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## Surface alloys of CuAu I: charge transfer and the electronic density of states

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**Abstract.** The electronic structure of the (001) surface of ordered low-temperature 50% Cu–Au alloy (CuAu I) with different surface compositions is investigated by using the tight-binding linearized muffin-tin orbital method. The charge distribution and the charge transfer of the CuAu I(001) surface are considered from various viewpoints. The calculated local density of states is compared with spectroscopic measurements. It is shown that the surface effect in the valence band photoemission spectrum of CuAu I could improve the agreement between theoretical and experimental spectra. Implications in surface physics and surface chemistry of the activation or deactivation of certain regions of the electronic energy spectrum of a surface by adjusting the temperature of the system are discussed.

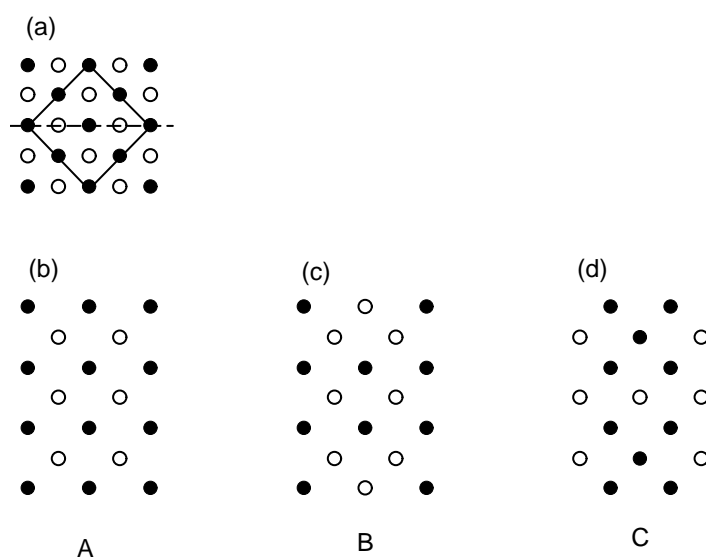
### 1. Introduction

Transition and noble-metal surfaces have been studied rather extensively in recent years. This is probably due to their interesting physical properties and various promising applications in technology. The ability to control surface reactions and to alter the reactivity of surfaces using tunable surfaces would have important implications. One possibility for altering the properties of surfaces is to use surface alloys with different concentrations [1] or surfaces having different structure or morphology [2]. The present work deals with the properties of the CuAu I(001) surface. In the Cu–Au alloy system there are two well characterized ordered phases: CuAu I (the low-temperature phase) and CuAu II (the higher-temperature phase) [3]. The (001) surface of CuAu I is an example of a surface whose concentration can be altered by varying the temperature. The surfaces of Cu–Au alloys have been found, experimentally [4–8] and theoretically [9–13], to exhibit a complex surface segregation. The oscillating segregation profile starts with a Au-enriched surface layer followed by a Au-depleted second layer and so on into the bulk with an exponentially decreasing amplitude. The characteristic decay length of the oscillations decreases with increasing temperature. Similar phenomena have been found also in surface alloys obtained by depositing Au on a Cu surface [14–16].

At low temperatures CuAu I forms an ordered bulk structure consisting of alternating Au-rich and Cu-rich (002) layers on the underlying tetragonally distorted fcc lattice. The experimental equilibrium lattice parameters of CuAu I are  $a = 3.966 \text{ \AA}$  and  $c/a = 0.926$  [17]. The layer-by-layer ordering is explained by a preference for unlike bonds between the constituents of the compound. Due to the lower surface energy, Au segregates to the surface and in this way forces the second layer to be Cu rich and so on. With increasing temperature the probability of finding Cu atoms in the surface layer increases. Tersoff [10] has investigated this temperature-driven surface desegregation of Au by means of Monte Carlo calculations.

According to Tersoff, the bulk ordering temperature  $T_c$  is 800 K which can be compared with the experimental value of 680 K. Below  $T_c$ , the surface contains mainly Au atoms; above  $T_c$ , Cu atoms emerge in the surface in greater quantities.

