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Isabelle Braems, F. Berthier, J. Creuze, R. Tetot, B. Legrand. Complete miscibility between different crystallographic structures Monte Carlo simulations of Cu-Ag deposited on Cu(001). *Physical Review B: Condensed Matter and Materials Physics (1998-2015)*, 2006, 74 (1-4), pp.113406. <10.1103/PhysRevB.74.113406>. <cea-02356014>

HAL Id: cea-02356014

<https://cea.hal.science/cea-02356014v1>

Submitted on 9 Dec 2019

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A paradoxical miscibility: Ag-Cu / Cu (001)

I. Braems,* F. Berthier, J. Creuze, and R. Tétot

LEMHE/ICMMO, UMR 8182, CNRS,

Université Paris-Sud, F 91405 Orsay Cedex, France

B. Legrand

SRMP-DMN, CEA Saclay, F 91191 Gif-sur-Yvette Cedex, France

(Dated: May 15, 2006)

Abstract

Monte Carlo simulations of an $\text{Ag}_c\text{Cu}_{1-c}$ monolayer deposited onto Cu(001) show that a 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.

PACS numbers: 68.35.Md, 68.55.-a, 68.18.Jk, 68.47.De

Keywords: Ag; Cu; Cu-Ag; Monte Carlo Simulations; Size-Mismatch Systems; Surface Alloy; Surface Phase Transition

For all binary systems with two different crystallographic structures in the dilute solutions, the bulk phase diagram always displays a two-phase region that involves either the terminal solid solutions or an intermediate ordered compound [1]. However, it is now well-known that the surface behavior can substantially differ from the bulk one. Binary alloys that phase separate in the bulk can favor a tendency to order in the surface, in particular when both components exhibit a strong size mismatch [2],[3]. One can then explain why two elements that are quite immiscible in the bulk can become miscible in all proportions in the surface [4]-[8]. Yet this result concerns only metals that share the same crystallographic structure.

To the best of our knowledge, there is no generalization of this result to metals with different bidimensional crystallographic structures. We present here a study derived from Monte Carlo simulations that reveals a complete miscibility in the surface plane between Cu and Ag when they are both deposited on a (001) Cu substrate. 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 (1x1), whereas the Ag monolayer exhibits a c(10x2) superstructure corresponding to a pseudo-hexagonal plane that is similar to a (111) plane of pure Ag [9]-[12]. The phase diagram of the co-deposition of an $\text{Ag}_c\text{Cu}_{1-c}$ 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 non-miscibility of metals of different structures remains valid in the surface.

To determine the shape of this phase diagram we perform Monte Carlo simulations 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 only apply to the atoms of the deposited monolayer. The Cu substrate is a film of 5 planes (001) of $N(001) = 400$ atoms with periodic conditions parallel to both (001) surfaces. Note that simulations with films made of 25 planes of 100 atoms have also been performed and did not lead to significant differences. The substrate lattice parameter has been computed beforehand by simulations on a tri-periodic simulation box at the temperatures to be considered here. To improve the statistics, an $\text{Ag}_c\text{Cu}_{1-c}$

monolayer is deposited on each free surface of the Cu film, so that the comparison between both monolayers permits 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% of sites less in the $c(10 \times 2)$ superstructure than in the (1×1) structure [10]. For $N(001) = 400$ atoms, 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 towards adatom positions [10], [15]-[16]. To keep the substrate covered by only one monolayer, these expelled atoms are then withdrawn of the simulation box and simulations are run again. They are carried on till 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 a 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].

