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Electronic theory for surface segregation: Noble-metal alloys

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A theory for segregation at the surface of noble-metal alloys is presented. The calculation involves a self-consistent solution of the tight-binding Hartree Hamiltonian within the cluster-Bethe-lattice approximation. The effects of electronic charge transfer on surface segregation are given particular attention. The theory is applied to the study of the systems AuAg, AuCu, and AgCu. Comparisons are made with existing experimental data.

I. INTRODUCTION

The chemical composition in the neighborhood of alloy surfaces has been intensively investigated in recent years.[1,2] In general, it is found that the surface gets richer in one of the elements as compared with the bulk chemical composition. This phenomenon, known as surface segregation, is of great interest in surface physics, in particular, with respect to catalysis,[3,4] corrosion,[5] etc.

Surface segregation has been studied theoretically using several phenomenological theories based on pair bond models[6-8] (PBM) and elastic-strain-energy calculations.[9,10] The pair bond model, the most commonly used, has been studied extensively. Theories that describe segregation over the whole range of temperatures taking into account long- and short-range order are now available.[11] These models predict that the surface gets richer with the elements of lower heat of vaporization (or lower cohesive energy).

Another effect that contributes to segregation but is not taken into account in the PBM is the difference in atomic volumes of the constituents. Elastic-strain-energy theories[9] for segregation in random binary alloys $A_x B_{1-x}$ predict that the element with lower concentration is the one that segregates. Recently, discussions that incorporate the bond breaking and volume effects have been published.[12-14]

For very dilute alloys a rule for segregation based on the melting curve of the binary system[15] has been proposed. In a more recent publication,[16] segregation is discussed in terms of the bulk variables used by Miedema to account for the heat of formation of alloys.[17]

In addition to the phenomenological theories mentioned above, surface segregation has also been studied within microscopic theories.[18,19] Kerker *et al.*[18] carried out a calculation for CuNi and NiFe, in a tight-binding Hamiltonian with no off-diagonal disorder. In those studies, the total free energy was minimized with the constraint that the total number of atoms in the alloy is fixed, but the conservation of the total number of electrons was not considered. More recently, Lambin and Gaspard[19] proposed a similar tight-binding theory for CuNi, in which both constraints are ignored.

In this contribution we present a microscopic theory for the electronic forces responsible for segregation at the surface of noble-metal alloys. The free energy is calculated from a tight-binding Hartree Hamiltonian with off-diagonal disorder. The electronic local density of states (LDS) is determined by using a generalization of the cluster-Bethe-lattice method (CBLM).[20]

The theory and calculation are described in Sec. II. Our general results as well as the application of our theory to the systems $\mathrm{Au}_x\mathrm{Ag}_{1-x}$, $\mathrm{Au}_x\mathrm{Cu}_{1-x}$, $\mathrm{Ag}_x\mathrm{Cu}_{1-x}$ $(0 \leq x \leq 1)$ are presented and discussed in Sec. III. Section IV contains the summary and conclusions.

II. THEORY AND CALCULATION

The internal energy of the alloy is the total energy of the electron-ion system. Here we assume that the relevant contribution to the internal energy is due to s electrons, since in noble metals, the electronic density of states at the Fermi level is mainly of s character.[21-23]

To describe the alloy $A_x B_y$ $(y=1-x)$, we choose as the Hamiltonian a single-band tight-binding Hartree model with intra-atomic electron-electron Coulomb interaction U:

$$H=\sum_{i\sigma} \epsilon_{i\sigma} n_{i\sigma} + \sum_{\substack{i\neq j\\ \sigma}} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} - E_{ee} , \tag{2.1}$$

where

$$\epsilon_{i\sigma} = \epsilon^0_{i\sigma} + U\langle n_{i-\sigma}\rangle \tag{2.2}$$

and

$$E_{ee} = \tfrac{1}{2} \sum_{i\sigma} (\epsilon_{i\sigma} - \epsilon^0_{i\sigma}) \langle n_{i\sigma}\rangle . \tag{2.3}$$

