

Electronic theory for surface segregation in  $\text{Cu}_x\text{Ni}_{1-x}$  alloy

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Surface segregation is studied for  $\text{Cu}_x\text{Ni}_{1-x}$  alloys using the tight-binding Hartree-Hamiltonian and a mixed Bethe-lattice model to determine the electronic energy. Results for the surface segregation at (100) and (111) surfaces of the alloy are presented and compared with existing experimental results. Also, results are given for the temperature dependence of the segregation. Furthermore, the effect of the surface segregation on the local electronic density of states and on the surface core-level shifts is calculated on the basis of our electronic theory.

## I. INTRODUCTION

In recent years the surface composition of metal alloys has been studied extensively. Particular attention has been given to investigation of the surface composition of Cu-Ni alloys.<sup>1-5</sup> In these alloys strong segregation of Cu atoms to the surface occurs. Obviously, such a segregation is of interest with respect to a study of the catalytic activity of such alloys.<sup>6</sup> Several theories of segregation in alloys have been proposed. Among the phenomenological theories, the pair bond models<sup>7-10</sup> for the interatomic interactions are most extensively used. According to this model, the constituent having the lower heat of vaporization segregates to the surface. However, it has been recently shown<sup>11-14</sup> that the use of surface energies to describe surface segregation gives a better agreement for a large number of systems including those with components of appreciably different molar volumes. Theories<sup>11,12,15</sup> taking into account both bond breaking and volume effects and including long-range and short-range atomic order<sup>16</sup> have also been presented. Microscopic electronic theories of segregation<sup>17-19</sup> presented so far use a tight-binding-type Hamiltonian. In a recent theory,<sup>19</sup> the tight-binding Hartree Hamiltonian with off-diagonal disorder is solved self-consistently to determine segregation in noble-metal alloys. It should be noted that this theory predicts correct segregation trends even for systems like Cu-Au alloy, the constituents of which differ appreciably in their molar volumes. In this paper we apply this theory to calculate surface segregation in  $\text{Cu}_x\text{Ni}_{1-x}$  alloy. Moreover, to describe the alloy system, we use for determining the electronic ener-

gy, four different sets of transfer functions in cluster-Bethe-lattice model (see Appendix A), whereas in Ref. 19 only three such transfer functions were used.

The surface segregation is determined by minimizing the free energy with respect to the alloy concentration. The minimization is performed with the constraints that the total number of atoms and electrons in the alloy is fixed. Thus, the segregation for (100) and (111) surfaces of Cu-Ni alloy, as well as the temperature dependence of the surface segregation is calculated and compared with existing experimental results. We demonstrate that the surface segregation is clearly reflected in the surface electronic-density of states (DOS).

Recently, there is increasing interest in the study of the core-level-binding energy shifts in metals<sup>20,21</sup> and alloys.<sup>22,23</sup> It has been pointed out that the surface core-level binding energy-shifts (SCLS) in alloys can be used to analyze the surface segregation in alloys. Therefore, in the present paper we use the electronic theory presented here to calculate the SCLS as a function of alloy composition including surface segregation.

In Sec. II we outline the electronic theory for surface segregation. In Sec. III we present for  $\text{Cu}_x\text{Ni}_{1-x}$  alloys results on segregation and its temperature dependence. Also, we discuss how segregation affects the surface DOS. In Sec. IV we discuss the effect of surface segregation on the SCLS in  $\text{Cu}_x\text{Ni}_{1-x}$  alloys. Section V gives a discussion of our results. Details on the mixed cluster-Bethe-lattice model, used to calculate the local density of states (LDOS) are presented in the Appendix A. In Appendix B the expression for the SCLS for alloy is derived.

## II. ELECTRONIC THEORY FOR SURFACE SEGREGATION

The internal energy  $E$  of the alloy is calculated by using the tight-binding Hartree Hamiltonian with intra-atomic electron-electron Coulomb interaction  $U$ . We take only the  $d$  band into account, because the electronic DOS of  $\text{Cu}_x\text{Ni}_{1-x}$  alloy system at the Fermi-level is mainly of  $d$  character.<sup>24</sup> The Hamiltonian is written as

$$H = \sum_{i,\sigma} \epsilon_{i\sigma} n_{i\sigma} + \sum_{\substack{i \neq j \\ \sigma}} t_{ij} c_{i\sigma}^\dagger c_{j\sigma}, \quad (1)$$

where

$$\epsilon_{i\sigma} = \epsilon_{i\sigma}^0 + U \langle n_{i-\sigma} \rangle. \quad (2)$$