Most of the theoretical investigations of Cu–Au alloys apply semiempirical methods, which can treat large systems, give the equilibrium geometric structure of the alloy and follow the dynamics of the system for a longer period. However, the accurate electronic structure, needed in analysing e.g. the chemical reactivity of the surfaces, is beyond the scope of the semiempirical methods. In the present work, we will concentrate only on chemical (concentration) effects, not on structural or dynamical effects, on the electronic structure of the CuAu I(001) surface. Generally, chemical composition is more important as regards surface-induced reactions than structural or dynamical properties. The electronic structure calculations are performed for three different compositions of the CuAu I(001) surface: an ideal low-temperature Au-terminated surface (denoted as A), 25 at.% Cu in the surface layer (denoted as B) and 25 at.% Au in the second layer (denoted as C). Figure 1 shows the relevant cross sections of the unit cells used in the calculations. Although the investigations are only for CuAu I, the results are expected to be useful for other Cu–Au alloys as well.



**Figure 1.** Cross sections of the unit cells used in the calculations (empty spheres are not shown). Black and white spheres correspond to Au and Cu atoms, respectively. A: ideal low-temperature CuAu I; B: extra Cu atoms in the surface layer; and C: extra Au atoms in the second layer. (a) Top view, (001) surface of CuAu I, black spheres: surface layer; white spheres: second layer. The unit cell (solid line) contains four atoms per layer. The dashed line shows the cross-section plane for the side-view cross sections (b)–(d) (seven-atomic-layer metal films). In (d) the origin is shifted compared to those in (b) and (c).

## 2. Method

The density functional theory (DFT) has proven to be a very useful tool in the study of surfaces and bonding of adsorbates on a surface [18, 19]. In the present work, the electronic structure calculations are based on the DFT within the local density approximation [20, 21]. For the exchange and correlation potential of the electron gas a Ceperley–Alder form is used [22, 23].

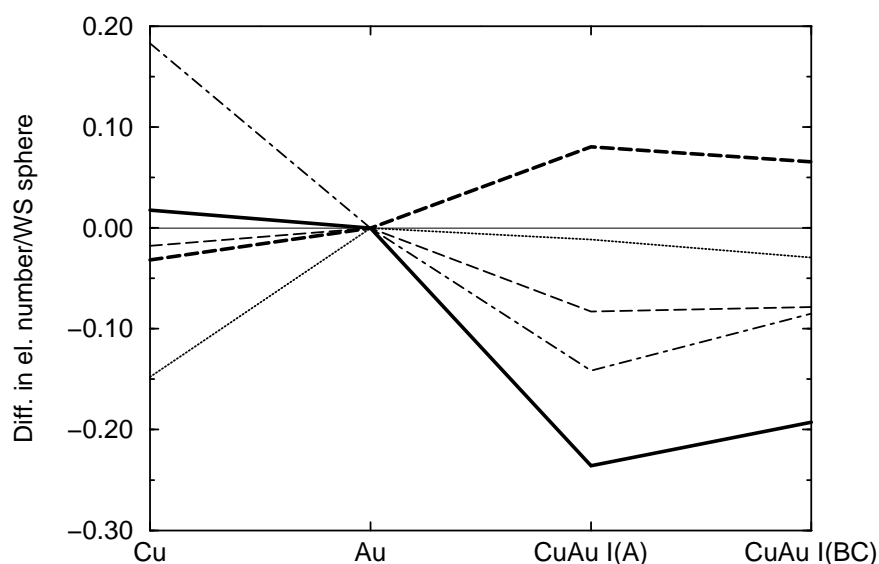
The calculations are performed using the scalar-relativistic tight-binding linear muffin-tin orbital method in the atomic-sphere approximation [24, 25]. The surface investigated is the (001)-oriented Au-terminated surface of CuAu I. In the calculations,  $\sqrt{2}a \times \sqrt{2}a$  surface unit cells are used allowing investigations for the 25 at.% ordered surface alloy. The experimental equilibrium lattice parameters and equal Wigner–Seitz (WS) radii for the atomic spheres of the constituents are used in the calculations.