Here $c^\dagger_{i\sigma}$ ($c_{i\sigma}$) is the creation (destruction) operator of an electron in the Wannier state of spin σ at the site i and $n_{i\sigma} \equiv c^\dagger_{i\sigma} c_{i\sigma}$. The symbols $\epsilon^0_{i\sigma}$ and t_{ij} denote the single site energy for the pure metal atoms and the hopping integral between nearest neighbors. The parameter $\epsilon^0_{i\sigma}$ takes the value $\epsilon^0_{A\sigma}$ ($\epsilon^0_{B\sigma}$) if the site i is occupied by an A (B) atom while t_{ij} can be t_{AA}, t_{BB}, or t_{AB} depending on the atoms in sites i and j.

The chemical composition of the system in the neighborhood of the surface is determined by minimizing the total free energy $F(x_1, x_2, \ldots)$ of the crystal with respect to the concentrations $x_1, x_2, \ldots$ of the first, second, etc., crystal layer parallel to the surface. The minization is carried out with the constraints that the number of atoms and the number of electrons remain fixed. In the following we consider a random system (no chemical order). For this case the free energy can be written as

$$F(x_1, x_2, \ldots) = \sum_{\lambda=1}^{\infty} \left(\int_{-\infty}^{\epsilon_F} \omega N^\lambda(\omega)\, d\omega - E^\lambda_{ee} \right) + k_B T \sum_\lambda (x_\lambda \ln x_\lambda + y_\lambda \ln y_\lambda)\,. \tag{2.4}$$

Here $N^\lambda(\omega)$ is the average LDS for sites in the λth plane, ϵ_F is the Fermi energy, k_B is the Boltzman constant, and T is the temperature.

The first term in Eq. (2.4) is the internal energy of the system and the last term corresponds to the entropy of a random alloy. The electronic contribution to the entropy as well as the temperature dependence of the internal energy is negligible and therefore not taken into account.

The conservation of the total number of A, B atoms and electrons are given by the constraints:

$$\sum_\lambda x_\lambda = (\mathrm{const}) \tag{2.5}$$

and

$$\sum_\lambda \int_{-\infty}^{\epsilon_F} N^\lambda(\omega)\, d\omega = (\mathrm{const})\,. \tag{2.6}$$

Lagrange multipliers allow us to determine segregation by minimizing

$$\mathfrak{F} = F - \mu \sum_\lambda x_\lambda - \nu \sum_\lambda \langle n^\lambda \rangle\,, \tag{2.7}$$

where $\langle n^\lambda \rangle$ is the average number of electrons per site in the λth plane,

$$\langle n^\lambda \rangle = \int_{-\infty}^{\epsilon_F} N^\lambda(\omega)\, d\omega\,, \tag{2.8}$$

and

$$\mu = \frac{\partial F}{\partial x_b}\,, \quad \nu = \epsilon_F = \frac{\partial F}{\partial \langle n_b \rangle}\,, \tag{2.9}$$

where the subindex b denotes bulk, i.e., $\lambda \to \infty$. The LDS can be obtained from the proper diagonal element of the one-particle Green's function

$$N^\lambda_I(\omega) = -\frac{1}{\pi}\, \mathrm{Im} \sum_\sigma G^\lambda_{ii,\sigma}(\omega)\,, \tag{2.10}$$

where I is equal to A (B) if the site i of the λth plane is occupied by an A (B) atom.

The average LDS is given by

$$N^\lambda(\omega) = x_\lambda N^\lambda_A(\omega) + y_\lambda N^\lambda_B(\omega)\,. \tag{2.11}$$

We evaluated the diagonal Green's function by means of the CBLM. In this method one substitues the infinite periodic lattice by an infinite system of connected atoms, with the same coordination number z as the lattice under consideration, but without closed rings of bonds. This lattice has the property that the one-particle Green's function in the binary alloy case can be written in terms of four transfer functions.[24,25] In particular, if the alloy is completely disordered, it is possible to write analytic expressions for the Green's functions.

