

Quantum interference effects on the segregation energy in diluted metallic alloys

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The electronic contribution ΔE to the segregation energy in diluted transition-metal alloys is investigated. It is shown that quantum interference effects on the electronic states, which take place in the near-surface region, significantly affect the screening of the potential of the minority alloy component and, as a consequence, the electronic contribution to the segregation energy. An analytical approximation to ΔE , valid for sufficiently large distances to the surface, is obtained, which evinces the relation between the spatial behavior of ΔE and specific features of the host Fermi surface.

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I. INTRODUCTION

It is experimentally well established that the chemical composition of an alloy in its near-surface region may differ from that in the bulk. The understanding of this phenomenon, known as surface segregation, is a subject of great interest in condensed matter physics, materials science, and catalytic chemistry. From the experimental point of view, attention has been focused on the study of detailed composition-depth profiles, which provide a fairly complete description of the segregation process. Several methods, such as low-energy electron, x-ray scattering diffraction, and atom-probe techniques, have been used to investigate the layer-by-layer atomic composition near the surface of various materials. It has been found that some alloys, such as Cu_3Au ,¹ Pt-Ru ,² Pt-Ni , and Pt-Rh ,³ exhibit complex surface segregation behavior, with the composition oscillating about the bulk value as a function of the distance z to the surface. The amplitude of the oscillations diminishes as z increases, making difficult the observation of such behavior well below the surface plane. Nevertheless, oscillations down to over ten atomic layers have been reported by Ren *et al.*⁴ in one Pt-Rh alloy.

Previous theoretical work on the problem of surface segregation has been based on either electronic structure calculations,⁵⁻⁷ mean-field theories for effective Ising models,^{3,8-11} theories related to the order-disorder transformation in alloys,^{12,13} or embedded-atom methods.¹⁴ However, several important points such as the connection between the oscillation periods and the electronic structure of the material have not been clearly established yet.

In this communication, we investigate the surface segregation of the minority component element of diluted metallic alloys. For such systems, we calculate the electronic contribution $\Delta E(z)$ to the segregation energy, defined as the change in total electronic energy associated with the exchange in position between an atom of the minority component within

the bulk and one atom of the host material placed at a distance z of the surface.⁵ We also derive an analytical approximation to $\Delta E(z)$, which makes clear the connection between the spatial behavior of this quantity and the geometry of the host Fermi surface (FS). According to such an expression, $\Delta E(z)$ should oscillate as a function of z with well-defined periods given by the extremal dimensions of the host Fermi surface in the direction perpendicular to the surface plane. As a consequence, the spatial behavior of $\Delta E(z)$ may depend on the orientation of the alloy surface. The oscillation amplitudes are found to decay as $1/z$ and to be determined basically by two factors—namely, the valence difference between host and impurity elements and the curvatures of the host FS at its extrema. The theory is illustrated by numerical and analytical calculations of $\Delta E(z)$ for a simple model, and the agreement between the two sets of results confirms the accuracy of the analytical approximation. The observed oscillatory behavior of the electronic contribution to the segregation energy is interpreted in terms of quantum interference effects near the host surface and their effects on the screening of the minority component potential.

II. ELECTRONIC CONTRIBUTION TO THE SEGREGATION ENERGY

The systems we consider are substitutional binary alloys $A_{1-x}B_x$, where A and B are transition-metal elements and $x \ll 1$ (diluted alloys). In this composition range, multiple-scattering processes involving two or more distinct B atoms can be neglected; hence, they may be regarded as isolated impurities in an otherwise pure A host. We regard the system as consisting of atomic planes parallel to the alloy surface, labeled by the index l . The surface plane corresponds to $l = 1$. The atomic positions within each plane are labeled \mathbf{R} . For simplicity, we assume that the atomic planes are equivalent; however, the extension of the theory to include the con-

cept of principal layers is straightforward.¹⁵ We are interested in calculating $\Delta E_l = \Delta E(l, d)$, where d is the interplane distance. Such a quantity can be readily obtained from electronic structure calculations.