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,

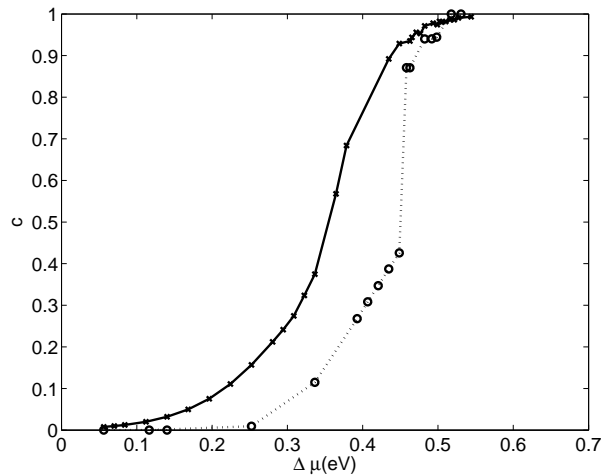


FIG. 1: Equilibrium isotherms expressing the concentration c as a function of the chemical potential difference $\Delta\mu$ (in eV) for a monolayer $\text{Ag}_c\text{Cu}_{1-c}$ adsorbed onto $\text{Cu}(001)$ at 650 (continuous line) and 300 K (dotted line). In this last case, the isotherm is obtained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

which indicates a complete miscibility of both elements at this temperature. The monolayer does nevertheless adopt the square structure (1x1) when it is copper-rich (Fig. 2a) and the pseudo-hexagonal structure c(10x2) when it is silver-rich (Fig. 2b). The number of expelled

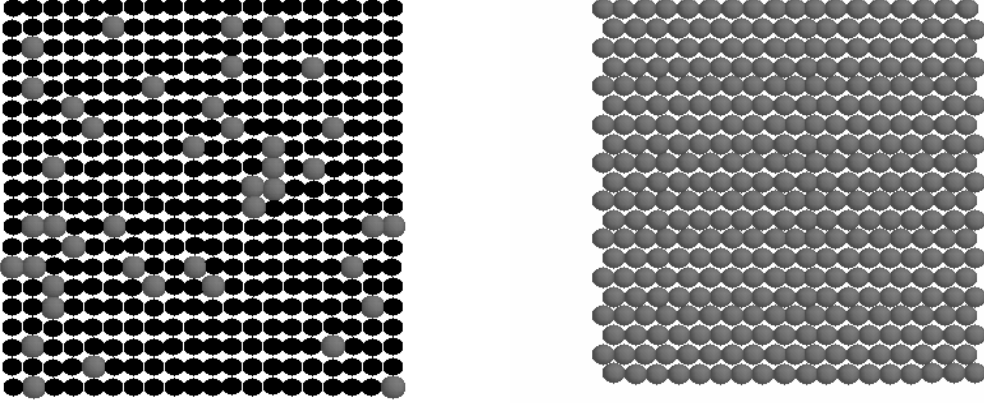


FIG. 2: Snapshots obtained at 650 K and quenched at 0 K in (a) the first regime ($c \approx 0.2$, (1x1) structure) and (b) in the c(10x2) structure. The Cu atoms are displayed in black and the Ag atoms in grey.

atoms quantifies the structural evolution of the monolayer as a function of c . We define an order parameter $\eta = 10(1 - \frac{N_{\text{layer}}}{N_{\text{substrate}}})$, that equals 0 in the (1x1) structure and 1 in the c(10x2) structure. Figure 3a 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 (1x1) of the substrate. During the second regime ($c > 0.28$), the number of expelled atoms increases linearly with c and reaches $\frac{1}{10}N_{\text{substrate}}$ (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 3b 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