In order to study the surface properties, we consider a mixed Bethe lattice.[25] The number of nearest neighbors is z_0 in the surface plane, z_1 between two adjacent planes, and z in the bulk ($z = z_0 + 2z_1$). We take the solid with the surface to be represented by two kinds of atoms: s (surface) and b (bulk). Any s atom is connected with z_0 other s atoms and z_1 b atoms; i.e., the surface coordination number is $z_0 + z_1$. Any b atom is connected with $z = z_0 + 2z_1$ other atoms.

In this model, when assuming that the hopping integrals t_{ij} do not depend on the location of sites i and j, it is also possible to write analytic expressions for the Green's function at sites located at the surface in terms of transfer functions that connect atoms at the surface, atoms between the surface and the second layer, and between bulk atoms.

The self-consistent calculation was carried out in such a way that in the bulk, the conditions

$$\int_{-\infty}^{\epsilon_F} [x_b N_A(\omega) + y_b N_B(\omega)]\, d\omega = \langle n_b \rangle \tag{2.12}$$

and

$$\int_{-\infty}^{\epsilon_F} N_A(\omega)\, d\omega = \langle n_A \rangle \tag{2.13}$$

are fulfilled. Here $\langle n_A \rangle$ is the number of electrons on atoms A in the bulk of the alloy. Similar conditions have to be fulfilled in the neighborhood of the surface:

$$\int_{-\infty}^{\epsilon_F} N^\lambda_I(\omega)\, d\omega = \langle n^\lambda_I \rangle \quad (I = A, B)\,.$$

For simplicity, and based on previous results,[11] we take only the surface layer to have concentration x_s different from the bulk value. The LDS at the surface depends on x_b and x_s as well as the LDS for the first plane parallel to the surface.

In the following, as we are interested in noble-metal alloys, we consider the half-filled band case, i.e., one electron per atom.

III. RESULTS AND DISCUSSION

A. General remarks

In Fig. 1 we show some results for the LDS in the bulk and at the (111) surface of a fcc crystal ($z_0 = 6, z_1 = 3$). The short- and the long-dashed lines correspond to the partial local density of states in A and B atoms, respectively, and the full lines correspond to the average density of states. We took $x_b = 0.5$, $U = 0$, $\delta/W_A = (\epsilon_B^0 - \epsilon_A^0)/W_A = 0.1$, $t_{BB} = 0.8 t_{AA}$, $t_{AB}^2 = t_{AA} t_{BB}$, and various surface concentrations x_s. The symbol $W_{A\,(B)}$ denotes the bandwidth of the pure element A (B). As expected, the surface local density of states is narrower than the bulk one because of the reduction in the number of nearest neighbors. This makes, in general, the electronic charge transfer between atoms at the surface stronger than in the bulk.

