

Surface composition of clean and oxygen-covered Au₃Cu alloy

H. C. Poon

Department of Physics, National University of Singapore, Kent Ridge, 0511 Singapore

B. C. Khanra* and T. S. King

Ames Laboratory and Department of Chemical Engineering, 231 Sweeney Hall, Iowa State University, Ames, Iowa 50011

(Received 13 October 1992; revised manuscript received 3 February 1993)

Surface segregation behavior of clean and oxygen-adsorbed Au₃Cu systems has been studied theoretically within the tight-binding formalism. It has been found that for the clean Au₃Cu system the top layer is Au enriched, while the second layer is Cu enriched. In the presence of a monolayer of oxygen atoms, on the other hand, there is a segregation reversal in the top layer which becomes Cu enriched. The above findings are in total agreement with the very recent experimental impact collision ion-scattering spectroscopic results.

I. INTRODUCTION

In bimetallic alloys, surface compositions are usually different from the bulk composition. In studies of heterogeneous catalysis employing bimetallic systems one must know this surface composition for a complete understanding of catalytic activity and selectivity. For a clean alloy surface there are several driving forces leading to the segregation of one of the components to the surface. Among them are the differences in surface energy of the individual metallic components, their relative atomic sizes, and the heats of solution in one another. Miedema¹ has shown empirically that the segregation forces originating from these three criteria account for the observed segregation behavior in most of the transition-metal alloys. Mukherjee and Moran-Lopez² have tried to explain the segregation behavior in a large number of transition-metal alloys from a simple tight-binding theory. Experimentally, Auger electron spectroscopy and low-energy ion-scattering techniques have been used to determine the surface composition of clean alloys with some success.

In a real heterogeneous catalytic system, the chemisorption of atoms and molecules on the alloy catalyst can cause a profound change in surface composition. This is due to the different strengths of the chemisorption bond of the adsorbate with different metallic components of the alloy. Under realistic reaction conditions, it is the knowledge of the composition of the adsorbate-covered alloy surface that is useful in understanding the catalytic activity rather than the surface composition of the clean alloy. Unfortunately, there is no easily implemented theory to treat this chemisorption-induced surface segregation. In the past, a simple semiempirical theory has been used³⁻⁶ in which the surface concentration $x_s(A)$ in an alloy A_xB_{1-x} could be obtained from the relation

$$\frac{x_s}{1-x_s} = \frac{x}{1-x} e^{Q/RT}, \quad (1)$$

where x is the bulk concentration of A ; $Q = Q_0 + (E_A - E_B)\Theta$ is the "heat of segregation" of A in the

presence of adsorbates; Q_0 is the heat of segregation for the clean A_xB_{1-x} alloy; E_A and E_B are the chemisorption energies of the adsorbate on A and B metals, respectively; and Θ is the adsorbate coverage. This approach suggests that the relative magnitudes of Q_0 and $(E_A - E_B)\Theta$ ultimately control the segregation of one component or the other to the surface. However, the equation (1) employing the heat of segregation oversimplifies the thermodynamics of segregation. Since Q appears as an exponent in the equation, the segregation behavior becomes very sensitive to the Q values. King and Donnelly⁷ and very recently Montejano-Carrizales and Moran-Lopez⁸ have used the pair-bond-type model to investigate surface segregation in the presence of chemisorbed species. The phenomenological approaches, however, do not describe segregation in terms of electronic properties of the system such as the electronic density of states and the internal electronic energy, etc. This may be done by microscopic electronic theory. For example, Modak and Khanra⁹ used the tight-binding formalism to study H-induced surface segregation in the Cu_xNi_{1-x} system. In that scheme a monolayer of hydrogen atoms was considered and the entire system was treated in the tight-binding formalism by considering only the d electrons. For simplicity of the calculation, the atoms were assumed to be chemisorbed on atop positions. The hopping interactions between metallic d orbitals and the hydrogen s orbital were adjusted to produce the correct H/Ni and H/Cu chemisorption properties. The adsorbate-adsorbate hopping interaction was arbitrarily chosen resulting in good agreement between theory and experiment. However, we feel it is difficult to extend this calculation to other complicated adsorbates such as oxygen and carbon monoxide because these molecules cannot be represented by only one orbital. Inclusion of more adsorbate orbitals in the scheme would require *a priori* knowledge of various hopping interactions between metallic and adsorbate orbitals, and between adsorbate orbitals themselves. It is difficult to determine these values from experimental results or to derive them theoretically. In addition, the assumption of

