. Sluiter and P. E. A. Turchi, *ibid.* **40**, 11 215 (1989).

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

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

[46] G. Tréglia and B. Legrand, Phys. Rev. B **35**, 4338 (1987).

[47] B. Legrand and G. Tréglia, in *The Structure of Solid Surfaces II*, edited by J. F. Van der Veen and M. A. Van Hove (Springer, Berlin, 1987), p. 167.

[48] G. Tréglia, B. Legrand, and F. Ducastelle, Europhys. Lett. **7**, 575 (1988).

[49] G. Tréglia, B. Legrand, and P. Maugain, Surf. Sci. **225**, 319 (1990).

[50] B. Legrand, G. Tréglia, and F. Ducastelle, Phys. Rev. B **41**, 4422 (1990).

[51] F. Ducastelle, B. Legrand, and G. Tréglia, Prog. Theor. Phys. Suppl. **101**, 159 (1990).

[52] G. Tréglia, B. Legrand, J. Eugène, B. Aufray, and F. Cabané, Phys. Rev. B **44**, 5842 (1991).

[53] A. Bieber and F. Gautier, J. Phys. Soc. Jpn. **53**, 2061 (1984); Z. Phys. B **57**, 335 (1984); Acta Metall. **34**, 2291 (1986); **35**, 1839 (1987).

[54] M. Asta, C. Wolverton, D. de Fontaine, and H. Dreyssé, Phys. Rev. B **44**, 4907 (1991); C. Wolverton, M. Asta, H. Dreyssé, and D. de Fontaine, *ibid.* **44**, 4914 (1991).

[55] F. Solal, R. Caudron, F. Ducastelle, A. Finel, and A. Loiseau, Phys. Rev. Lett. **58**, 2245 (1987).

[56] V. Kumar and K. H. Bennemann, Phys. Rev. Lett. **53**, 278 (1984); J. M. Sanchez and J. L. Moran-Lopez, Phys. Rev. B **32**, 3534 (1985); Surf. Sci. **157**, L297 (1985).

[57] J. L. Moran-Lopez, F. Mejia-Lira, and K. H. Benneman, Phys. Rev. Lett. **54**, 1936 (1985); J. M. Sanchez, F. Mejia-Lira, and J. L. Moran-Lopez, *ibid.* **57**, 360 (1986).

[58] A. Berera, H. Dreyssé, L. T. Wille, and D. de Fontaine, J. Phys. F **18**, L49 (1988); A. Berera, Phys. Rev. B **42**, 4311 (1990).

[59] J. Friedel, in *The Physics of Metals*, edited by J. M. Ziman (Cambridge University Press, London, 1969), p. 138.

[60] R. Haydock, Solid State Phys. **35**, 215 (1980); *The Recursion Method and Its Applications*, edited by D. G. Pettifor and D. L. Weaire (Springer, Berlin, 1985).

[61] N. R. Burke, Surf. Sci. **58**, 349 (1976).

[62] T. L. Einstein and J. R. Schrieffer, Phys. Rev. B **7**, 3629 (1973).

[63] R. Pandit and M. Wortis, Phys. Rev. B **25**, 3226 (1982).

[64] J. Vrijen and S. Radelaar, Phys. Rev. B **17**, 409 (1978); S. an Mey, Z. Metallk. **78**, 502 (1987); S. Srikanth and K. T. Jacob, Mater. Sci. Technol. **5**, 427 (1989).

[65] J. L. Murray, Bull. Alloy Phase Diagrams **2**, 335 (1982).

[66] M. Sluiter and P. E. A. Turchi, in *Alloy Phase Stability and Design*, edited by G. M. Stocks, D. D. Pope, and A. F. Giamei, MRS Symposia Proceedings No. 186 (Materials Research Society, Pittsburgh, 1991).

[67] H. Dreyssé, G. Ceder, D. de Fontaine, and L. T. Wille, Vacuum **41**, 446 (1990).