The surface of CuAu I is simulated by using a repeated-slab technique. In a slab calculation the surface of a semi-infinite solid is approximated by a surface of a metal film. To preserve the periodicity of the structure investigated, the system considered is simulated by alternating metal and vacuum films. To test that the results obtained for the present model system are valid approximations for the properties of the surface of the semi-infinite bulk CuAu I, the convergence of the quantities investigated with respect to relevant calculational parameters has to be considered. In the present case the density of states (DOS) of the surface atomic layer is used as a test quantity. The surface DOS is calculated as a function of thickness of the metal film, thickness of the vacuum between the adjacent metal films and number of  $k$ -points. According to these test calculations, metal film seven atomic layers thick, a vacuum region in between the adjacent metal films equivalent to three atomic layers and 42  $k$ -points in the Brillouin zone integrations lead to the required accuracy in the calculations.

### 3. Results and discussion

#### 3.1. Charge transfer through the surface

The trends in the surface properties of metallic materials can be investigated by considering the difference in surface charge between different materials. Figure 2 shows the average number



**Figure 2.** The average number of electrons per atom of the surface layer and the first vacuum layer of the compounds investigated with respect to the corresponding pure Au values. Thick dashed line: the difference in the total number of electrons of the first vacuum layer. Thick solid line: the difference in the total number of electrons of the surface layer. Thin dotted, dashed and dash-dotted lines refer to the s, p and d electrons of the surface layer, respectively.

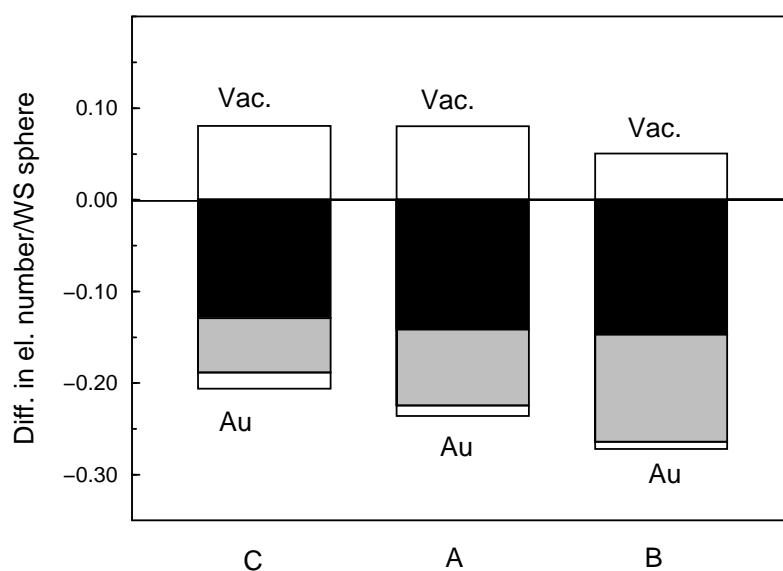
of electrons per atom of the surface layer and the first vacuum layer of the metals investigated with respect to the corresponding values for pure Au. Since Cu and Au are the constituents of CuAu I, it is natural to start the discussion of surface charge transfer by considering the surfaces of pure Cu and Au. The electronic charge of the pure Cu surface is slightly more localized (perpendicular to the surface) than that of the pure Au surface. This localization can be seen in figure 2 as a transfer of electrons from the first vacuum layer to the surface atomic layer when going from pure Au to pure Cu.

