

Complete miscibility between different crystallographic structures: Monte Carlo simulations of Cu-Ag deposited on Cu(001)

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Monte Carlo simulations of an $\text{Ag}_c\text{Cu}_{1-c}$ monolayer deposited onto Cu(001) show that complete miscibility of two elements adopting different crystallographic structures can be observed in the surface, while experimental bulk phase diagrams preclude a similar phenomenon in the bulk. While the deposited pure Ag monolayer is pseudo-hexagonal and the pure Cu monolayer is square and pseudomorphic, for intermediate concentrations at sufficiently high temperatures a disordered state appears in which square and hexagonal environments, respectively due to Cu and Ag, coexist. As a result, the surface phase diagram does not present any miscibility gap at 650 K.

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It is now well established that a strong size mismatch between two metallic elements can notably disrupt the extension of three-dimensional thermodynamics to the surface case. Thus, when the two metals share the same crystallographic structure, binary alloys that phase separate in the bulk can favor a tendency to order in the surface.^{1,2} One can then explain why two elements that are quite immiscible in the bulk can become miscible in all proportions in the surface.³⁻⁷ To the best of our knowledge, the possibility of complete solubility between elements with different bidimensional crystallographic structures has not been demonstrated. Three-dimensional thermodynamics universally claims that the bulk phase diagram of a binary system with two different crystallographic structures in the dilute solutions always displays a two-phase region that involves either the terminal solid solutions or an intermediate ordered compound.⁸ Can we imagine that this rule is infringed in the surface and that a solid solution can be stabilized over the whole range of concentration? In such a case, what structure can accommodate such a miscibility? In particular, can an amorphous structure be thermodynamically more stable than a two-phase region constituted of two crystallographic structures?

To answer these questions, we chose a strong-size-mismatch system for which the two elements have different two-dimensional crystallographic structures. The deposition of Cu-Ag onto the Cu(001) plane is a perfect candidate. While Cu and Ag share the same crystallographic structure (fcc) in the bulk, they adopt different structures as pure monolayers when deposited onto Cu(001), mainly because of the strong size mismatch ($\frac{r_{\text{Ag}}}{r_{\text{Cu}}}=1.13$). The Cu monolayer is pseudomorphic with a square lattice (1×1), whereas the Ag monolayer exhibits a $c(10 \times 2)$ superstructure corresponding to a pseudo-hexagonal plane that is similar to the (111) plane of pure Ag.⁹⁻¹² The phase diagram of the codeposition of a $\text{Ag}_c\text{Cu}_{1-c}$ monolayer onto Cu(001) should reveal a phase separation between a copper-rich solid solution with a square structure and a silver-rich solid solution with a hexagonal structure, if the rule about the nonmiscibility of metals of different structures remains valid in the surface.

We present here a study derived from Monte Carlo simulations that reveals complete miscibility in the surface plane between Cu and Ag when they are both deposited on a (001) Cu substrate. These simulations are carried out at two temperatures (650 and 300 K) in the pseudo-grand-canonical ensemble by imposing the chemical potential difference $\Delta\mu = \mu_{\text{Ag}} - \mu_{\text{Cu}}$.¹³⁻¹⁵ Two kinds of events are proposed. Atomic displacements affect the whole set of atoms of the system (substrate and deposited monolayer), and switches of chemical nature apply only to the atoms of the deposited monolayer. The Cu substrate is a film of five (001) planes of $N_s = 400$ atoms per plane with periodic conditions parallel to both (001) surfaces. Note that simulations with films made of 25 planes of 100 atoms per plane have also been performed and did not lead to significant differences. The substrate lattice parameter was computed beforehand by simulations on a triperiodic simulation box at the temperatures to be considered here. To improve the statistics, a $\text{Ag}_c\text{Cu}_{1-c}$ monolayer is deposited on each free surface of the Cu film, so that the comparison between the two monolayers permits one to test the convergence. The Ag concentration in the deposited monolayer is defined by $c = \frac{N_{\text{Ag}}}{N_{\text{layer}}}$, where N_{Ag} is the number of Ag atoms in the monolayer and N_{layer} is the total number of sites inside the monolayer. Due to the difference of atomic radii between Ag and Cu, there are 10% fewer sites in the $c(10 \times 2)$ superstructure than in the (1×1) structure.¹⁰ For a substrate layer of $N_s = 400$ sites, N_{layer} then varies between 400 when $c=0$ and 360 when $c=1$. This variation occurs by spontaneous expulsion of atoms of the monolayer toward adatom positions.^{10,15,16} To keep the substrate covered by only one monolayer, these expelled atoms are then withdrawn from the simulation box and simulations are run again. They are carried on until the concentration and the number of atoms in the monolayer remain constant and identical between both surfaces of the film ($|\delta c| < 0.01$ and $|\delta N_{\text{layer}}| < 1$). The computation of the energy relies on an N -body interatomic potential that is derived from the second-moment approximation of the tight-binding scheme,^{17,18} the parameters for the Cu-Ag interaction being chosen in order to reproduce the experimental solubility limits.¹⁹