chemisorption at atop positions makes the generality of the segregation studies limited. In the present work we propose a tight-binding scheme that overcomes some of these difficulties in order to study surface segregation in the presence of more complex adsorbates. In essence, we use the tight-binding theory of Mukherjee *et al.*¹⁰ for a clean surface; but here we modify the surface-surface and surface-bulk hopping parameters to take into account the effect of chemisorption. This modification is dependent on the strength of chemisorption of the adatom on the individual metals and it produces results in reasonably good agreement with the recent experimental study to investigate the oxygen-covered Au₃Cu alloy¹¹ using the impact collision ion-scattering spectroscopic (ICISS) technique. The experiment showed that in the case of a clean surface, the top two layers are enriched in Au and Cu, respectively. But in the presence of a monolayer of oxygen there is a surface composition reversal; the top layer was enriched with copper and the second layer was enriched with gold.

II. THEORETICAL FORMALISM

A. Clean surface

Band-structure calculations¹² using fully relativistic Korringa-Kohn-Rostoker (KKR) and KKR-coherent-potential-approximation methods have shown that for the Au-Cu alloy only the *d* states are substantially affected when one of the atoms in pure Cu is replaced by Au. The *sp* contributions to the electronic properties of the system would, therefore, remain approximately constant when the concentrations are varied. An earlier electronic theory² used only the *d*-band density of states (DOS) of pure metals to predict the segregation behavior in 702 transition-metal alloys. Although the *d* band was assumed to be of rectangular shape, the predictions agreed in all of the known cases except for a few containing magnetic elements. On the basis of the above work^{2,12} we consider here only the *d* electrons of the system. However, unlike the scheme in Ref. 2 we calculate the local DOS for the calculation of energy instead of assuming for it a rectangular shape. For a segregating alloy system $A_x B_{1-x}$ the layer compositions may be derived by minimizing the total free-energy \mathcal{F} of the system with respect to the layer compositions x_1, x_2, \dots, x , etc. If x_λ is the concentration of *A* components in the λ th layer, the free-energy functional for the system may be written as^{9,10,13}

$$\mathcal{F} = \sum_{\lambda=1}^{\infty} \left[\int_{-\infty}^{E_F} \{ E \rho_\lambda(E) dE - E_\lambda^{ee} \} + k_B T [x_\lambda \ln x_\lambda + (1-x_\lambda) \ln(1-x_\lambda)] - \mu x_\lambda - E_F \langle n_\lambda \rangle \right], \quad (2)$$

where the quantity in curly brackets is the internal energy of the atoms. The quantity $k_B T [x_\lambda \ln x_\lambda + (1-x_\lambda) \ln(1-x_\lambda)]$ is the entropy contribution to the free energy. The terms μx_λ and $E_F \langle n_\lambda \rangle$ appear in the energy expression from the constraints that the total

number of atoms and electrons in the system are conserved. E_F and μ are the Fermi energy and the chemical potential of the system, respectively. E_λ^{ee} is the correction to the internal energy due to the Hartree-Fock approximation given by

$$E_\lambda^{ee} = \frac{1}{2} \sum_{\sigma=\text{spin}} U \langle n_\lambda^{-\sigma} \rangle \langle n_\lambda^{\sigma} \rangle, \quad (3)$$

where U is the intra-atomic electron-electron Coulomb interaction. We assume that since the *d* band remains filled for noble-metal alloy systems, such as Au₃Cu, this correction is a constant and need not be considered explicitly.

The electronic density of states $\rho_\lambda(E)$ may be calculated from the diagonal part of the Green function as

$$\rho_\lambda^i(E) = -\frac{1}{\pi} \sum_{\sigma} \text{Im} G_\lambda^{ii,\sigma}, \quad (i = A, B) \quad (4)$$

where the Green functions are evaluated from Dyson's equation as

$$E \langle i | G | j \rangle = \delta_{ij} + \sum_n \langle i | H | n \rangle \langle n | G | j \rangle \quad (5)$$

with the tight-binding Hamiltonian

$$H = \sum_i \varepsilon_i |i\rangle \langle i| + \sum_{i,j(i \neq j)} t_{ij} |i\rangle \langle j|, \quad (6)$$

where ε_i and t_{ij} represent the *i*th site energy and the hopping interaction between the *i*th and the *j*th site, respectively. The intermediate sites between the *i*th and *j*th sites are given by *n*.