Here,  $c_i^\dagger$  and  $c_i$  are usual creation and destruction operators for electrons with spin  $\sigma$  in Wannier state at site  $i$  occupied by  $\langle n_{i\sigma} \rangle$  electrons.  $\epsilon_{i\sigma}^0$  and  $t_{ij}$  are the single-site energy for the pure metal and hopping integral between nearest neighbors, respectively.  $\epsilon_{i\sigma}^0$  can have values  $\epsilon_{A\sigma}^0$  or  $\epsilon_{B\sigma}^0$  if the site is occupied by an  $A$  or  $B$  atom, respectively. The hopping integral  $t_{ij}$  can have values  $t_{AA}$ ,  $t_{BB}$ , or  $t_{AB}$  depending on the type of atoms on sites  $i$  and  $j$ . The alloy composition at the surface is determined by minimizing the free energy  $F(x_1, x_2, \dots, x_b)$  of the crystal with respect to the concentrations  $x_1, x_2, \dots$  of first, second, . . . crystal layers parallel to the surface. The constraints, that the number of atoms and the number of electrons are fixed, are included in the free-energy expression using Lagrange multipliers. Thus, we minimize the expression

$$\begin{aligned} \mathcal{F}(x_1, x_2, \dots) = & F(x_1, x_2, \dots) \\ & - \mu \sum_{\lambda=1}^{\infty} x_\lambda - \nu \sum_{\lambda=1}^{\infty} \langle n_\lambda \rangle. \end{aligned} \quad (3)$$

Here,  $\langle n_\lambda \rangle$  denotes the average number of electrons on an atom on  $\lambda$ th plane. The Lagrange-multipliers  $\mu$  and  $\nu$  are related to the bulk parameters of the alloy and are given by

$$\mu = \frac{\partial F}{\partial x_b}, \quad \nu = \frac{\partial F}{\partial \langle n_b \rangle} \equiv E_F. \quad (4)$$

The free energy  $F(x_1, x_2, \dots)$  is given by

$$F(x_1, x_2, \dots) = \sum_{\lambda=1}^{\infty} E_\lambda(x_1, x_2, \dots) - TS, \quad (5)$$

where  $E_\lambda$  is the internal energy of an atom in the

$\lambda$ th layer parallel to the surface. In the present model,

$$E_\lambda = \int_{-\infty}^{E_F} E \rho_\lambda(E) dE - E_{ee}^\lambda. \quad (6)$$

Here,  $\rho_\lambda(E)$  is average LDOS in the  $\lambda$ th layer,  $E_F$  is the Fermi energy, and  $E_{ee}^\lambda$  is the correction term in the energy for the  $\lambda$ th layer, due to Hartree-Fock approximation and is given for an atom at site  $i$  by

$$E_{ee}^\lambda(i) = \frac{1}{2} \sum_{\sigma} (\epsilon_{i\sigma} - \epsilon_{i\sigma}^0) \langle n_{i\sigma} \rangle. \quad (7)$$

The temperature dependence of the internal energy is negligible and therefore not taken into account. The configurational entropy of the random alloy system is given by

$$S = -k_B \sum_{\lambda} [x_\lambda \ln x_\lambda + (1-x_\lambda) \ln(1-x_\lambda)]. \quad (8)$$

The LDOS is determined from the diagonal element of the one-particle Green's function  $G_{ii,\sigma}(E)$ :

$$\rho_\lambda^i(E) = -\pi^{-1} \text{Im} \sum_{\sigma} G_{ii,\sigma}(E), \quad i = A, B. \quad (9)$$

The average LDOS is in the  $\lambda$ th layer given by

$$\rho_\lambda(E) = x_\lambda \rho_\lambda^A(E) + (1-x_\lambda) \rho_\lambda^B(E). \quad (10)$$

The diagonal Green's function  $G_{ii,\sigma}(E)$  is evaluated by a mixed Bethe-lattice model,<sup>19</sup> as described in Appendix A.

Now, from Eq. (3) it is clear that an analytical solution of the equation  $\partial \mathcal{F} / \partial x_i = 0$  is not possible. Therefore, the equilibrium concentration  $x_S (= x_1)$  at the surface is obtained by minimizing  $\mathcal{F}(x_1, x_2, \dots)$  with respect to  $x_1$  numerically.