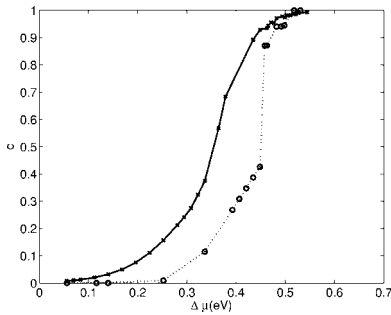


FIG. 1. Equilibrium isotherms expressing the concentration c as a function of the chemical potential difference $\Delta\mu$ (in eV) for a monolayer $\text{Ag}_c\text{Cu}_{1-c}$ adsorbed onto $\text{Cu}(001)$ at 650 K (continuous line) and 300 K (dotted line). In this latter case, the isotherm is obtained only for increasing values of $\Delta\mu$.

Figure 1 depicts the variation of the monolayer concentration c as a function of $\Delta\mu$ at 650 and 300 K.

Consider first $T=650$ K. We do not observe any discontinuity of this isotherm, which indicates a complete miscibility of both elements at this temperature. The monolayer does nevertheless adopt the square structure (1×1) when it is copper rich [Fig. 2(a)] and the pseudohexagonal structure ($c(10\times 2)$) when it is silver rich [Fig. 2(b)].

The number of expelled atoms quantifies the structural evolution of the monolayer as a function of c . We define an

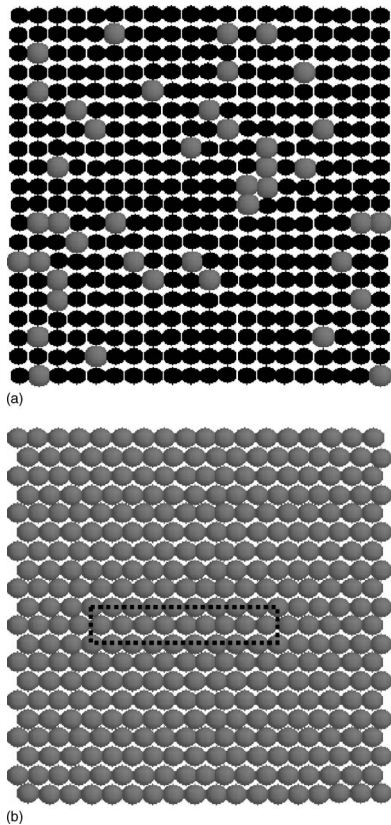


FIG. 2. Snapshots obtained at 650 K and quenched at 0 K in (a) the first regime [$c\approx 0.2$, (1×1) structure] and (b) the $c(10\times 2)$ structure (with one primitive cell dotted). The Cu atoms are displayed in black and the Ag atoms in gray.