We follow the approach of Riedinger and Dreysse⁵ and assume that the change in the electronic potential due to the introduction of the B atom is restricted to the impurity site, which is a good approximation for the sort of metallic systems we are interested in. Thus, within the framework of the tight-binding model, the Hamiltonian of the system can be written as

$$H = H_A + \sum_{\mu} |l\mathbf{R}\mu\rangle v_{l,\mu} \langle l\mathbf{R}\mu|, \quad (1)$$

where H_A is the host Hamiltonian, $|l\mathbf{R}\mu\rangle$ represents an atomic function with orbital quantum number μ centered on the site (l, \mathbf{R}) occupied by the impurity, and $v_{l,\mu}$ is the change in the electronic potential on such site. We recall that, since H_A has translational symmetry parallel to the surface plane, $v_{l,\mu}$ does not depend on \mathbf{R} .

The condition of global charge neutrality requires the change in the number of occupied states in the system to be equal to $\Delta n = n_B - n_A$, where n_A and n_B are, respectively, the numbers of valence electrons per atom (electronic concentration) of A and B . This condition leads to a simple relation between Δn and $v_{l,\mu}$, known as Friedel's sum rule, which may be regarded as a self-consistency condition on v . In the case of transition metals, two additional approximations may be introduced at this point.⁵ First, since the screening of the impurity potential is carried out mostly by the d states, the changes in the s and p potentials on the impurity site can be ignored to a first approximation. Second, since crystal field effects on the d states are usually small, the dependence of v on the orbital index μ can be neglected. Thus, we are left with a single parameter v_l describing the change in the d potential on the site occupied by the impurity. By imposing global charge neutrality we find that

$$\Delta n = -\frac{1}{\pi} \text{Im Tr} \ln\{[1] - v_l [G_{l,l}(E_F)]\}, \quad (2)$$

where $[1]$ is the identity matrix, Tr stands for the trace over the d orbitals, $[G_{l,l}(E_F)]$ is the host Green's function matrix for states with d symmetry at an arbitrary site \mathbf{R} in plane l , and E_F is the Fermi energy. It is worth noting that, in contrast to the case in which the impurity is in the bulk of the A material, the potential v in the above equation depends on the impurity position relative to the surface plane. As discussed below, such a dependence is due to quantum interference effects which take place in the near-surface region. In the present work, Eq. (2) is used to obtain v_l for different positions l , in each case for fixed valence difference Δn .

Having determined v_l , the total electronic energy of the system when the impurity is positioned in the atomic plane l can be readily obtained from ordinary scattering theory. It is given by the expression

$$E_l = E_A + E_F \Delta n + \frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \text{Im Tr} \ln\{[1] - v_l [G_{l,l}(\omega)]\}, \quad (3)$$

where E_A is the total electronic energy of the pure A material. Thus, $\Delta E_l = E_l - E^{(b)}$, where $E^{(b)}$ is the total electronic energy of the system when the impurity is in the bulk of the A material, which can be written as

$$\Delta E_l = \frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \text{Im Tr} \ln\{([1] - v_l [G_{l,l}(\omega)]) \times \{[1] - v_b [G_{0,0}^{(b)}(\omega)]\}^{-1}\}. \quad (4)$$

Here v_b and $[G_{0,0}^{(b)}(\omega)]$ represent, respectively, the change in the d potential and the local Green's function matrix for states with d symmetry for the impurity in the bulk of the A material. The former can be obtained from Eq. (2) by replacing $[G_{l,l}(E_F)]$ with $[G_{0,0}^{(b)}(\omega)]$.

As explained at length in the next section, for $l \gg 1$ the numerical calculations of v_l and $[G_{l,l}(E_F)]$ become extremely time consuming. In addition, in such a range of values of l , the integration over energy in Eq. (4) involves large cancellations and has to be carried out with extremely high accuracy. On the other hand, as we show below, for sufficiently large values of l , those difficulties can be overcome and simple analytical expressions for v_l , $[G_{l,l}(E_F)]$, and ΔE_l can be derived. Even more interesting, such analytical expressions for v_l and ΔE_l establish a clear connection between the spatial behavior of these two quantities and specific features of the electronic structure of the host material.