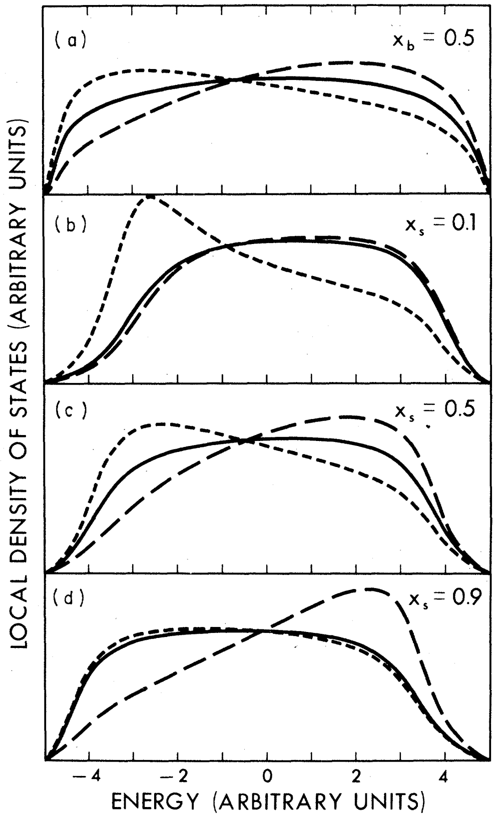

FIG. 1. Local density of states on A atoms (short dashed line), on B atoms (long dashed line), and the average (full line). The parameters used are $U = 0$, $\delta/W_A = 0.1$, $\gamma = 0.8$, $x_b = 0.5$. We show the bulk density of states (a), and the surface density of states for $x_s = 0.1$ (b), $x_s = 0.5$ (c), and $x_s = 0.9$ (d).

In Fig. 2 we present the phase diagram for segregation. The coordinates are δ/W_A and $\gamma = W_B/W_A$. Notice that we always take $\epsilon_A^0 < \epsilon_B^0$.

We show results for $U = 0$ (full line), U/W_A

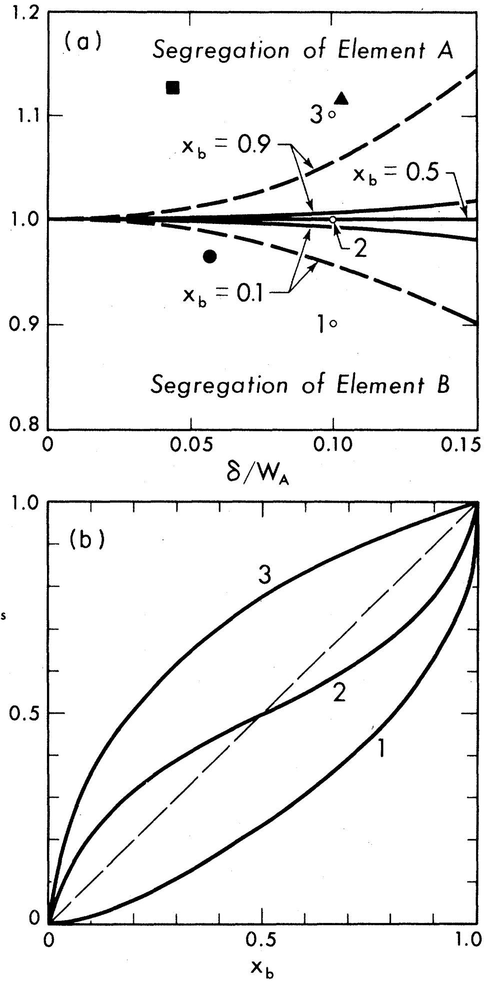

FIG. 2. (a) Phase diagram for segregation in alloys of metals with one s-electron. The coordinates are $\gamma = W_B/W_A$ and $\delta/W_A = \epsilon_B^0 - \epsilon_A^0/W_A$. We show results for $U = 0$ (dashed lines) and $U/W_A = 0.1333$ (solid lines) and for various bulk concentrations. For $x_b = 0.5$ the results for $U = 0$ and $U \neq 0$ coincide. The points marked with a triangle, a square, and a circle correspond approximately to AuCu, AgCu, and AuAg, respectively. (b) Results for segregation in alloys with parameters marked with 1, 2, and 3 in the above figure, $U = 0$ and $T = 700$ K.

$=0.1333$ (broken line), and $x_b=0.1$, 0.5, and 0.9. In the region above a given line the element that segregates is the element A and in the region below, the opposite occurs. For $\delta=0$, we find that the component with narrower band is the one in which the surface gets richer. This is in accordance with the predictions of the PBM if the cohesive energy in our model is calculated from the s bands, i.e., the narrower the bands, the smaller the cohesive energy.