## III. RESULTS FOR SURFACE SEGREGATION

The essential parameters needed for the calculation of the surface segregation of Cu are the bandwidths of the pure elements of the alloy, the mean energies of the  $d$  band, and the number of  $d$  electrons. The  $d$  bandwidths are taken to be 3.34 eV (Ref. 24) for Cu and 4.3 eV for Ni. The difference between the mean energies is taken as  $\epsilon_{\text{Ni}}^0 - \epsilon_{\text{Cu}}^0 = 1.8$  eV,<sup>24</sup> and the band fillings are taken equal to 10 electrons per atom for Cu, and 9.4 electrons<sup>24</sup> per atom for Ni. The intra-atomic Coulomb interaction  $U$  is taken to be 2 eV.

In Fig. 1 we present results for the surface con-

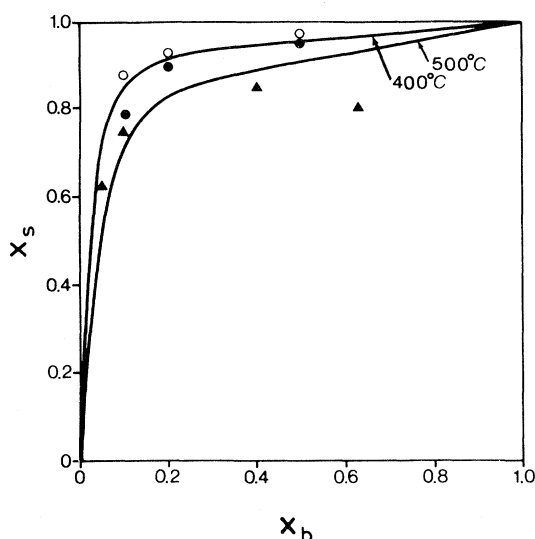


FIG. 1. The surface concentration  $x_s$  of Cu as a function of its bulk concentration  $x_b$  on (111) surface of  $\text{Cu}_x\text{Ni}_{1-x}$  alloy at 400 and 500°C. Experimental values refer to Brongersma *et al.*<sup>3</sup> Open circles: at 400°C, Full circles: at 500°C; and Sinfelt *et al.* (Ref. 6) (triangles).

centration  $x_s$  of Cu at a (111) surface for the two different temperatures 400°C and 500°C. As mentioned in the theory the calculation took into account intrasite electron-electron Coulomb interaction  $U$ . The electronic charge transfer from bulk to surface is calculated self-consistently. For comparison also results for  $U=0$  are shown in Fig. 2. The temperature dependence of the Cu concentration at the (111) surface of Cu-Ni alloy ( $x_b=0.107$ ) is shown in Fig. 3 and compared with the existing low-energy ion-scattering spectroscopy (LEIS) results.<sup>3</sup> In Fig. 4 we compare the segregation on (111) and (100) surfaces of Cu-Ni alloy.

In Fig. 5(a) we show the total bulk DOS for  $x_b=0.62$ . For comparison results are shown for  $x_b=0.62$  obtained by Stocks *et al.*<sup>24</sup> using coherent potential approximation (CPA). One notes that detailed structure in the DOS is not present in our calculation, but the main features of the DOS compare well. In Fig. 5(b) we illustrate how the surface segregation affects the surface DOS. Instead of curve 2, which would give the DOS in the absence of surface segregation, one obtains a DOS shown by curve 1 as a result of segregation. In Fig. 5(c) we show the surface DOS for two different surface concentrations. The full curve refers to  $x_s=0.91$  and the dashed curve to  $x_s=0.83$ .

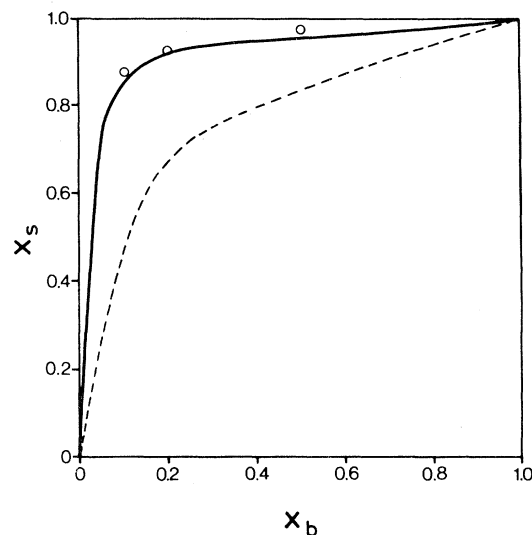


FIG. 2. The surface concentration  $x_s$  of Cu as a function of its bulk concentration  $x_b$  on (111) surface of  $\text{Cu}_x\text{Ni}_{1-x}$  alloy at 400°C. The full curve refers to the Coulomb interaction  $U=2$  eV and dashed curve to  $U=0$ .