III. ANALYTICAL APPROXIMATION

We first notice that the argument of the logarithmic function in Eq. (4) is expected to approach $[1]$ as l increases. Thus, for $l \gg 1$, the expression for ΔE_l can be approximated by

$$\Delta E_l \approx \frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \text{Im Tr} \{([1] - v_l [G_{l,l}(\omega)]) \{([1] - v_b [G_{0,0}^{(b)}(\omega)]\}^{-1} - [1])\}, \quad (5)$$

which reduces to

$$\Delta E_l \approx \frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \text{Im Tr} \{v_b [G_{0,0}^{(b)}(\omega)] - v_l [G_{l,l}(\omega)] \{([1] - v_b [G_{0,0}^{(b)}(\omega)]\}^{-1}\}. \quad (6)$$

We show below that, as expected, v_l and $[G_{l,l}(\omega)]$ approach v_b and $[G_{0,0}^{(b)}(\omega)]$, respectively, with increasing l . Let us look first at the behavior of $[G_{l,l}(\omega)]$. In the case in which interplane hoppings are restricted to nearest-neighbor planes, it can be shown that

$$[G_{l,l}(\omega)] = [G_{0,0}^{(b)}(\omega)] - \Omega_{2d} \int \frac{d^2 q}{(2\pi)^2} [G_{l,0}^{(b)}(\mathbf{q}, \omega)] \cdot [G_{0,0}^{(b)}(\mathbf{q}, \omega)]^{-1} \cdot [G_{0,l}^{(b)}(\mathbf{q}, \omega)], \quad (7)$$

where Ω_{2d} is the area of the Wigner-Seitz cell of the two-

dimensional (2D) lattice defined within the atomic planes and \mathbf{q} is a 2D wave vector parallel to the atomic planes. For fixed values of \mathbf{q} and ω , the matrix elements of $[G_{l,0}^{(b)} \times (\mathbf{q}, \omega)]$ and $[G_{0,l}^{(b)}(\mathbf{q}, \omega)]$ are oscillatory functions of l . This follows from the analytic expressions for the Green's function in layered systems derived by Umerski.¹⁶ The oscillation period is given by $\lambda(\omega, \mathbf{q}) = 2\pi/k(\mathbf{q}, \omega)$, where $k(\mathbf{q}, \omega)$ is determined by solving the material's dispersion relation $\omega = E(\mathbf{q}, k)$, which we assume to have a single sheet in reciprocal space; the extension to cases with more than one sheet is straightforward.^{16,17} In such a case, the terms in the summation over \mathbf{q} on the right-hand side of Eq. (7) can be expanded in a Fourier series:

$$\begin{aligned} & [G_{l,0}^{(b)}(\mathbf{q}, \omega)] \cdot [G_{0,0}^{(b)}(\mathbf{q}, \omega)]^{-1} \cdot [G_{0,l}^{(b)}(\mathbf{q}, \omega)] \\ &= \sum_{s \geq 2} [c_s(\mathbf{q}, \omega)] \exp[isk(\mathbf{q}, \omega)ld], \end{aligned} \quad (8)$$

where $[c_s(\mathbf{q}, \omega)]$ is a matrix of Fourier coefficients. For large l and fixed ω , the exponential in Eq. (8) oscillates rapidly as a function of \mathbf{q} , which leads to large cancellations when the integration over \mathbf{q} is carried out. This is the underlying reason why the numerical calculation of $[G_{l,l}(\omega)]$ becomes increasingly difficult as larger values of l are considered, as pointed out in the previous section. As a consequence, the nonvanishing contributions to the \mathbf{q} integral in Eq. (7) come just from the neighborhood of points \mathbf{q}_0^α in \mathbf{q} space which render $k(\mathbf{q}, \omega)$ stationary. By expanding $k(\mathbf{q}, \omega)$ in a Taylor series about \mathbf{q}_0^α up to second order in \mathbf{q} and approximating the remaining \mathbf{q} -dependent factors by their values at \mathbf{q}_0^α , the integral over the parallel wave vector reduces to Gaussian integrals and can be evaluated analytically.¹⁸ Then, the expression for $[G_{l,l}(\omega)]$ reduces to

$$[G_{l,l}(\omega)] = [G_{0,0}^{(b)}(\omega)] + \sum_{\alpha} \sum_{s \geq 2} \frac{1}{sld} [A_s(\mathbf{q}_0^\alpha, \omega)] \exp[isk_0^\alpha(\omega)ld], \quad (9)$$

where

$$[A_s(\mathbf{q}_0^\alpha, \omega)] = \frac{\Omega_{2d}}{2\pi} [c_s(\mathbf{q}_0^\alpha, \omega)] \frac{s}{(|k_{xx}^\alpha| |k_{yy}^\alpha|)^{1/2}}.$$