In this work, the diagonal Green functions and, hence, the local density of states are determined by using a generalization of the cluster-Bethe-lattice method.¹⁴⁻¹⁸ In this method, one substitutes the system of connected atoms with the same coordination number *Z* as the lattice under consideration, but without closed rings of bonds. The advantage of this method is that the one-particle Green function in the binary alloy may be expressed in terms of four transfer functions; and in the case of the disordered alloy the Green functions can be expressed analytically.^{17,18} The effect of short-range order on segregation behavior is not considered in the present work.

In the execution of the above scheme for segregation studies one must consider the energetic difference between the surface atoms and bulk atoms due to their different environments. In general, the hopping integrals vary with the coordination number *Z* as $1/\sqrt{Z}$.¹⁹ This would show the surface hopping integrals to have larger values than the bulk hopping integrals. The tight-binding Ising model calculation by Legrand, Treglia, and Ducastelle²⁰⁻²² predicts that for the fcc(111) and fcc(100) surfaces the surface-surface and surface-bulk hopping interactions are 1.5 times larger than the bulk hopping interactions. For the fcc(110) surface the surface hopping integrals are twice the bulk hopping integrals. With this approach they could explain the segregation behavior of Pt-Ni (100), (110), and (111) surfaces.²⁰ They also used this scheme with some success for the Pt-Rh system.²² In this work we use the same increase for surface-surface

and surface-bulk hopping interactions with respect to the bulk-bulk hopping interactions as used by Legrand, Treglia and Ducastelle.²⁰⁻²² Let this increment parameter (i.e., the ratio of the surface-surface or surface-bulk hopping parameter to the bulk-bulk hopping parameter) be α_0 . We have calculated the surface composition for $\alpha_0 = 1.2-1.6$ and show that the surface composition in a clean alloy agrees very well with the experimental results for $\alpha_0 = 1.4-1.6$.

B. Adsorbate-covered surface

In the presence of chemisorbed species the energetics of the system must be considered carefully. In the case of oxygen on Au_3Cu , the oxygen atoms interact strongly with copper but not with gold. The existence of the chemisorption bond with the surface Cu atoms would cause a redistribution of the electronic charge density around the surface atoms. This will greatly modify the surface-surface and surface-bulk hopping interactions. In the tight-binding scheme the hopping integrals are directly proportional to the cohesive energy. In the process of chemisorption of a monolayer of oxygen on Cu atoms there is a net gain in energy E_c where E_c is the chemisorption energy of an oxygen atom on Cu. From the point of view of pure energetics we may intuitively associate this chemisorption with a virtual increase in surface cohesive energy of a Cu atom and hence an increase in the surface-surface and surface-bulk hopping interactions. Considering the bulk and surface cohesive energies of Cu as 3.47 and 2.797 eV, respectively,⁷ and E_c for oxygen on Cu as 3.08 eV,⁵ the effective values of the surface-surface and surface-bulk hopping interactions are of the order of 2.5 times the value of the bulk-bulk hopping interactions in Cu. For the Au surface atoms the hopping interaction remains unaffected by oxygen chemisorption. The overall effect of using the chemisorption-modified surface-surface and surface-bulk hopping interactions in the calculations is the following: In a clean Au-Cu alloy the Au atoms segregate to the surface because of the higher surface-surface and surface-bulk hopping interactions in Au compared to their values in Cu. But in the presence of chemisorbed oxygen atoms, the values of the surface-surface and surface-bulk hopping interactions in Cu become larger than the corresponding values in Au, and this leads to surface enrichment with Cu atoms.

In this work we have calculated the surface compositions for $\alpha = 1.5-2.5$ to find how the results vary as a function of α . The main advantage of this approach is that we may proceed with the segregation calculation in the same way as in the case of the absence of chemisorption, but now with a modified hopping interaction which is proportional to the surface cohesive energy. This approach avoids an unnecessary complexity involved in considering the adsorbed monolayer directly in the tight-binding scheme.