The corresponding bulk concentration is  $x_b=0.2$ . These two different surface concentrations  $x_s$  correspond to the two different temperatures 400°C and 500°C, respectively. In Fig. 5(d) we compare the surface DOS for  $x_b=0.2$ ,  $x_s=0.91$  (dashed curve) with that of pure copper (full curve).

In Fig. 6 we show the SCLS ( $\Delta_c^S$ ) for Ni as a function of Cu concentration, calculated from Eq. (15). These results together with the SCLS are discussed in Sec. V.

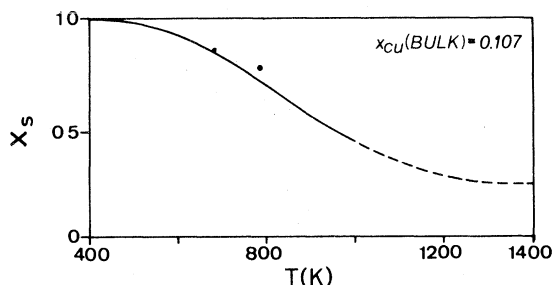


FIG. 3. The surface concentration  $x_s$  of Cu on (111) surface of  $\text{Cu}_x\text{Ni}_{1-x}$  alloy with bulk Cu concentration  $x_b=0.107$ , as a function of temperature. Experimental points are taken from Brongersma *et al.* (Ref. 3).

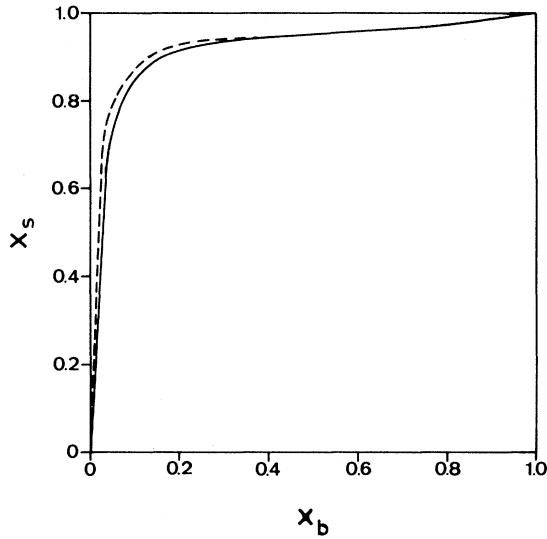


FIG. 4. The surface concentration  $x_s$  of Cu as a function of its bulk concentration  $x_b$  at 400°C for (111) surface (full line), and for (100) surface (dashed line).

#### IV. ELECTRONIC THEORY FOR SURFACE CORE-LEVEL-BINDING ENERGY SHIFT (SCLS)

In the following we analyze the effect of surface segregation on SCLS. This is of interest for an analysis of surface segregation from SCLS data. The SCLS for  $A$  and  $B$  in  $A_xB_{1-x}$  alloy can be given as (see Appendix B)

$$\Delta_c^S(A) = E^s(A^*, A_xB_{1-x}) - E^s(A, A_xB_{1-x}) \quad (11)$$

and

$$\Delta_c^S(B) = E^s(B^*, A_xB_{1-x}) - E^s(B, A_xB_{1-x}) \quad (12)$$

Here,  $E^s(A^*, A_xB_{1-x})$  denotes the surface enthalpy (difference in energy of an atom in the bulk and in the surface) of  $A^*$  in the alloy  $A_xB_{1-x}$ ,  $A^*$  ( $B^*$ ) denotes the core-ionized  $A$  ( $B$ ) atom. If  $A$  and  $B$  are the neighboring elements in the Periodic Table, then  $B^* = A$  (which is the case for Cu-Ni alloy).

Therefore Eq. (12) becomes

$$\Delta_c^S(B) = E^s(A, A_xB_{1-x}) - E^s(B, A_xB_{1-x}) \quad (13)$$

Now, in terms of the LDOS  $\rho_s^i(b)$  at surface (bulk), the surface enthalpy can be written as

$$E^s(A, A_xB_{1-x}) = \int_{-\infty}^{E_F} (E - \epsilon_A^s) \rho_s^A(E) dE - \int_{-\infty}^{E_F} (E - \epsilon_A^b) \rho_b^A(E) dE - [E_{ee}^s(A) - E_{ee}^b(A)] \quad (14)$$

where  $E_{ee}(A)$  denotes the correction term in energy for  $A$  atom due to Hartree-Fock approximation, given by Eq. (7). Therefore, Eq. (13) can be written as