The difference in the surface charge between Cu and Au that is obtained can be explained, at least partially, by the missing valence–core orthogonalization in the case of the Cu 3d radial wave function compared to the Au 5d radial wave function. This effect is clearly discernible in figure 2, which shows a sharp rise in the number of d-type valence electrons within the surface atomic layer when going from pure Au to pure Cu. The charge rearrangement obtained can be compared with the depletion of the d-type electrons in the surface of Au compared to the corresponding bulk value [26]. The contracted d-type valence charge of Cu pushes the Cu s-type valence charge further away from the atomic core region, which actually leads to transfer of the valence electrons from the surface layer to the vacuum. However, this compensation is not complete and the total valence charge transfer leads to a slightly higher electronic charge in the surface atomic layer and a lower electronic charge in the first vacuum layer for the Cu surface compared to the Au surface.

Due to the substantial transfer of electrons from the surface atomic layer to the vacuum, the polarization of the surface charge is higher in CuAu I(A) than in pure Au (or in pure Cu). The above charge transfer is mainly due to the 5d- and 6p-type electrons of Au. The active role of the 5d and 6p electrons can be explained by the steeper slope of the pressure-versus-volume curve of the 5d- and 6p-type wave functions compared to that of the 6s-type wave function [24]. Because the lattice of CuAu I is compressed compared to the lattice of pure Au, the existing difference in the pressure-versus-volume behaviour among the partial wave functions in CuAu I leads to the protrusion of the 5d- and 6p-type valence charge into the vacuum. In CuAu I(BC) (both B- and C-type sites exist on the surface), the average surface charge polarization is slightly lower, resulting from extra Cu atoms in the surface layer of CuAu I(BC) compared to CuAu I(A).

### 3.2. Atom-resolved charge transfer

A more detailed picture of the charge transfer on the surfaces can be obtained by considering the charge transfer on an atomic scale. Figure 3 shows the difference in the number of electrons between the Au atom on the surface of a CuAu I compound and the Au atom on the surface of pure Au. Similarly the difference for the first vacuum layer between the compounds and pure Au is shown. The transition from CuAu I(A) to CuAu I(BC) induces the redistribution of the surface charge in the following way. In the neighbourhood of the second-layer Au (case C) the electron number of the first-layer Au atoms is higher whereas the number of electrons in the vacuum remains unchanged. In the neighbourhood of the first-layer Cu (case B) the electron number of Au atoms and the vacuum is lower and the first-layer Cu atom gets more electrons compared to the Cu atoms in the surface of pure Cu. In this way Cu atoms (not shown in figure 3) in the CuAu I surface act as electron concentration centres. The concentration of the electrons into Cu sites is due to the different spatial distribution of the valence charge in Au and Cu sites and occurs in bulk CuAu I as well. Cu atoms are smaller than Au atoms which implies that in CuAu I at a particular atomic site the contribution to the charge density coming from the neighbouring atomic sites is larger for Cu than for Au. The charge transfer obtained in this case is opposite to the prediction based on the electronegativities of the constituents.



**Figure 3.** The difference in the number of electrons between the Au atom on the surface of a CuAu I compound and the Au atom on the surface of pure Au. A similar quantity for the empty spheres ('Vac.') of the first vacuum layer is also shown. A, B and C refer to the notation in figure 1. For the Au the contribution coming from s (white), p (grey) and d (black) electrons is also shown. For vacuum only the difference in total number of electrons is shown.

The electronegativities of Cu and Au are 1.9 and 2.4, respectively. However, there is no contradiction in this, because in this case the accumulation of electrons at Cu sites is mainly due to the size effect rather than the difference in the chemical reactivity of the atoms. Figure 3 also shows the response of the partial charges (s, p, d) of Au to the changes in the chemical composition of the surroundings. The d part is rather inert whereas the s and p parts show opposite trends to each other. Table 1 shows the trends in partial charges for bulk, surface and the first vacuum layer.

**Table 1.** The number of valence electrons of WS spheres ( $N^t$  total;  $N^s$ ,  $N^p$ ,  $N^d$  partial numbers). The bulk values of Au (Cu) are 0.828, 0.818 and 9.354 (0.722, 0.768 and 9.506) for  $N^s$ ,  $N^p$  and  $N^d$ , respectively. The bulk values refer to the central layer of the pure Au and Cu films.