III. RESULTS

In the present calculation the parameters used are the hopping parameters t_{ij} , the site energies ϵ_i ($i = A$ or B), and the temperature T . The hopping parameters for the bulk are related to the bandwidths of pure metals. The

bandwidths of Au and Cu are taken to be 5.3 and 3.1 eV, respectively.^{13,23} The difference in site energies of Cu and Au was taken to be 1.4 eV.^{13,23} The calculations were performed for $T = 300$ K. We calculated the composition of the top two layers of the Au_3Cu system with and without adsorbed oxygen atoms by numerical minimization of the free energy given by Eq. (2) as a function of composition of these two layers. In Sec. II A it was shown for a clean alloy surface for a fcc(100) surface that the surface-surface and the surface-bulk hopping interactions would be approximately equal to 1.5 times the hopping parameters in the bulk²⁰⁻²² ($\alpha_0 \approx 1.5$). We present in Table I the computed results of the top two layer compositions for several values of α_0 . We note that for α_0 in the range of 1.4-1.5 the top layer is Au enriched while the second layer is Cu enriched as observed in the ICISS experiment by Nakanishi *et al.*¹¹ The experiment predicted a top-layer Au concentration of 0.95 and second-layer Au concentration of 0.05. The calculated results are in very good agreement with the experimental results for the top layer. For the second layer the present calculation shows a somewhat higher Au concentration than found in the experiment, but the experiment as well as the theory both show Cu enrichment in the second layer.

In Fig. 1 we plot a typical local density of states for an Au atom, a Cu atom, and the average alloy in the bulk and in the surface regions. The average alloy density is calculated by the approximation¹⁰

$$\rho_{\text{alloy}}(E) = x\rho_A(E) + (1-x)\rho_B(E) \text{ for the bulk,}$$

and

$$\rho_{\text{alloy}}^s(E) = x_s\rho_A^s(E) + (1-x_s)\rho_B^s(E) \text{ for the surface.}$$

For convenience, the zero of energy in the density of states versus energy plots is considered to be located at the midpoint between the d -band maxima of Au and Cu. To calculate the surface density of states we consider two values of α_0 . In one case, $\alpha_0 = 1$ corresponds to the case where the surface-surface and surface-bulk hopping interactions are the same as bulk-bulk hopping interactions. In the second, $\alpha_0 = 1.5$ corresponds to the surface-linked hopping interactions that are 1.5 times stronger than the bulk-bulk interaction. The concentration profile is assumed to be $x_1(\text{Au}) = 0.9$, $x_2(\text{Au}) = 0.3$, and $x(\text{Au}) = 0.75$ for both Figs. 1(b) and 1(c). The bandwidth of the local density of states of an atom is a monotonically increasing function of the interaction strength with its

TABLE I. Composition of the top two layers of Au_3Cu for different strengths of surface-surface and surface-bulk hopping interactions.

α_0	$x_1(\text{Au})$	$x_2(\text{Au})$
1.2	0.6	0.2
1.3	0.7	0.3
1.4	0.9	0.3
1.5	0.9	0.3
1.6	0.9	0.4

neighbors. As seen from Fig. 1, the bandwidth of a surface atom with $\alpha_0=1$ is narrower than that of a bulk atom since the former has fewer neighbors. The band edges for surface DOS's are, however, the same as in the bulk. When α_0 is increased from 1 to 1.5, the bandwidth of a surface atom increases again. From a comparison of Figs. 1(b) and 1(c) it may be noted that higher binding-energy states are populated more for $\alpha_0=1.5$ than for $\alpha_0=1.0$. This makes the state corresponding to Fig. 1(c) energetically more favorable than the state corresponding to Fig. 1(b).

In the presence of a chemisorbed oxygen species, the density of states are calculated for $\alpha(\text{Cu-Cu})=2.5$ and compared with the density of states for clean surfaces. Some typical density-of-states plots are shown in Fig. 2. The concentration profile is assumed to be $x_1(\text{Au})=0.1$, $x_2(\text{Au})=0.3$, and $x(\text{Au})=0.75$ for both Figs. 2(a) and 2(b). Here we observe the same trends as before: higher binding-energy states are populated more for the higher $\alpha(\text{Cu-Cu})$ value. This again makes the state correspond-

ing to Fig. 2(b) energetically more favorable than the one corresponding to Fig. 2(a). The lack of structures in the local DOS curves in Figs. 1 and 2 arise from the neglect of closed rings of bonds in the Bethe-lattice scheme used in this work.