For $\gamma=1$ ($W_A=W_B$) and $x_b=0.5$, we find that the surface composition is equal to the bulk value and is independent of δ. It can be shown analytically that this result comes from the symmetry of this special case; i.e., $x_b=0.5$, $W_A=W_B$, and $\epsilon_F=\delta/2$. As soon as one moves away from $x_b=0.5$, segregation depends on δ. This is shown in Fig. 2 for $x_b=0.1$ and $x_b=0.9$. We also present here our results for the self-consistent calculation of our model with intra-atomic Coulomb interaction different from zero. We see from these results that the effect of $U\neq 0$ is to enhance segregation. This makes the predictions of this model even more different from the ones of the PBM in which the phase diagram is independent of x_b and the boundary is given by $\gamma=1$. In Fig. 2(b) we present results of x_s as a function of x_b for $U=0$, $\delta/W_A=0.1$, $T=700\,\mathrm{K}$, and different values of γ. We see that for $\gamma=1$ (curve 2) at $x_b=0.5$ there is no segregation. For $x_b\neq 0.5$ the element that segregates is the minority component. Far from $\gamma=1$ (curves 1 and 3) the element with the narrower band tends to go to the surface over the whole range of bulk concentrations, again in accordance with the PBM.

B. Application to $\mathrm{Au}_x\mathrm{Ag}_{1-x}$, $\mathrm{Au}_x\mathrm{Cu}_{1-x}$, and $\mathrm{Ag}_x\mathrm{Cu}_{1-x}$

The three noble metals Au, Ag, and Cu are systems with fcc crystal structure and, as noted above, the electronic density of states at the Fermi level is mainly due to s electrons.[21-23] We therefore apply the theory of the previous section to study segregation in these systems.

The $\mathrm{Au}_x\mathrm{Ag}_{1-x}$ system shows a complete mutual solubility in both the liquid and the solid alloy with no known short-range order.[26] Then the assumption that the system is completely random should be a good approximation. The parameters we used in the calculation are given in Table I. The difference $\delta=\epsilon^0_{\mathrm{Au}}-\epsilon^0_{\mathrm{Ag}}=0.9$ corresponds to the difference in work function.[27] The value for the Au bandwidth is the same as the one used by Gelatt and Ehrenreich[28] to study charge transfer in the bulk atoms of this system. We choose a narrower band for Ag based on the assumption that t_{ij} decays exponentially with the distance between atoms and the fact that the Ag lattice parameter is slightly bigger than the Au one.[29] With these parameters the alloy is located in the point marked with a full circle in the phase diagram of Fig. 2(a).

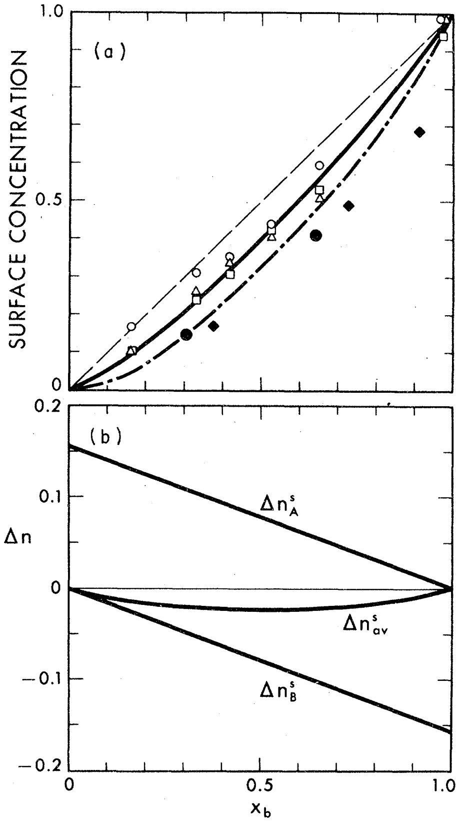

FIG. 3. (a) Surface composition (dashed-dotted line) and the average surface composition $\bar{x}_s=(x_s+x_b)/2$ (full line) as a function of bulk composition calculated for $\mathrm{Au}_x\mathrm{Ag}_{1-x}$ with parameters given in Table I and $T=700$ K. Experimental values: Overbury and Somorjai (Ref. 30; open triangle, open circle, open square), Nelson (Ref. 31; full circle), and Kelley *et al.* (Ref. 32; full square). (b) Surface charge transfer on A, B and the average as a function of bulk composition.