Case	First vacuum layer				Surface layer			
	$N^t$	$N^s$	$N^p$	$N^d$	$N^t$	$N^s$	$N^p$	$N^d$
Au	0.226	0.084	0.095	0.048	10.729	0.837	0.535	9.358
Cu	0.194	0.090	0.075	0.030	10.747	0.689	0.517	9.541
CuAu I(A)	0.306	0.120	0.124	0.062	10.493	0.826	0.452	9.216
CuAu I(C)	0.307	0.119	0.124	0.063	10.523	0.819	0.475	9.229
CuAu I(B), Cu	0.276	0.112	0.111	0.054	10.828	0.697	0.494	9.637
CuAu I(B), Au					10.458	0.829	0.418	9.211

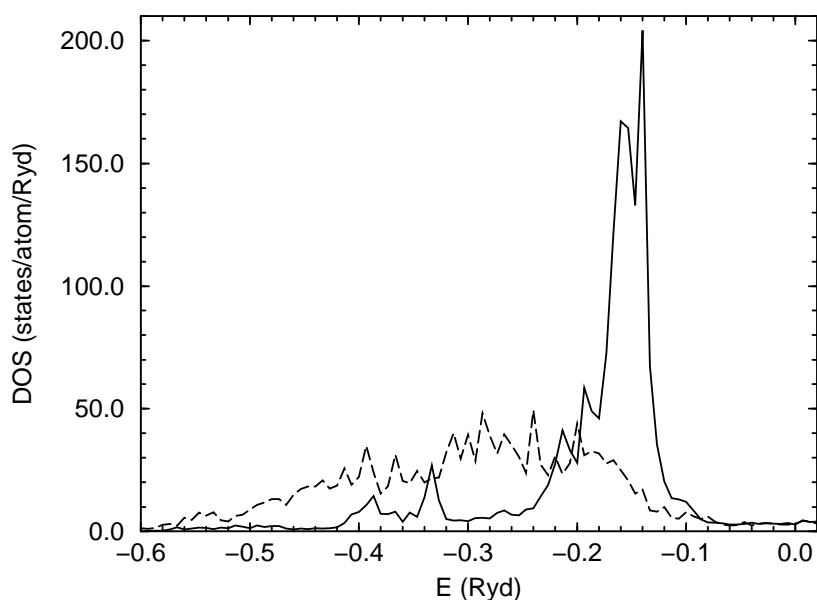
### 3.3. Charge transfer in energy space

To shed more light on the chemical properties of surfaces it is useful to consider the redistribution of the surface valence charge in the energy space. This can be done by using the

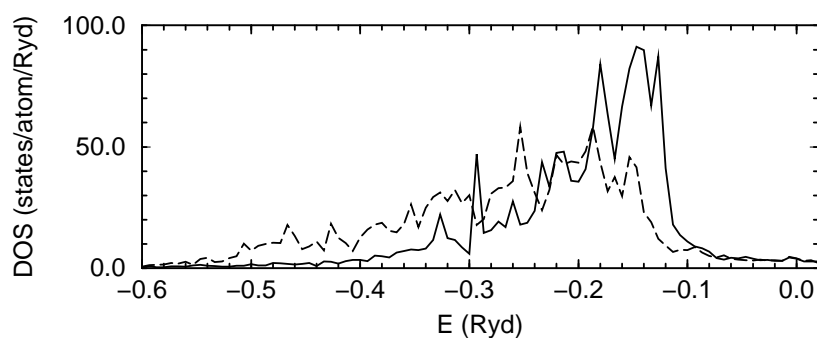
atomically resolved density of states:

$$\rho(E) = \sum_i^{\text{occup}} \int_{\Omega} |\psi_i(\vec{r})|^2 d^3r \delta(E - E_i) \quad (1)$$

where  $\Omega$  is the volume of the WS sphere of the atom considered,  $\psi_i(\vec{r})$  and  $E_i$  are the wave function and the energy of the electronic state  $i$  and the sum is taken over the occupied electronic states of the system. Figure 4(a) shows the total DOS of two surface atoms, a Cu atom of CuAu I(B) and a Au atom of CuAu I(C). As figure 4(a) shows, the maximum of the Cu DOS is about 0.15 Ryd higher in energy than the maximum of the Au DOS. Due to the relatively short range of the Cu 3d wave functions compared with the Au 5d wave functions, the interaction between the Cu 3d and Au 5d states in CuAu I is not strong. This leads to the relatively weak mixing of the Cu 3d and Au 5d bands in CuAu I, not only on the surface but in the bulk as well.