We calculated the Au concentration in the top two layers using $\alpha(\text{Cu-Cu})=2.5$ and $\alpha(\text{Au-Au})=1.5$. The Au concentrations in the top two layers were found to be 0.1 and 0.5, respectively. The ICISS experiment gives these values as 0.05 and 0.95, respectively. The calculated results indicate that the top layer is Cu enriched and, thus, that there is a complete segregation reversal in the top layer under a monolayer of oxygen. In the second layer, the calculated Au concentration is less than that found in the experiment indicating a Cu enrichment also in the second layer in the presence of chemisorption. For intermediate coverages ($0 < \Theta < 1$) of oxygen we did not perform any explicit calculation. However, if a variation of $\alpha(\text{Cu-Cu})$ from 1.5 to 2.5 is any indication of increasing the coverage from 0.0 to 1.0, we find the Au concentration in the top two layers as shown in Fig. 3. We do not compare them with the experimental Au concentration versus oxygen coverage results because the relationship between the theoretical parameter α and the experimental parameter Θ is not known.

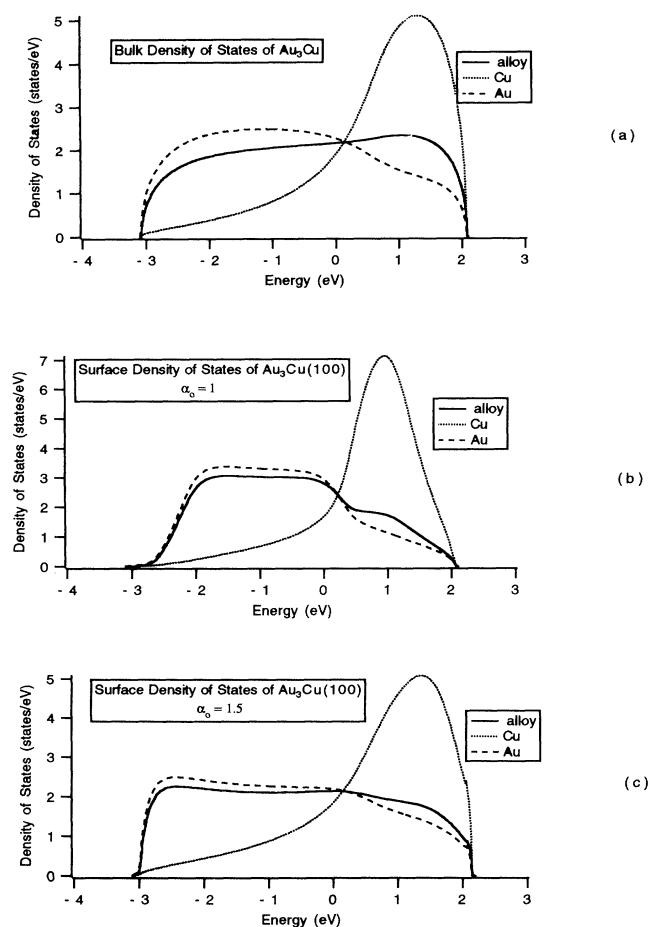


FIG. 1. Local density of states in (a) a bulk atom, (b) an atom of the first layer with $\alpha_0=1.0$, and (c) an atom of the first layer with $\alpha_0=1.5$ for $\text{Au}_3\text{Cu}(100)$. The atom can be either Au, Cu, or an "alloy." It is assumed that $x_1(\text{Au})=0.9$; $x_2(\text{Au})=0.3$; $x(\text{Au})=0.75$.