Here, $k_{\xi\xi}^\alpha = \partial^2 k / \partial q_\xi^2$ at $\mathbf{q} = \mathbf{q}_0^\alpha$ ($\xi = x, y$), $k_0^\alpha(\omega) = k(\mathbf{q}_0^\alpha, \omega)$, and

$$\zeta = \begin{cases} i & \text{if } k_{xx} > 0 \text{ and } k_{yy} > 0, \\ -i & \text{if } k_{xx} < 0 \text{ and } k_{yy} < 0, \\ 1 & \text{if } k_{xx} \cdot k_{yy} < 0. \end{cases}$$

q_x and q_y are the components of \mathbf{q} in an orthogonal system of axes chosen to diagonalize the Taylor expansion of the argument of the exponential in Eq. (8). According to Eq. (9), $[G_{l,l}(\omega)]$ approaches $[G_{0,0}^{(b)}(\omega)]$, upon increasing l , as expected. Using this result, it can be shown (see the Appendix) that

$$\Delta v_l = v_l - v_b = \sum_{\alpha} \sum_{s \geq 2} \frac{1}{sld} \text{Im}\{B_s(\mathbf{q}_0^\alpha, E_F) \exp[isk_0^\alpha(E_F)ld]\}, \quad (10)$$

where

$$B_s(\mathbf{q}_0^\alpha, E_F) = \frac{v_b}{\pi \rho_i(E_F)} \text{Tr}([A_s(\mathbf{q}_0^\alpha, E_F)] \{[1] - v_b [G_{0,0}^{(b)}(E_F)]\}^{-1}). \quad (11)$$

Here $\rho_i(E_F) = -(1/\pi) \text{Im Tr}([G_{0,0}^{(b)}(E_F)] \{[1] - v_b [G_{0,0}^{(b)}(E_F)]\}^{-1})$ is the local density of states on the site of an impurity located in the bulk. On the basis of Eqs. (7) and (10), the expression for ΔE_l in Eq. (6) can be approximated by

$$\begin{aligned} \Delta E_l &\approx \frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \text{Im Tr}\{[-\Delta v_l G_{0,0}^{(b)}(\omega) - v_b \delta G_{l,l}(\omega)] \\ &\quad \times [1 - v_b G_{0,0}^{(b)}(\omega)]^{-1}\}, \end{aligned}$$

where we have kept terms up to order $1/l$ and $[\Delta G_{l,l}(\omega)] = [G_{l,l}(\omega)] - [G_b(\omega)]$. We recall that both $[\Delta G_{l,l}(\omega)]$ and Δv_l decrease as $1/l$ for $l \gg 1$ [cf. Eqs. (9) and (10)]. Therefore,

$$\begin{aligned} \Delta E_l &\approx \Delta v_l \left(-\frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \text{Im Tr}([G_{0,0}^{(b)}(\omega)] \right. \\ &\quad \left. \times \{[1] - v_b [G_{0,0}^{(b)}(\omega)]\}^{-1}) \right) \\ &\quad + \frac{v_b}{l} \left(-\frac{1}{\pi} \sum_{\alpha} \sum_{s \geq 2} \frac{1}{sd} \int_{-\infty}^{E_F} d\omega \text{Im Tr}([A_s(\mathbf{q}_0^\alpha, \omega)] \right. \\ &\quad \left. \times \{[1] - v_b [G_{0,0}^{(b)}(\omega)]\}^{-1} \times \exp[isk_0^\alpha(\omega)ld] \right). \end{aligned} \quad (12)$$