[68] H. Dreyssé, L. T. Wille, and D. de Fontaine, Solid State Com-

mun. **78**, 355 (1991).

[69] J. A. Blackman, D. M. Esterling, and N. F. Berk, Phys. Rev. B **4**, 2412 (1971); D. A. Papaconstantopoulos, A. Gonis, and P. M. Laufer, *ibid.* **40**, 12 196 (1989).

[70] H. Shiba, Prog. Theor. Phys. **46**, 77 (1971).

[71] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[72] P. Turchi, G. Tréglia, and F. Ducastelle, J. Phys. F **13**, 2543 (1983).

[73] C. M. M. Nex, Comput. Phys. Commun. **34**, 101 (1984); R. Haydock and C. M. M. Nex, J. Phys. C **18**, 2235 (1985); M. Foulkes and R. Haydock, *ibid.* **19**, 6573 (1986); M. U. Luchini and C. M. M. Nex, *ibid.* **20**, 3125 (1987).

[74] N. Beer and D. G. Pettifor, in *Electronic Structure of Complex Systems*, edited by P. Phariseau and W. M. Temmerman (Plenum, New York, 1982).

[75] P. van der Plank and W. M. H. Sachtler, J. Catal. **7**, 300 (1967); **12**, 35 (1968); W. M. H. Sachtler and P. van der Plank, Surf. Sci. **18**, 62 (1969); V. Ponec and W. M. H. Sachtler, J. Catal. **24**, 250 (1972).

[76] K. Watanabe, M. Hashiba, and T. Yamashina, Surf. Sci. **61**, 483 (1976).

[77] D. T. Ling, J. N. Miller, I. Lindau, W. E. Spicer, and P. M. Stefan, Surf. Sci. **74**, 612 (1978).

[78] Y. S. Ng, T. T. Tsong, and S. B. McLane, Jr., Phys. Rev. Lett. **42**, 588 (1979); J. Appl. Phys. **51**, 6189 (1980); J. Vac. Sci. Technol. **17**, 154 (1980).

[79] L. E. Rehn, S. Danyluk, and H. Wiedersich, Phys. Rev. Lett. **43**, 1764 (1979).

[80] K. Wandelt and C. R. Brundle, Phys. Rev. Lett. **46**, 1529 (1981).

[81] P. J. Durham, R. G. Jordan, G. S. Sohal, and L. T. Wille, Phys. Rev. Lett. **53**, 2038 (1984).

[82] N. Q. Lam, H. A. Hoff, H. Wiedersich, and L. E. Rehn, Surf. Sci. **149**, 517 (1985).

[83] T. Sakurai, T. Hahizume, A. Jimbo, A. Sakai, and S. Hyodo, Phys. Rev. Lett. **55**, 514 (1985).

[84] L. E. Rehn, H. A. Hoff, and N. Q. Lam, Phys. Rev. Lett. **57**, 780 (1986).

[85] H. H. Brongersma, P. A. J. Ackermans, and A. D. van Langeveld, Phys. Rev. B **34**, 5974 (1986).

[86] T. Sakurai, T. Hashizume, A. Kobayashi, A. Sakai, S. Hyodo, Y. Kuk, and H. W. Pickering, Phys. Rev. B **34**, 8379 (1986).

[87] T. Berghaus, C. Lunau, H. Neddermeyer, and V. Rogge, Surf. Sci. **182**, 13 (1987).

[88] V. Rogge and H. Neddermeyer, Phys. Rev. B **40**, 7559 (1989).

[89] R. G. Donnelly and T. S. King, Surf. Sci. **74**, 89 (1978).

[90] J. Urias and J. L. Moran-Lopez, Surf. Sci. **128**, L205 (1983).

[91] H. F. Lin, C. L. Wang, and C. Y. Cheng, Solid State Commun. **59**, 253 (1986); C. Y. Cheng, Phys. Rev. B **34**, 7400 (1986).

[92] L. T. Wille and P. J. Durham, Surf. Sci. **164**, 19 (1985).