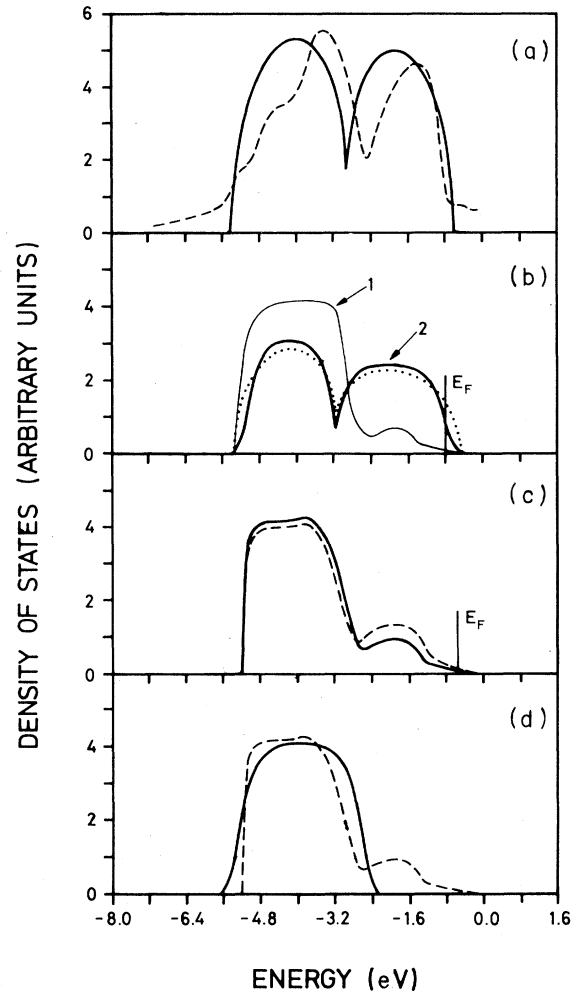


FIG. 5. Various results for the electronic density of states at (111) surface of  $Cu_xNi_{1-x}$  alloy. (a) shows the total DOS in bulk for  $x_b=0.62$  (full curve). For comparison the dashed curve refers to CPA calculations by Stocks *et al.* (Ref. 24) again for  $x_b=0.62$ . (b) shows the average DOS for  $x_b=0.5$ . The dotted curve refers to bulk DOS. Curves 1 and 2 refer to the DOS at the surface for  $x_s=0.95$  and  $x_s=0.5$ , respectively. Note,  $x_s=0.95$  is the calculated surface concentration for  $x_b=0.5$ . (c) shows the average DOS with  $x_b=0.2$  at surface with  $x_s=0.91$  (full curve) with  $x_s=0.83$  (dashed curve). These two surface concentrations are calculated  $x_s$  for  $x_b=0.2$  at 400 and 500°C, respectively. (d) shows the comparison of DOS at surface for  $x_b=0.2$ ,  $x_s=0.91$  (dashed curve) with that of pure Cu (full curve).

$$\Delta_c^S(B) = \int_{-\infty}^{E_F} E(\Delta\rho^A(E) - \Delta\rho^B(E))dE - (n_A^s\epsilon_A^s - n_A^b\epsilon_A^b - n_B^s\epsilon_B^s + n_B^b\epsilon_B^b) - [E_{ee}^s(A) - E_{ee}^b(A) - E_{ee}^s(B) + E_{ee}^b(B)], \quad (15)$$

where

$$\Delta\rho^i(E) = \rho_s^i(E) - \rho_b^i(E),$$

$$n_i^{s(b)} = \int_{-\infty}^{E_F} \rho_{s(b)}^i(E) dE.$$

Equation (15) is used to calculate the SCLS for Ni in  $\text{Cu}_x\text{Ni}_{1-x}$  alloy. A similar expression for SCLS for Cu can also be written, but in the present formulation it is not possible to calculate it, because one needs the surface enthalpy of Zn (next higher element of Cu) in  $\text{Cu}_x\text{Ni}_{1-x}$  alloy.  $\Delta_c^S(B)$  is the heat of segregation of  $A$  in the alloy  $A_xB_{1-x}$ .<sup>22</sup>

## V. DISCUSSION

For simplicity, we have assumed in the calculation only the surface concentration to be different from the bulk (the monolayer model). From experiments<sup>3-5</sup> and the calculations based on bond-breaking model,<sup>13</sup> the concentrations in the second, third, . . . layers are found to be very nearly equal to the bulk value, and therefore the monolayer model is a good approximation for Cu-Ni alloy.