TABLE I. Input parameters for the calculations in $\mathrm{Au}_x\mathrm{Ag}_{1-x}$, $\mathrm{Au}_x\mathrm{Cu}_{1-x}$, and $\mathrm{Ag}_x\mathrm{Cu}_{1-x}$ systems.

Parameters	Value (eV)
Au bandwidth	14
Ag bandwidth	13.5
Cu bandwidth	15.6
$\epsilon^0_{\mathrm{Ag}}-\epsilon^0_{\mathrm{Au}}$	0.9
$\epsilon^0_{\mathrm{Cu}}-\epsilon^0_{\mathrm{Au}}$	1.5
$\epsilon^0_{\mathrm{Cu}}-\epsilon^0_{\mathrm{Ag}}$	0.6
U	2

In Fig. 3(a) we show results for segregation at $T=700\,\mathrm{K}$. We plot the results for the concentration in the first layer x_s (thick broken line) and the results for the average concentration of the first and second layers, $\bar{x}_s = (x_s + x_b)/2$. Our results for the average concentration should be compared with the experimental results,[30-33] since the experiment tests at least two atomic layers.

In Fig. 3(b) we present results for the electronic charge transfer in atoms at the surface:

$$\Delta n_I^s = \langle n_I^s \rangle - 1 \quad (I = A, B), \tag{3.1}$$

$$\Delta n_{\mathrm{av}}^s = x_0 \Delta n_A^s + y_0 \Delta n_B^s . \tag{3.2}$$

These are the results of the self-consistent calculation at the equilibrium value x_s for each value x_b. Notice that these results are plotted as a function of x_b.

The $\mathrm{Au}_x\,\mathrm{Cu}_y$ system is rich in order-disorder phenomena with phase transitions at $\mathrm{Au}_{0.25}\mathrm{Cu}_{0.75}$, $\mathrm{Au}_{0.5}\mathrm{Cu}_{0.5}$, and $\mathrm{Au}_{0.75}\mathrm{Cu}_{0.25}$. The critical transition temperatures are 663, 683, and 472 K, respectively.[26] Therefore our theory is only applicable above these temperatures, where the long-range order vanishes and the short-range order is small.

Experiments on segregation have been performed at temperatures below and above the transition temperatures.[34, 35] Van Santen *et al.*[34] reported no segregation on $\mathrm{Au}_{0.25}\mathrm{Cu}_{0.75}$ and $\mathrm{Au}_{0.75}\mathrm{Cu}_{0.25}$. Later, McDavid and Fain[35] performed experiments on polycrystalline samples, finding a strong segregation of gold over the whole concentration range. More recently, Shaw and Fain[36] reported experimental results on an $\mathrm{Au}_{0.25}\mathrm{Cu}_{0.75}$ (111) single crystal. They find again that the surface gets enriched in Au atoms but it is significantly below the value obtained from polycrystalline samples ($x_s = 0.39$ vs $x_s = 0.64$).