For sufficiently large values of l , the exponential in the last integrand oscillates very rapidly as a function of the ω , leading once more to large cancellations, this time when the integration over energy is carried out. Thus, the main contribution to this integral comes from the neighborhood of E_F , where there may be an incomplete oscillation period. Then, $k_0^\alpha(\omega)$ may be expanded in a Taylor series about E_F and the integral over ω carried out analytically.¹⁸ As a result, an additional dependence on $1/l$ appears in the second term on the right-hand side of Eq. (12). Thus, the leading term in the expression for ΔE_l in the asymptotic region ($l \gg 1$) is given by

$$\Delta E_l \approx \frac{n_i^{(b)}}{ld} \sum_{\alpha} \sum_{s \geq 2} \frac{1}{s} \text{Im}\{B_s(\mathbf{q}_0^\alpha, E_F) \exp[2isk_0^\alpha(E_F)ld]\}, \quad (13)$$

where

$$n_i^{(b)} = -\frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \operatorname{Im} \operatorname{Tr} \{ [G_{0,0}^{(b)}(\omega)] \{ [1] - v_b [G_{0,0}^{(b)}(\omega)] \}^{-1} \} \quad (14)$$

is the density of particles at the site of an impurity atom in the bulk of the host material.

We remark that according to Eqs. (13) and (10), for sufficiently large distances to the surface, the electronic contribution to the segregation energy and change in the screened impurity potential are related by the equation

$$\Delta E_l \approx n_i^{(b)} \Delta v_l,$$

which clearly establishes the relation between the quantum interference effects in the near-surface region, the screening of the impurity potential, and the segregation energy. In addition, Eqs. (13) and (10) imply that both Δv_l and ΔE_l should oscillate as a function of distance $z=(l-1)d$ to the surface, with decaying amplitude and with a superposition of well-defined periods given by

$$\lambda_{as} = \frac{2\pi}{s k_0^\alpha(E_F)}, \quad (15)$$

where $s \geq 2$ and $k_0^\alpha(E_F) = k(\mathbf{q}_0^\alpha, E_F)$ are the extremal dimensions of the host Fermi surface in the direction perpendicular to the host surface. Therefore, depending on the geometry of the host Fermi surface, the oscillation periods may be either long or short in the scale of the interplane distance. It is clear from Eqs. (10) and (13) that the main contributions to both Δv_l and ΔE_l are expected to come from the first Fourier terms in each series. In both cases, however, the amplitude of the oscillations depends on the curvatures of the host Fermi surface at the extremal points and decays as $1/z$ towards the bulk.

In the following section, we apply the above theory to a rather simple model and calculate the segregation energy based on both Eqs. (4) and (13). The comparison between the results of the two calculations will enable us to assess the accuracy of the asymptotic approximation and to confirm the above-mentioned relation between the behavior of ΔE_l and the geometry host Fermi surface.

IV. RESULTS AND CONCLUSIONS

In this section we present results for a simple model in which the atoms of the system occupy sites of an underlying simple cubic lattice and the electronic structure is described by a single-band tight-binding model with hopping t between nearest-neighbor sites. We recall that for such model the host Fermi surface is given by

$$E_F = \epsilon_A + 2t[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)],$$

where ϵ_A is the host site energy and a is the lattice parameter. In which follows, the energy unit is taken such that $t = -0.5$ and $\epsilon_A = 0$.

We first deal with the case in which the surface has (001) orientation. The electronic density n_A of the host material is chosen equal to 0.5, which corresponds to $E_F = 0$. In such a