[93] S. Mukherjee and J. L. Moran-Lopez, Progr. Surf. Sci. **25**, 139 (1987).

[94] S. M. Foiles, Phys. Rev. B **32**, 7685 (1985); **40**, 11 502 (1989).

[95] J. Eymery and J. C. Joud, Surf. Sci. **231**, 419 (1990).

[96] R. Najafabadi, H. Y. Wang, D. J. Srolovitz, and R. LeSar, Acta Metall. Mater. **39**, 3071 (1991); H. Y. Wang, R. Najafabadi, D. J. Srolovitz, and R. LeSar, Phys. Rev. B **45**, 12 028 (1992).

[97] M. A. Krivoglaz, *Theory of X-Ray and Thermal Neutron Scattering by Real Crystals* (Plenum, New York, 1969); P. C. Clapp and S. C. Moss, Phys. Rev. **142**, 418 (1966); **171**, 754 (1968); S. C. Moss and P. C. Clapp, *ibid.* **171**, 764 (1968). For an extension of the Krivoglaz-Clapp-Moss approach see D. M. Kroll and H. Wagner, *ibid.* **42**, 6531 (1990).

[98] V. Gerold and J. Kern, Acta Metall. **35**, 393 (1987); W. Schweika and H. G. Haubold, Phys. Rev. B **37**, 9240 (1988); W. Schweika and A. E. Carlsson, *ibid.* **40**, 4990 (1989).

[99] D. de Fontaine and J. Kulik, Acta Metall. **33**, 145 (1985).

[100] J. Kanamori and Y. Kakehashi, J. Phys. (Paris) Colloq. **38**, C7-274 (1977).

[101] R. H. Brown and A. E. Carlsson, Solid State Commun. **61**, 743 (1987).

[102] H. Dreyssé, L. T. Wille, and D. de Fontaine (unpublished).

[103] S. M. Kuo, A. Seki, Y. Oh, and D. N. Seidman, Phys. Rev. Lett. **65**, 199 (1990); J. G. Hu and D. N. Seidman, *ibid.* **65**, 1615 (1990).

[104] V. M. Tapilin, Surf. Sci. **206**, 405 (1988).

[105] J. Kudrnovsky, B. Wenzien, V. Drchal, and P. Weinberger, Phys. Rev. B **44**, 4068 (1991); J. Kudrnovsky, P. Weinberger, and V. Drchal, *ibid.* **44**, 6410 (1991); V. Drchal, J. Kudrnovsky, L. Udvardi, P. Weinberger, and A. Pasturel, *ibid.* **45**, 14 328 (1992).

[106] M. S. Daw and M. I. Baskes, Phys. Rev. Lett. **50**, 1285 (1983); Phys. Rev. B **29**, 643 (1984); S. M. Foiles, M. I. Baskes, and M. S. Daw, *ibid.* **33**, 7983 (1986).

[107] J. B. Pendry, *Low-Energy Electron Diffraction* (Academic, London, 1974); L. T. Wille and P. J. Durham, J Phys F **13**, L117 (1983); J. H. Kaiser, P. J. Durham, R. J. Blake, and L. T. Wille, J. Phys. C **21**, L1159 (1988); J. M. MacLaren, S. Crampin, D. D. Vvedensky, and J. B. Pendry, Phys. Rev. B **40**, 12 164 (1989).

[108] A. Gonis, X. G. Zhang, J. M. MacLaren, and S. Crampin, Phys. Rev. B **42**, 3798 (1990); X. G. Zhang, P. J. Rous, J. M. MacLaren, A. Gonis, M. A. Van Hove, and G. A. Somorjai, Surf. Sci. **239**, 103 (1990); S. Crampin, R. Monnier, T. Schulten, G. H. Schadler, and D. D. Vvedensky, Phys. Rev. B **45**, 464 (1992).

[109] A. Zunger, S. H. Wei, L. G. Ferreira, and J. E. Bernard, Phys. Rev. Lett. **65**, 353 (1990).