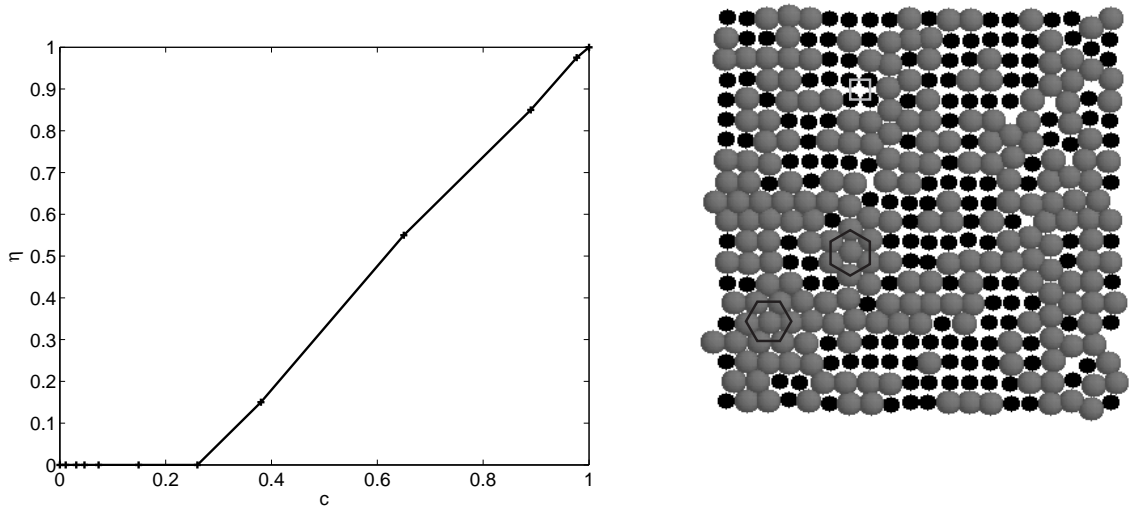


FIG. 3: (a) Evolution of the structural order parameter η (see text) as a function of c at 650 K; (b) a snapshot obtained at 650 K and quenched at 0 K in the second regime ($c \approx 0.6$). The Cu atoms are displayed in black and the Ag atoms in grey; the hexagons and the square stand respectively for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

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. 4a). In the first regime, the Cu and Ag atoms share the same crystallographic environment ($Z_{\text{Ag}} = Z_{\text{Cu}} \approx 4$). In the second regime, the environment of the Ag atoms becomes more and more hexagonal, while the environment of the Cu atoms remains mostly square ($Z_{\text{Ag}} > Z_{\text{Cu}}$), the difference with a 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 homo-atomic nearest-neighbors for an Ag atom (Z_{AgAg}) with the one obtained from a random distribution, where this quantity equal cZ_{Ag} (Fig. 4b). The first regime is close to a random distribution, while the second regime displays a strong tendency to favor homo-atomic bonds.

The configuration displayed on Fig. 3b is very similar to what could be observed during