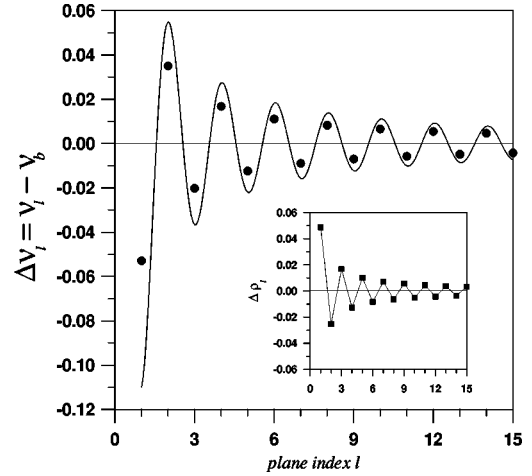


FIG. 1. Change in the electronic potential at the impurity site relative to the bulk value, $\Delta v_l = v_l - v_b$, as a function of the index l of the atomic plane where the impurity is positioned (solid circles). The energy unit is taken such that $t = -0.5$. The distance of the impurity to the surface plane is $z = (l-1)d$, where d is the interplane distance. The solid curve represents the analytical approximation to Δv_l (see text). The surface plane has (001) orientation. The inset shows the change $\Delta \rho_l$ in the local density of states at the Fermi energy $\rho_l(E_F)$ with respect to the bulk value $\rho_b(E_F)$ of the unperturbed host material as a function of l .

case, the extrema of the host FS have extrema along the direction perpendicular to the surface are located at $\mathbf{q}_0^{1,2} = (0, \pm \pi/a)$ and $\mathbf{q}_0^{3,4} = (\pm \pi/a, 0)$. The extremal dimension of the FS at the four points is $k_0^\alpha(E_F) = k_z = \pi/2a$, which according to Eq. (15) corresponds to $\lambda = 2d$. Figure 1 shows $\Delta v_l = v_l - v_b$ as a function of l (solid circles), for $n_B = 0.4$, with v_l and v_b obtained from Eq. (2). As regard the determination of v_l , the Green's function matrix element $G_{l,l}(E_F)$, which enters Eq. (2), has been calculated from Eq. (7). We remark that for the values of l in Fig. 1, it was necessary to consider more than 3.3×10^7 \mathbf{q} points in the irreducible wedge of the two-dimensional Brillouin zone to achieve convergence. It is clear that Δv_l oscillates with a period predicted by the analytical approximation, which is represented by the solid line. The agreement between the numerical and analytical results is quite good, even close to the surface.

It is worth commenting at this point on the spatial behavior of Δv_l . According to Thomas-Fermi theory, the screening of an impurity potential by an electron gas is carried out mostly by the states at the Fermi energy. In fact, the screened potential of a Coulomb charge is

$$V_{scr}(r) = \frac{e^{-k_0 r}}{r},$$

where $k_0 = 4\pi e^2 \rho(E_F)$. Here, $\rho(E_F)$ is the density of states (DOS) at the Fermi energy. For the electronic density of ordinary metals, the screening length $\lambda_{scr} = 2\pi/k_0$ turns out to be of order 1 Å, which fully justifies the assumption that the change in the electronic potential due to the introduction of the impurity is restricted to the impurity site. In the bulk of a crystalline material, the amplitude of the electronic states is

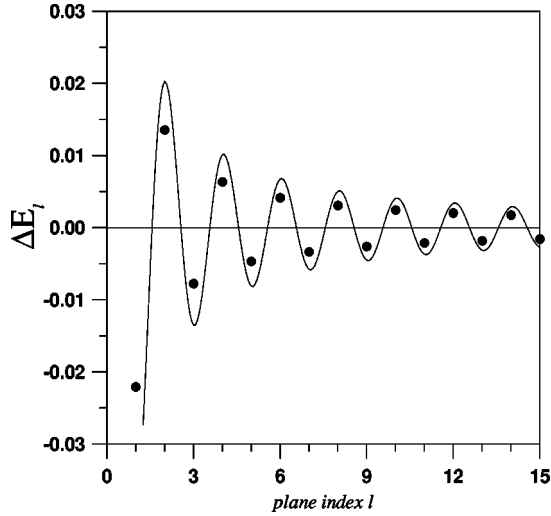


FIG. 2. Electronic contribution to the segregation energy ΔE_l as a function of the index l of the atomic plane where the impurity positioned (solid circles). The solid curve represents the analytical approximation to ΔE_l (see text). The energy unit is taken such that $t=-0.5$. The distance of the impurity to the surface plane is $z=(l-1)d$, where d is the interplane distance. The surface plane has (001) orientation.