As can be seen from Fig. 1, our surface segregation results are in good agreement with the results obtained from the LEIS experiment,<sup>3</sup> which precisely measures the surface concentration. Figure 2 shows that our results obtained for  $U=0$  are in bad agreement with experiment. This indicates the importance of Coulomb interactions between the electrons. We find that due to  $U \neq 0$ , surface

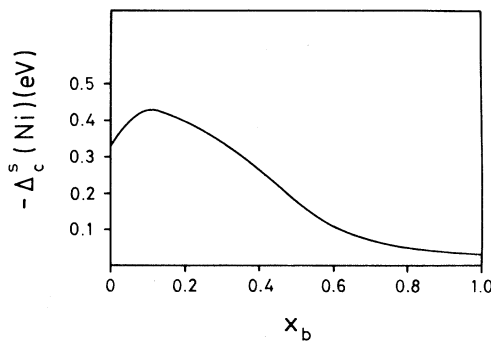


FIG. 6. The surface core-level shift for Ni [ $\Delta_c^S(\text{Ni})$ ] as a function of bulk Cu concentration.

segregation of Cu is enhanced. A similar effect has also been obtained earlier.<sup>19</sup>

Our results shown in Fig. 4 indicate slight enhancement of Cu surface segregation on the more opened (100) surface as compared to a (111) surface, a fact which is observed experimentally.<sup>25</sup> From the results of DOS in Fig. 5 it is obvious that with increasing concentration the peak in the average DOS centered on Cu increases. Consequently, one expects strong Cu peaks in the energy-distribution curves of photoelectron emitted from a Cu rich Cu-Ni alloy surface, as observed.<sup>26</sup> Figure 5(c) illustrates that with increasing temperature the Cu peak will decrease, since the Cu concentration on the surface decreases. Figure 5(d) shows that in the case of very strong surface segregation of Cu, the average DOS at the surface looks almost similar to that of pure Cu.

In Fig. 6 we show the surface core-level binding energy shift for Ni on (111) surface calculated from Eq. (15). So far, no experimental results are available. However, it is interesting to note that the results of our self-consistent electronic calculation show a similar trend as those recently obtained by Kumar *et al.*<sup>22</sup> using a phenomenological model. For transition metals, Desjonqueres *et al.*<sup>21</sup> have explained the origin of the SCLS as a consequence of the atomic  $d$ -level shifts at the surface in order to preserve charge neutrality. Though in our calculation a somewhat different approach is used, we also note that the change in atomic  $d$  levels  $\epsilon_d$  for Ni at the surface is similar to the curve shown in Fig. 6. For small bulk Cu concentrations, a big shift is observed in the surface-core-level of Ni, which can be understood from the DOS curves shown in Fig. 5. In the bulk there will be large DOS near the Fermi energy, whereas at the surface, because of small Ni concentrations, a small DOS will be at  $E_F$ . So, to preserve the charge neutrality Ni level should be shifted to higher energies. As the bulk Cu concentration increases, the shift reduces. This is because the surface DOS is expected to remain almost unchanged because of small variation in surface concentration, as the bulk concentration is increased.

As the surface composition is different in different crystal planes, the SCLS is also expected to be different. In our calculation for surface enthal-

pies, we have considered only  $d$  electrons. However, there will also be some contribution from  $s$  electrons, particularly important for Cu. Since in the expression for SCLS only the difference in surface enthalpies appear, we feel that this will get canceled, as the contribution of  $s$  electrons is almost constant throughout the transition-metal series. Finally, we have not considered the possibility of a different  $s$ - $d$  charge configuration at the surface. This may lead to some change in SCLS.

The results of our simple tight-binding calculation are encouraging, as our calculated surface composition is in good agreement with experiment. As the importance of the SCLS in the study of segregation has already been pointed out,<sup>22,23</sup> we suggest that experiments should be done to measure SCLS in alloys, to supplement already-used techniques available in the study of surface segregation.