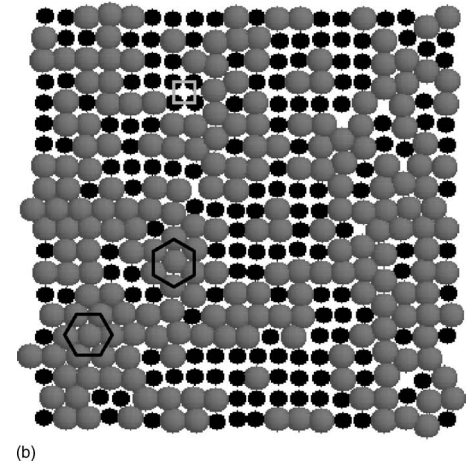
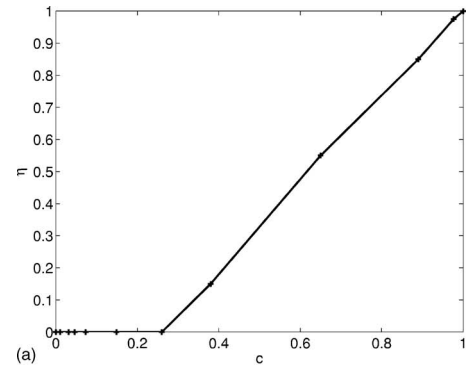


FIG. 3. (a) Evolution of the structural order parameter η (see text) as a function of c at 650 K; (b) a snapshot obtained at 650 K and quenched at 0 K in the second regime ($c\approx 0.6$). The Cu atoms are displayed in black and the Ag atoms in gray; the hexagons and the square stand, respectively, for the two different variants of the Ag environment and for the Cu environment.

order parameter $\eta=10\left(1-\frac{N_{\text{layer}}}{N_s}\right)$, which equals 0 in the (1×1) structure and 1 in the $c(10\times 2)$ structure. Figure 3(a) shows that η varies continuously with c and that its variation exhibits two regimes. In the first regime ($0 < c < 0.28$) where no atom is expelled ($\eta=0$), the monolayer keeps the square structure (1×1) of the substrate. During the second regime ($c > 0.28$), the number of expelled atoms increases linearly with c and reaches $\frac{1}{10}N_s$ (corresponding to $\eta=1$) for $c=1$. The continuity of $\eta(c)$ at 650 K indicates that the monolayer structure varies continuously from a square lattice to a hexagonal one, while the continuity of $c(\Delta\mu)$ at that temperature implies a complete miscibility of two elements of different 2D crystallographic structure.

What structure does the monolayer adopt for intermediate concentrations that would lead to this complete miscibility? Figure 3(b) displays a snapshot of the Monte Carlo simulations in the second regime ($c\approx 0.6$). We observe the formation of hexagonal environments for Ag atoms whereas the Cu atoms tend to keep a square environment. This can be quantified by representing the number of nearest neighbors for Cu and Ag atoms (respectively Z_{Cu} and Z_{Ag}) as a function of c [Fig. 4(a)]. In the first regime, the Cu and Ag atoms share the same crystallographic environment ($Z_{\text{Ag}}=Z_{\text{Cu}}\approx 4$). In the

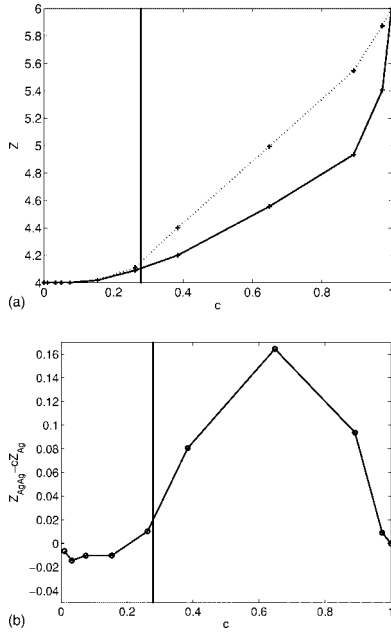


FIG. 4. Evolution as a function of c at 650 K of (a) the number of nearest-neighbor atoms for a Cu atom (Z_{Cu} , continuous line) and for a Ag atom (Z_{Ag} , dotted line) and (b) the local order defined for a Ag atom as the difference $Z_{AgAg} - cZ_{Ag}$ between the number of homoatomic nearest neighbors and the one obtained for a random distribution. The vertical line indicates the limit between the two regimes.

second regime, the environment of the Ag atoms becomes more and more hexagonal, while the environment of the Cu atoms remains mostly square ($Z_{Ag} > Z_{Cu}$), the difference from perfect square lattice being due to the Cu atoms in a mixed environment. Finally, at the end of the second regime ($c > 0.9$), the Cu solutes are surrounded by Ag atoms, and the hexagonal environment is common to both kinds of atoms.