the same at all lattice sites and so is the local density of states. However, in the near-surface region, quantum interference between states with the Fermi energy which are incident on, and reflected by, the surface modulates the amplitude of those states, giving rise to a position-dependent local density of states at E_F —i.e., $\rho(z, E_F)$. According to Thomas-Fermi theory, this should affect the screening of the impurity potential. At those positions where $\rho_l = \rho(ld, E_F)$ is larger, the screened potential is expected to be weaker and vice versa. This point is entirely confirmed by the data in Fig. 1, which shows in the inset $\Delta\rho_l(E_F) = \rho_l(E_F) - \rho_b(E_F)$ as a function of l , where $\rho_l(E_F) = \rho(ld, E_F)$ and $\rho_b(E_F)$ is the bulk density of states of the pure A material.

Figure 2 shows ΔE as a function of the plane index l (solid circles) calculated from Eq. (4), for the same set of parameters as in Fig. 1. Also, in this case, it was necessary to consider more than 3.3×10^7 \mathbf{q} points in the irreducible wedge of the two-dimensional Brillouin zone to achieve convergence in the calculation of $G_{l,l}(\omega)$, within the range of values of l in the figure. The solid line represents the analytical approximation given by Eq. (13). We find that ΔE oscillates with the predicted period and that the two sets of results are in quite good agreement, even for relatively small values of l .

Finally, to illustrate the dependence of both the screening of the impurity potential and the segregation energy on surface orientation, which arises as a consequence of the nonsphericity of the host FS, we consider the case of a (110) surface. The 2D Brillouin zone now corresponds to the region defined by the relations $-\pi\sqrt{2}/2a \leq q_x \leq \pi\sqrt{2}/2a$ and $-\pi/a \leq q_y \leq \pi/a$, and the host FS has extrema at the points $\mathbf{q}_0^{1,2} = (0, \pm\pi/a)$ and $\mathbf{q}_0^3 = (0, 0)$. The corresponding extremal dimensions are $k_0^{1,2}(E_F) = \pi/(3d)$ and $k_0^3(E_F) = 2\pi/(3d)$; thus, both $\Delta\nu$ and ΔE are expected to oscillate as a function of l

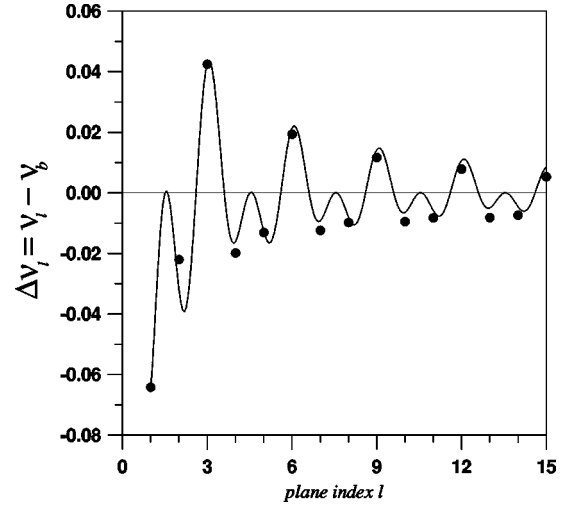


FIG. 3. Change in the electronic potential at the impurity site relative to the bulk value, $\Delta\nu_l = \nu_l - \nu_b$, as a function of the index l of the atomic plane where the impurity positioned (solid circles). The energy unit is taken such that $t=-0.5$. The distance of the impurity to the surface plane is $z=(l-1)d$, where d is the interplane distance. The solid curve represents the analytical approximation to $\Delta\nu_l$ (see text). The surface plane has (110) orientation.

with a superposition of two periods—namely, $\lambda_{1,2} = 3d$ and $\lambda_3 = 3d/2$, where $d = a\sqrt{2}/2$. This is confirmed by the results in Figs. 3 and 4, which show, respectively, $\Delta\nu$ and ΔE plotted as functions of l (both for $n_A = 0.5$ and $n_B = 0.4$). In these figures, solid circles represent the results of numerical calculations, whereas solid lines correspond to analytical approximations. The agreement between the two sets of results is quite good. The present results give support to the work of Dreysee and Riedinger,⁶ who have numerically studied the