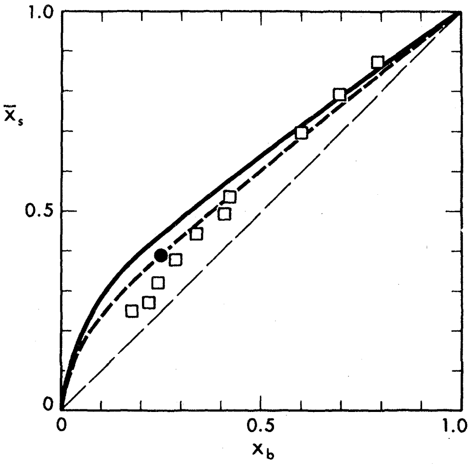

FIG. 4. Average surface composition as a function of bulk composition calculated for $\mathrm{Au}_x\mathrm{Cu}_{1-x}$ with parameters of Table I and $T = 700$ K (full line), and with $U = 0$ (dashed line). Experimental results: McDavid and Fain (Ref. 35; open square) and Shaw and Fain (Ref. 36; full circle).

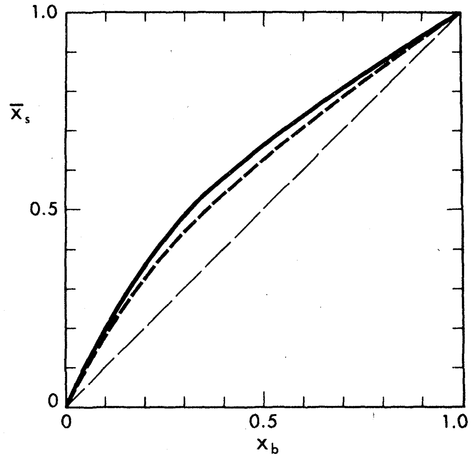

FIG. 5. Average surface composition as a function of bulk composition calculated for $\mathrm{Ag}_x\mathrm{Cu}_{1-x}$ with parameters of Table I, $T = 700$ K (full line), and with $U = 0$ (dashed line).

The values used for the microscopic parameter are given in Table I. The energy difference between the spectroscopic s levels[20-37] of Au and Cu was used for δ, and the bandwidths are similar to those used to calculate the order-disorder phase transition of these systems in a band model.[20] This alloy is marked with a full triangle in Fig. 2(a).

Our results are presented in Fig. 4. We took $T = 700$ K, and the two curves correspond to the surface average concentration $\bar{x}_s$ when $U = 0$ (broken line) and $U = 2$ eV (solid line). We see that our theory gives results in good agreement with the available experimental results in contrast with the PBM which predicts Cu segregation.[38] The plotted experimental results are the average concentration (open squares) for polycrystalline samples[35] and the calculated first layer concentration using the results[36] from a single crystal (single full circle).

The $\mathrm{Ag}_x\,\mathrm{Cu}_y$ alloy has properties completely different from the two systems already discussed. This alloy in its solid phase separates into two phases[26] except for very low ($0 < x < 0.05$) and very high ($0.87 < x < 1$) Ag concentrations. Our theory can be applied only in these regions of the phase diagram where the components are miscible.

Experimental results for segregation in polycrystalline samples have been published.[39] They report that the results depend very much on the sample preparation, but they show that there is a trend toward Ag segregation.

Our results are displayed in Fig. 5. The parameters are those used in the two systems discussed above. The two curves correspond to $U = 0$ (broken line) and $U = 2$ (solid line). Even though our results have meaning only at low and high concentrations, results are shown for the whole concentration range.

IV. SUMMARY AND CONCLUSIONS

We have introduced a band-theory method for calculating segregation at surfaces of random noble-metal binary alloys. The calculation was performed so that both the number of atoms and the number of electrons are conserved. These are constraints that have to be included in any theory of segregation. The theory allowed us to calculate the self-consistent charge transfer in the bulk and at the surface and thereby to study how charge transfer influences segregation.

The theory was applied to study segregation at the surface of $\mathrm{Au}_x\mathrm{Ag}_y$, $\mathrm{Au}_x\mathrm{Cu}_y$, and $\mathrm{Ag}_x\mathrm{Cu}_y$. We find, in general, good agreement with the available experimental results, a feature not present in other models.

Extensions of this theory to include order-disorder effects are straightforward, as are applications to transition-metal alloys.

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