#### ACKNOWLEDGMENTS

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#### APPENDIX A: DETERMINATION OF DIAGONAL GREEN'S FUNCTION IN MIXED BETHE-LATTICE MODEL

As discussed earlier by Kittler and Falicov,<sup>27</sup> in the bulk of the alloy one has only four different types of sites in the Cayley tree, since the branching ratios at a site depend only on the type of the atom at that site and its parent atom. In the bulk, the ratio of the Green's function at a particular site to that of its parent, depending upon whether the link is made via an  $A$ - $A$ ,  $A$ - $B$ ,  $B$ - $A$ , or  $B$ - $B$  bond, are denoted by  $\delta_1$ ,  $\delta_2$ ,  $\delta_3$ , and  $\delta_4$ , respectively, and are given by

$$\begin{aligned}\delta_1 &= t_{AA} \{ E - \epsilon_A^b - (Z-1)[xt_{AA}\delta_1 + (1-x)t_{AB}\delta_3] \}^{-1}, \\ \delta_2 &= t_{AB} \{ E - \epsilon_A^b - (Z-1)[xt_{AA}\delta_1 + (1-x)t_{AB}\delta_3] \}^{-1}, \\ \delta_3 &= t_{AB} \{ E - \epsilon_B^b - (Z-1)[xt_{AB}\delta_2 + (1-x)t_{BB}\delta_4] \}^{-1}, \\ \delta_4 &= t_{BB} \{ E - \epsilon_B^b - (Z-1)[xt_{AB}\delta_2 + (1-x)t_{BB}\delta_4] \}^{-1},\end{aligned}\tag{A1}$$

where  $Z$  is the coordination number in the bulk. Now, to describe the surface we need three other sets of such transfer functions [Eq. (A1)], depending upon whether the link is made between two surface atoms, between a surface and a bulk atom, and vice versa. The corresponding sets of transfer functions are denoted by  $(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$ ,  $(\beta_1, \beta_2, \beta_3, \beta_4)$ , and  $(\gamma_1, \gamma_2, \gamma_3, \gamma_4)$  and are given by

$$\begin{aligned}\alpha_1 &= t'_{AA} \{ E - \epsilon_A^s - (Z_0-1)[x_1 t'_{AA} \alpha_1 + (1-x_1) t'_{AB} \alpha_3] - Z_1 [xt_{AA} \beta_1 + (1-x)t_{AB} \beta_3] \}^{-1}, \\ \alpha_2 &= (t'_{AB}/t'_{AA}) \alpha_1, \\ \alpha_3 &= t'_{AB} \{ E - \epsilon_B^s - (Z_0-1)[x_1 t'_{AB} \alpha_2 + (1-x_1) t'_{BB} \alpha_4] - Z_1 [xt_{AB} \beta_2 + (1-x)t_{BB} \beta_4] \}^{-1}, \\ \alpha_4 &= (t'_{BB}/t'_{AB}) \alpha_3.\end{aligned}\tag{A2}$$

Here,  $t'_{ij}$  denotes the hopping integral on the surface;  $Z_0$  and  $Z_1$  are the numbers of nearest neighbors in the surface plane and between two adjacent planes, respectively.  $x$  and  $x_1$  are the bulk and the surface concentrations, respectively.

Similarly, the set of transfer functions connecting a surface atom to a bulk atom are given by

$$\begin{aligned}\beta_1 &= t_{AA} \{ E - \epsilon_A^b - (Z_1-1)[xt_{AA}\gamma_1 + (1-x)t_{AB}\gamma_3] - (Z_0+Z_1)[xt_{AA}\delta_1 + (1-x)t_{AB}\delta_3] \}^{-1}, \\ \beta_2 &= (t_{AB}/t_{AA}) \beta_1, \\ \beta_3 &= t_{AB} \{ E - \epsilon_B^b - (Z_1-1)[xt_{AB}\gamma_2 + (1-x)t_{BB}\gamma_4] - (Z_0+Z_1)[xt_{AB}\delta_2 + (1-x)t_{BB}\delta_4] \}^{-1}, \\ \beta_4 &= (t_{BB}/t_{AB}) \beta_3.\end{aligned}\tag{A3}$$

and the set of transfer functions connecting a bulk-atom to a surface atom is given by

$$\begin{aligned}\gamma_1 &= t_{AA} \{ E - \epsilon_A^s - Z_0 [x_1 t'_{AA} \alpha_1 + (1-x_1) t'_{AB} \alpha_3] - (Z_1 - 1) [x t_{AA} \beta_1 + (1-x) t_{AB} \beta_3] \}^{-1}, \\ \gamma_2 &= (t_{AB}/t_{AA}) \gamma_1, \\ \gamma_3 &= t_{AB} \{ E - \epsilon_B^s - Z_0 [x_1 t'_{AB} \alpha_2 + (1-x_1) t'_{BB} \alpha_4] - (Z_1 - 1) [x t_{AB} \beta_2 + (1-x) t_{BB} \beta_4] \}^{-1}, \\ \gamma_4 &= (t_{BB}/t_{AB}) \gamma_3.\end{aligned}\tag{A4}$$