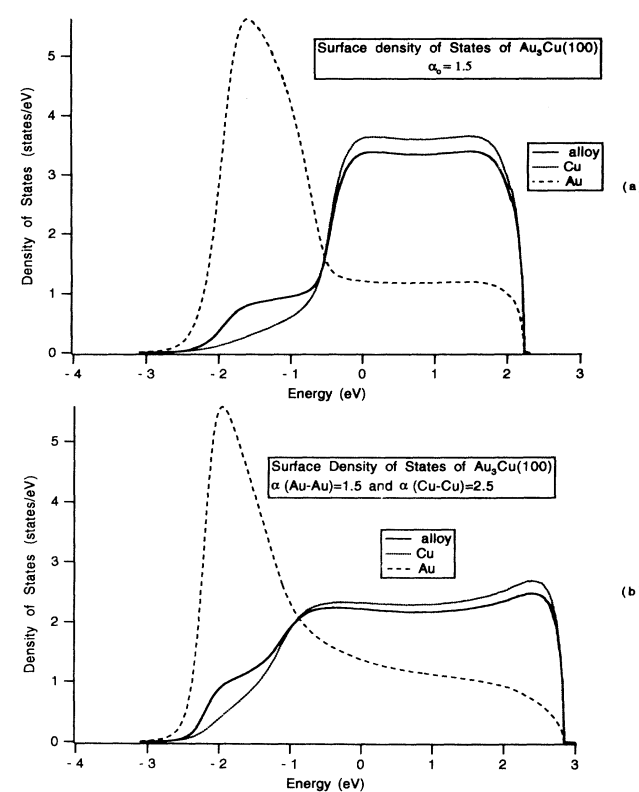


FIG. 2. Local density of states in an atom of the first layer with (a) $\alpha_0(\text{Au-Au})=1.5$ and $\alpha_0(\text{Cu-Cu})=1.5$; (b) $\alpha(\text{Au-Au})=1.5$ and $\alpha(\text{Cu-Cu})=2.5$ for $\text{Au}_3\text{Cu}(100)$. The atom can be either Au, Cu, or an "alloy." It is assumed that $x_1(\text{Au})=0.1$, $x_2(\text{Au})=0.3$, $x(\text{Au})=0.75$.

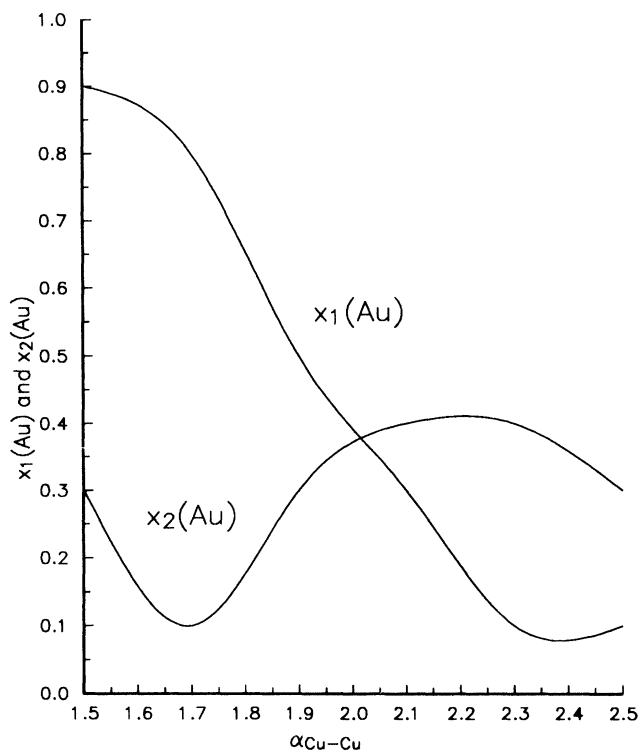


FIG. 3. Au concentration in the top two layers as a function of α .

IV. CONCLUSIONS

We have presented a simple tight-binding model to calculate the surface composition of Au_3Cu alloys in the presence of adatoms. We consider only the d electrons of the system. The effect of the chemisorbed species has

been incorporated through a modification of surface-surface and surface-bulk hopping interactions in the tight-binding scheme. This method avoids a direct inclusion of the chemisorbed layer in the tight-binding scheme making the calculation relatively simple and efficient. Also, in order to include the chemisorbed layer directly in the calculation one must have a knowledge of the various hopping parameters. The present calculation avoids this difficulty.