(a)



(b)

**Figure 4.** The total DOS of a surface atom. (a) The Cu atom of CuAu I(B) (solid curve) and Au atom of CuAu I(C) (dashed curve). (b) Pure Cu (solid curve) and pure Au (dashed curve).

The weak mixing between the Cu 3d and Au 5d bands leads to the formation of a pseudogap between the Cu and Au d bands [27].

Comparing figure 4(a) with the bulk DOS of Cu in CuAu I [27] reveals that the Cu DOS at the surface is more localized and shifted to the lower binding energies than the corresponding DOS in bulk CuAu I. Taking this result into account could improve the agreement between the experimental and theoretical valence band photoemission spectra of CuAu I obtained by Qiu *et al* [28]. Qiu *et al* estimated that less than 14% of the contribution of the Cu signal to the total photocurrent comes from the surface layer. The surface effect would increase the intensity of the Cu peak of the theoretical total photoemission spectrum on the low-binding-energy side, suggesting a better agreement between the calculated spectrum and the experiment.

The narrowing of the d band of the surface alloy compared to the bandwidth of the corresponding bulk alloy was shown for the Cu(001)–Au structure by Wang *et al* [14]. Our results are in qualitative agreement with the angle-resolved photoelectron spectrum of Au/Cu(001) [29], which shows the shifting of the low-binding-energy peak to higher energies with increasing Au content of the surface alloy up to the level of half a monolayer of Au. On increasing the Au content beyond the half-monolayer level, de-alloying of the Au is observed, leading to the gradual disappearance of the Cu-related low-binding-energy peak in the measured spectrum.

The interaction between the surface and the atoms and molecules adsorbed on the surface depends on the electronic structure of the adsorbates and the surface. The interaction of the resonance states of the adsorbate with the electronic states of the substrate depends on the local DOS of the surface. The interaction between the surface and the adsorbate affects the broadening and hybridization of the electronic states of the adsorbate, leading to changes in the energetics of the adsorbate depending on the type of the adsorbate [19]. Depending on the intensity of the surface DOS and the spatial extent of the corresponding wave functions, the adsorbate is bound more strongly or weakly to the surface. For instance, if there is a resonance state of the adsorbate at about 0.25–0.30 Ryd below the Fermi level of CuAu I(BC), the interaction with the surface depends strongly on whether the adsorbate is on the (B) or (C) site of the surface. This difference in the interaction is typical for CuAu I, since there is not such a significant difference between the surface DOS of pure Au and pure Cu (figure 4(b)). It should be pointed out that the electronic structure of the surface of CuAu I could not be predicted just by considering the electronic structures of pure Cu and Au surfaces. The DOS at Cu and Au sites is significantly changed upon alloying due to the change in the lattice parameter and in the chemical environment of the atoms.

#### 4. Conclusions

Controlling the surface composition of CuAu I by temperature adjustment suggests several applications. Due to the different electronic properties of Cu and Au atoms the response of the CuAu I surface to various processes could be altered. A tunable surface could also be useful in the investigation of various diffusion processes. A Cu atom in the surface layer of CuAu I acts as a kind of temperature-driven switch for the electronic structure. Similar segregation phenomena have been observed e.g. in PtNi [10] (and see references therein). However, due to the partially occupied d band in PtNi, the properties of the PtNi surface are expected to differ from those of the CuAu I surface. Regarding the valence band photoemission spectra of CuAu I, the correct balance between the bulk and surface contributions of the spectrum should be taken into account in a detailed comparison of experimental and theoretical results.



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