These sets of nonlinear equations are solved iteratively. The one-particle Green's-functions in the bulk [ $G_{00}^{i,b}(E)$ ] and at the surface [ $G_{00}^{i,s}(E)$ ] are obtained using the relations

$$G_{00}^{A,s}(E) = \{ E - \epsilon_A^s - Z_0 [x_1 t'_{AA} \alpha_1 + (1-x_1) t'_{AB} \alpha_3] - Z_1 [x t_{AA} \beta_1 + (1-x) t_{AB} \beta_3] \}^{-1},\tag{A5}$$

$$G_{00}^{B,s}(E) = \{ E - \epsilon_B^s - Z_0 [x_1 t'_{AB} \alpha_2 + (1-x_1) t'_{BB} \alpha_4] - Z_1 [x t_{AB} \beta_2 + (1-x) t_{BB} \beta_4] \}^{-1},$$

$$G_{00}^{A,b}(E) = \{ E - \epsilon_A^b - Z [x t_{AA} \delta_1 + (1-x) t_{AB} \delta_3] \}^{-1},\tag{A6}$$

$$G_{00}^{B,b}(E) = \{ E - \epsilon_B^b - Z [x t_{AB} \delta_2 + (1-x) t_{BB} \delta_4] \}^{-1},$$

These sets of equations (A5) and (A6) are used to determine LDOS at surface and bulk, respectively, using Eq. (9).

## APPENDIX B: EXPRESSION FOR SCLS IN ALLOY

In deriving Eqs. (11) and (12) we adopt the approach of Johansson and Mårtensson,<sup>28</sup> in which one assumes (i) that the final core-ionized state is fully screened by valence electrons and (ii) the screening charge distribution around the core-ionized state is the same as that of a  $(Z+1)$  atom where  $Z$  is the atomic number in the initial state. The bulk core-level binding-energy of  $A$  component in binary alloy  $A_x B_{1-x}$  is written as<sup>22,23</sup>

$$\begin{aligned}E_{c,F}^b(A, A_x B_{1-x}) &= -E_{\text{coh}}^b(A^*, A_x B_{1-x}) \\ &\quad + E_{\text{coh}}^b(A, A_x B_{1-x}) + E_{c \rightarrow v}(A).\end{aligned}\tag{B1}$$

Similarly for  $B$  atom, one finds

$$\begin{aligned}E_{c,F}^b(B, A_x B_{1-x}) &= -E_{\text{coh}}^b(B^*, A_x B_{1-x}) \\ &\quad + E_{\text{coh}}^b(B, A_x B_{1-x}) + E_{c \rightarrow v}(B).\end{aligned}\tag{B2}$$

Here,  $-E_{\text{coh}}^b(A^*, A_x B_{1-x})$  is the cohesive energy of  $A^*$  (core-ionized  $A$  atom) in the alloy.  $E_{c \rightarrow v}$  is

the excitation energy of the core-electron  $c$  into the valence electron  $v$ . Similarly, the core-level binding energies for the surface atoms are written as

$$\begin{aligned}E_{c,F}^s(A, A_x B_{1-x_1}) &= -E_{\text{coh}}^s(A^*, A_x B_{1-x_1}) \\ &\quad + E_{\text{coh}}^s(A, A_x B_{1-x_1}) + E_{c \rightarrow v}(A),\end{aligned}\tag{B3}$$

and

$$\begin{aligned}E_{c,F}^s(B, A_x B_{1-x_1}) &= -E_{\text{coh}}^s(B^*, A_x B_{1-x_1}) \\ &\quad + E_{\text{coh}}^s(B, A_x B_{1-x_1}) + E_{c \rightarrow v}(B).\end{aligned}\tag{B4}$$

The superscripts  $b$  and  $s$  in Eqs. (B1)–(B4) refer to bulk and surface, respectively. The SCLS of  $A$  is written as

$$\begin{aligned}\Delta_c^S(A) &= E_{c,F}^s(A, A_x B_{1-x_1}) - E_{c,F}^b(A, A_x B_{1-x}) \\ &= E^s(A^*, A_x B_{1-x}) - E^s(A, A_x B_{1-x}),\end{aligned}\tag{B5}$$

and similarly for  $B$ ,

$$\Delta_c^S(B) = E^s(B^*, A_x B_{1-x}) - E^s(B, A_x B_{1-x}),\tag{B6}$$

where  $E^s(A, A_x B_{1-x})$  denotes the surface enthalpy of  $A$  in the alloy  $A_x B_{1-x}$ .

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