Within the limitations of the tight-binding scheme with only d orbitals and the approximations made for the calculation, the present work predicts the surface composition in the top layer of the Au_3Cu alloy in the presence and in the absence of an oxygen monolayer. This method predicts segregation reversal in the top layer, in general agreement with the experimental ICISS results. The calculation correctly predicts the composition of the second layer for the clean alloy. However, in the presence of chemisorbed oxygen the calculation shows the second layer to be Cu enriched while the experiment shows it to be Au enriched.

Further improvement of the model can be made by taking into account the metallic d as well as the s electrons. Secondly, inclusion of more layers in the free-energy minimization may also affect the second-layer equilibrium concentration. Furthermore, a better knowledge of chemisorption energy E_c on both components at various oxygen coverages would also augment the predictive power of the present model.

ACKNOWLEDGMENTS

This work was partly supported by the Biological and Chemical Technologies Research Program (Advanced Industrial Concepts Division) of the U.S. Department of Energy through the Ames Laboratories which is operated for the U.S. DOE by Iowa State University under Contract No. W-7405-Eng-82.

*Author to whom all correspondence should be addressed.

¹A. R. Miedema, *Z. Metallk.* **69**, 455 (1978).

²S. Mukherjee and J. L. Moran-Lopez, *Surf. Sci.* **189/190**, 1135 (1987).

³F. L. Williams and D. Nason, *Surf. Sci.* **45**, 333 (1974).

⁴E. E. Latta and H. P. Bonzel, *Interfacial Segregation* (American Society for Metals, Metals Park, OH, 1979).

⁵D. Tomanek, S. Mukherjee, V. Kumar, and K. H. Bennemann, *Surf. Sci.* **114**, 11 (1982).

⁶S. Modak and B. C. Khanra, *Chem. Phys. Lett.* **134**, 39 (1987).

⁷T. S. King and R. G. Donnelly, *Surf. Sci.* **141**, 417 (1984).

⁸J. M. Montejano-Carrizales and J. L. Moran-Lopez, *Surf. Sci.* **265**, 209 (1992).

⁹S. Modak and B. C. Khanra, *Phys. Rev. B* **34**, 5909 (1986).

¹⁰S. Mukherjee, J. L. Moran-Lopez, V. Kumar, and K. H. Bennemann, *Phys. Rev. B* **25**, 730 (1982).

¹¹S. Nakanishi, K. Kawamoto, N. Fukuoka, and S. Umezawa, *Surf. Sci.* **261**, 342 (1992).

¹²B. Ginatempo, G. Y. Guo, W. M. Temmerman, J. B. Staunton, and P. J. Durham, *Phys. Rev. B* **42**, 2761 (1990).

¹³H. C. Poon and B. C. Khanra, *Solid State Commun.* **80**, 361 (1991).

¹⁴J. D. Joannopoulos and F. Yndurain, *Phys. Rev. B* **10**, 5164

(1974).

¹⁵F. Yndurain and J. D. Joannopoulos, *Phys. Rev. B* **11**, 2957 (1975).

¹⁶C. A. Balseiro and J. L. Moran-Lopez, *Phys. Rev. B* **21**, 349 (1980).

¹⁷R. C. Kittler and L. M. Falicov, *Phys. Rev. B* **18**, 2506 (1978); *J. Phys. C* **9**, 4259 (1976).

¹⁸J. L. Moran-Lopez and L. M. Falicov, *Phys. Rev. B* **20**, 3900 (1979); M. O. Robbins and L. M. Falicov, in *Alloy Phase Diagrams*, edited by L. H. Bennett, T. B. Massalski, and B. C. Giessen, MRS Symposia Proceedings No. 19 (Materials Research Society, Pittsburgh, 1983), p. 53.

¹⁹D. Tomanek, A. A. Aligia, and C. A. Balseiro, *Phys. Rev. B* **32**, 5051 (1985).

²⁰B. Legrand, G. Treglia, and F. Ducastelle, *Phys. Rev. B* **41**, 4422 (1990).

²¹G. Treglia, B. Legrand, and F. Ducastelle, *Europhys. Lett.* **7**, 575 (1988).

²²B. Legrand and G. Treglia, *Surf. Sci.* **236**, 398 (1990).

²³O. K. Andersen, in *The Electronic Structure of Complex Systems*, Vol. 113 of *NATO Advanced Study Institute, Series B: Physics*, edited by W. M. Temmerman and P. Phariseau (Plenum, New York, 1991).