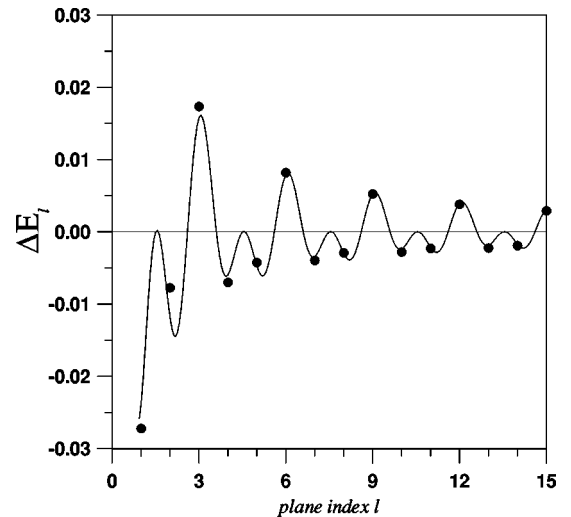


FIG. 4. Electronic contribution to the segregation energy ΔE_l as a function of the index l of the atomic plane where the impurity positioned (solid circles). The energy unit is taken such that $t=-0.5$. The solid curve represents the analytical approximation to ΔE_l (see text). The distance of the impurity to the surface plane is $z=(l-1)d$, where d is the interplane distance. The surface plane has (110) orientation.

influence of surface orientation on the band contribution to the segregation energy. The dependence of ΔE on the surface orientation in the case of diluted alloys is made totally clear by the analytical expression in Eq. (13).

In conclusion, we have investigated the electronic contribution to the segregation energy in diluted metallic alloys. We have shown that quantum interference effects which occur in the near-surface region significantly affect the screening of the potential of the minority alloy component and, consequently, the segregation energy. As we have demonstrated numerically and analytically, in such a region, both $\Delta\nu$ and ΔE exhibit an oscillatory behavior as functions of l , with well-defined periods determined by the geometry of the host Fermi surface and the relative orientation of the surface. This is a clear example of the important role played by quantum interference effects due to sharp changes in the electronic potential, which appear near surfaces and in most nanostructured systems.

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APPENDIX

We first notice that Eq. (2) (Friedel’s sum rule) can be rewritten as

$$\Delta n = -\frac{1}{\pi} \text{Im Tr} \ln\{[1] - \nu_b[G_{0,0}^{(b)}(E_F)] - \Delta\nu_l[G_{0,0}^{(b)}(E_F)] - \nu_b[\Delta G_{l,l}(E_F)] + \Delta\nu_l[\Delta G_{l,l}(E_F)]\}, \quad (16)$$

where $[\Delta G_{l,l}(E_F)] = [G_{l,l}(E_F)] - [G_{0,0}^{(b)}(E_F)]$. Since both $\Delta\nu_l$ and $[\Delta G_{l,l}(E_F)]$ are expected to vanish as l increases, for sufficiently large values of l the last term in the argument of the logarithmic function in the above equation can be neglected. Then, Eq. (16) reduces to

$$-\frac{1}{\pi} \text{Im Tr} \ln\{[1] - \{\Delta\nu_l[G_{0,0}^{(b)}(E_F)] + \nu_b[\Delta G_{l,l}(E_F)]\} \times \{[1] - \nu_b[G_{0,0}^{(b)}(E_F)]\}^{-1}\} = 0.$$

Moreover, for $l \gg 1$, the latter equation can be approximated by

$$\frac{1}{\pi} \text{Im Tr} \{ \{\Delta\nu_l[G_{0,0}^{(b)}(E_F)] + \nu_b[\Delta G_{l,l}(E_F)]\} \times \{[1] - \nu_b[G_{0,0}^{(b)}(E_F)]\}^{-1} \} = 0,$$

from which we get

$$\Delta\nu_l \rho_l(E_F) = \frac{\nu_b}{\pi} \text{Im Tr} \{ [\Delta G_{l,l}(E_F)] \{ [1] - \nu_b[G_{0,0}^{(b)}(E_F)] \}^{-1} \}.$$

Making use of Eq. (9), we immediately obtain the expression for $\Delta\nu_l$ in Eq. (10).

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