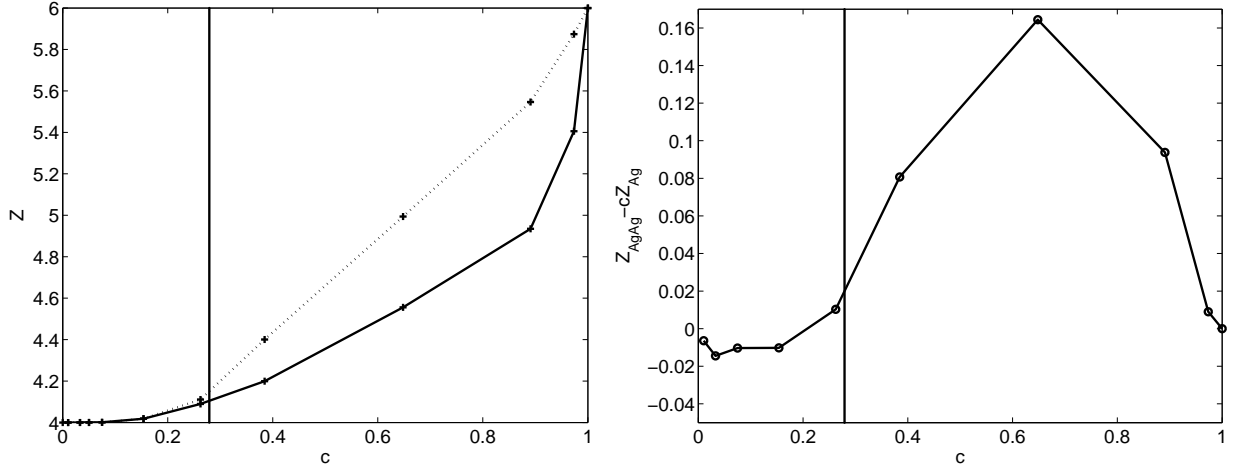


FIG. 4: Evolution as a function of c at 650 K of (a) the number of nearest-neighbors atoms for a Cu atom (Z_{Cu} , in continuous line) and for an Ag atom (Z_{Ag} , in dotted line) and (b) the local order defined for a Ag atom as the difference $Z_{\text{AgAg}} - cZ_{\text{Ag}}$ between the number of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

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 artefact due to a slow convergence of the simulations towards 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 from 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. 3b.

ii) the isotherm $c(\Delta\mu)$ is perfectly reversible in $\Delta\mu$. This also shows that the existence in the second regime of hexagonal environments relative to different variants of the $c(10 \times 2)$ structure (Fig 3b) is definitely an equilibrium phenomenon and not an artefact 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 clear up 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, $E_{\text{Ag}}^{\text{ads}}$ (resp. $E_{\text{Cu}}^{\text{ads}}$) is the adsorption energy for an Ag-pure monolayer in the $c(10 \times 2)$ structure (resp. 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 MC 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 a good agreement with the evolution of the short-range order with the concentration depicted on Fig. 4b, and with experimental observations that reveal a tendency to favor hetero-atomic bonds in the first regime [11]. Moreover, the inversion of the tendency to favor homo-atomic bonds in the bulk to hetero-atomic bonds in the surface (1×1) is in a good agreement with previous calculations [2], [3]. The common-tangent rule permits to predict 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. 3a).

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.

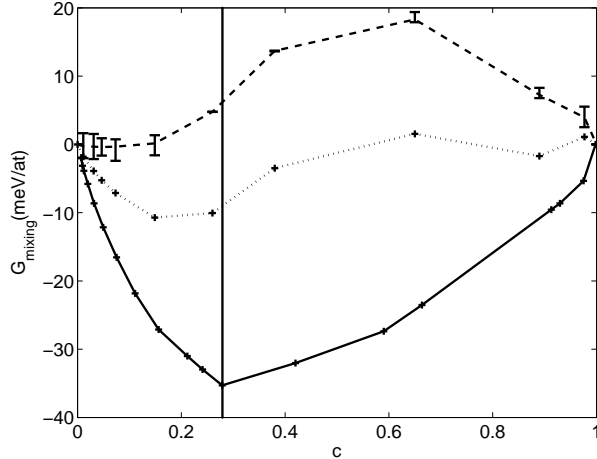


FIG. 5: Free mixing enthalpy $G_{\text{mixing}}(c)$ for a monolayer $\text{Ag}_c\text{Cu}_{1-c}$ as a function of c at 0 (dashed line), 300 (dotted line) and 650 K (continuous line). The vertical line indicates the limit between both regimes.

The experimental observations that exist on the Ag-Cu / Cu(001) system corroborate largely our results. Indeed, while annealing an 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 hetero-atomic 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 an experimental study 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 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 a total miscibility at sufficiently high temperature for the Cu-Ag / Cu (001) system and this despite the structural change observed between the low 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, we showed that two elements of different 2D crystallographic structures can be totally miscible as an alloyed monolayer deposited on a substrate. 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 the room temperature and the continuity of the segregation isotherms of Cu(Ag) (001) for temperatures larger than 525 K. SEXAFS experiments may bring to the fore the differential evolution of the coordination numbers of the Cu and Ag atoms as a function of the concentration of the alloyed monolayer.

The authors wish to thank Guy Tréglia (CRM-CNRS, Marseille) for very fruitful discussions.

* Electronic address: isabelle.braems@lemhe.u-psud.fr (I. Braems); Corresponding author.
Tel.: +33-1-69-15-46-77 ; fax: +33-1-69-15-48-19.

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