To determine whether this difference of crystallographic environment is accompanied by a local chemical order, we compare now the number of homoatomic nearest neighbors for a Ag atom (Z_{AgAg}) with the one obtained from a random distribution, where this quantity equals cZ_{Ag} [Fig. 4(b)]. The first regime is close to a random distribution, while the second regime displays a strong tendency to favor homoatomic bonds.

The configuration displayed on Fig. 3(b) is very similar to what could be observed during a phase-separation kinetics of the monolayer into two phases, the first one being copper rich and square and the second one being silver rich and pseudo-hexagonal. However, the complete miscibility observed in the Monte Carlo simulations is not an artifact due to a slow convergence of the simulations toward a phase-separated state, since the two following results hold.

(i) Introducing a monolayer (for $c \approx 0.7$) in a two-phase state that contains on one hand the $c(10 \times 2)$ superstructure with pure silver rows and on the other hand a (1×1) superstructure that is either copper pure, or that corresponds to a random configuration with $c \approx 0.28$, always leads to a final state that is similar to the one depicted on Fig. 3(b).

(ii) The isotherm $c(\Delta\mu)$ is perfectly reversible in $\Delta\mu$. This

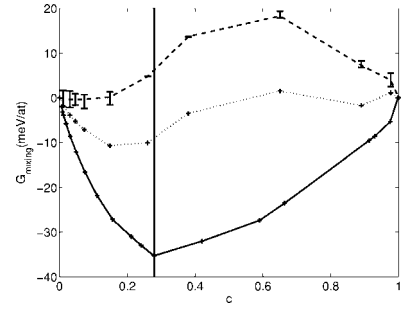


FIG. 5. Free mixing enthalpy $G_{\text{mixing}}(c)$ for a monolayer $\text{Ag}_c\text{Cu}_{1-c}$ as a function of c at 0 K (dashed line), 300 K (dotted line), and 650 K (continuous line). The vertical line indicates the limit between both regimes.

also shows that the existence in the second regime of hexagonal environments relative to different variants of the $c(10 \times 2)$ structure [Fig. 3(b)] is definitely an equilibrium phenomenon and not an artifact due to simulations that would be trapped in this kind of configuration. These configurations are indeed observed both while increasing $\Delta\mu$ from a (1×1) copper-pure monolayer or by diminishing $\Delta\mu$ from an ideal and monovariant $c(10 \times 2)$ silver-pure superstructure.

To clarify the origin of this total miscibility and determine the influence of the temperature onto it, we calculate the mixing energy (per atom of the adsorbed monolayer) defined as

$$E_{\text{mixing}}(c) = E^{\text{ads}}(c) - cE_{\text{Ag}}^{\text{ads}} - (1-c)E_{\text{Cu}}^{\text{ads}}.$$

The adsorption energy per adsorbed atom $E^{\text{ads}}(c)$ is computed as $\frac{\Delta E(c)}{N_{\text{layer}}}$, where $\Delta E(c)$ is the energy difference between a final state where the substrate is covered by the adsorbed monolayer $\text{Ag}_c\text{Cu}_{1-c}$ and an initial state constituted of the substrate alone. In a similar way, $E_{\text{Ag}}^{\text{ads}}$ ($E_{\text{Cu}}^{\text{ads}}$) is the adsorption energy for a Ag-pure monolayer in the $c(10 \times 2)$ structure [a Cu-pure monolayer in the (1×1) structure]. We then estimate the mixing free energy $G_{\text{mixing}}(c) = E_{\text{mixing}} - TS_{\text{mixing}}$ by adding the mixing entropy S_{mixing} computed within the Bragg-Williams approximation: $S_{\text{mixing}} = -k[c \ln(c) + (1-c) \ln(1-c)]$. Figure 5 indicates that $G_{\text{mixing}}(c)$ is convex on the whole range of concentration at 650 K, which confirms that the total miscibility observed in the Monte Carlo simulations is an equilibrium phenomenon. The mixing energy at 0 K is computed by averaging the energies of a large number of configurations obtained at 650 K then relaxed at 0 K with the help of a quenched molecular dynamics algorithm.²⁰ It is shown that at 0 K $E_{\text{mixing}}(c)$ is convex in the first regime ($c < 0.28$) and concave in the second regime ($c > 0.28$). These curvatures are in good agreement with the evolution of the short-range order with the concentration depicted on Fig. 4(b), and with experimental observations that reveal a tendency to favor heteroatomic bonds in the first regime.¹¹ Moreover, the inversion of the tendency to favor homoatomic bonds in the bulk to heteroatomic bonds in the (1×1) surface is in good agreement with previous calculations.^{1,2} The common-tangent rule permits one to pre-

dict a miscibility gap between 0.07 and 1 at 0 K, these limits becoming closer to 0.25 and 0.95 at 300 K. Note that these values differ from the stability limits of the structures (1×1) and $c(10 \times 2)$ given by the function $\eta(c)$ [Fig. 3(a)].

The computation of $G_{\text{mixing}}(c)$ at different temperatures indicates that its concave part disappears around 525 K, which gives an estimation of the critical temperature of the system Cu-Ag/Cu(001). To confirm the existence of a miscibility gap at low temperatures, we computed the same isotherm at 300 K by increasing progressively $\Delta\mu$ (see Fig. 1). The discontinuity of the resulting isotherm points out the presence of a first-order phase transition at 300 K, accompanied by a hysteresis cycle, the determination of its exact width being out of the scope of this paper.

The experimental observations that exist on the Ag-Cu-/Cu(001) system corroborate largely our results. Indeed, while annealing a Ag deposit onto Cu(001) between 300 and 475 K, Sprunger *et al.*¹¹ observe the incorporation of Ag atoms in the surface plane of the substrate. The derived microstructure is a two-phase state made of islands that are quite Ag-pure in a $c(10 \times 2)$ structure that coexist with a phase of concentration $c \approx 0.13$ of a (1×1) structure. Despite this phase separation, the authors observe a tendency to favor heteroatomic bonds in the solid solution dilute in silver ($c < 0.13$), which fully confirms the curvature of $E_{\text{mixing}}(c)$ in this regime (Fig. 5).

Moreover, our results can be related to several experimental studies of the segregation of the Cu(Ag) (001) system.^{21–24} Indeed, due to the strong surface segregation of the Ag atoms, one can observe via low energy electron diffraction (LEED) spectroscopy and AES techniques an Ag-pure surface plane adopting the $c(10 \times 2)$ structure onto a bulk that is almost Cu pure. For $T > 525$ K, these surface segregation isotherms are continuous, which is in a very good agreement with the prediction of total miscibility at sufficiently high temperature for the Cu-Ag/Cu(001) system

and this despite the structural change observed between the lower branch [(1×1) structure] and the upper branch [$c(10 \times 2)$ structure] of the isotherm. Note that this kind of study cannot be performed at lower temperature as the time necessary to reach equilibrium is too large.^{21–24}

To sum up, the results obtained via Monte Carlo simulations account for both the phase separation observed during the studies of growth of Ag/Cu(001) close to room temperature and the continuity of the segregation isotherms of Cu(Ag) (001) for temperatures larger than 525 K. We suggest complementary surface extended x-ray absorption fine-structure (SEXAFS) experiments to study the differential evolution of the coordination numbers of the Cu and Ag atoms as a function of the concentration of the alloyed monolayer. This will bring to the fore the specific environment of the amorphous state that accommodates the complete miscibility of two elements of different 2D crystallographic structures. Note that this result is to be generalized in two directions. First, a similar behavior is expected for any $AB/A(001)$ system with a comparable size mismatch (greater than or equal to 10%) and such that the difference in the surface energies $\gamma_A - \gamma_B$ is large enough to prevent the incorporation of B atoms in the first layers of the substrate at temperatures where the amorphous superficial phase is stable. The Ag-Ni/Ni(001) system, where the Ag-pure monolayer adopts a pseudohexagonal superstructure $c(8 \times 2)$, is therefore another potential candidate for experimental studies.²⁵ Second, besides the surface, the stability of an amorphous solid solution and complete miscibility between two elements of different crystallographic structures are expected to be observed in grain boundaries. A comparative study of the (001) surface and grain boundaries of (001) orientation for the Cu-Ag system should elucidate this point.

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