

Core-level shifts and the electronic structure of  $\text{Cu}_3\text{Au}$ 

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The bulk Au  $4f$  core levels in  $\text{Cu}_3\text{Au}$  have a binding energy 0.48 eV higher than they have in pure Au. The Au atoms on the  $\{100\}$  surface of the alloy exhibit a core-level shift of  $-0.4$  eV, whereas the  $5d$  valence orbitals are identical in energy for bulk and surface atoms in the alloy. This is contrary to the generally accepted models for surface core-level shifts in noble metals and serves as evidence for a strong  $s-d$  rehybridization between the bulk and surface of the alloy.

Small metal particles and alloys are known to be very good catalysts for chemical reactions, often with much higher activity than homogeneous single-crystal surfaces. In order to understand the special activity of these systems one has to understand the effects of geometry and/or charge transfer between the various components of the system on the electronic structure. High-resolution core-level spectroscopy offers a way of monitoring local changes in the electronic structure. Empirically it was established that atoms on surfaces, steps, or in clusters all exhibit different core-level binding energies, reflecting changes in the valence electronic structure at these sites.<sup>1-3</sup>

We have studied the valence bands and core levels of the single-crystal alloy  $\text{Cu}_3\text{Au}$  with two different surface orientations:  $\{100\}$  and  $\{111\}$ . We report here the results obtained from the  $\{100\}$  surface. Apart from the effects of alloying, the  $\{100\}$  surface of this single-crystal alloy offers the unique possibility to study an array of homogeneously dispersed Au atoms. The generally accepted structure of this surface at room temperature consists of two  $c(2 \times 2)$  sublattices of Au and Cu atoms with a pure Cu layer underneath as the second layer of the crystal.<sup>4</sup>

The experiments were performed at the National Synchrotron Light Source (NSLS) using a plane-grating monochromator.<sup>5</sup> The crystals were cleaned by Ar-ion bombardment followed by annealing at 500 K for 30 min. The surface conditions were checked by Auger and low-energy-electron diffraction spectroscopies.

Electron distribution curves (EDC) of the valence band were measured with a double-pass cylindrical-mirror analyzer in the angle-integrated mode for a series of photon energies and are shown in Fig. 1. The Au  $5d$ -derived features are located at 6.4 and 5.1 eV below  $E_F$ , independent of photon energy. Thus the  $5d$  spin-orbit splitting is greatly reduced compared with solid Au films (2.7 eV) and actually is close to the value observed for isolated Au atoms on a carbon substrate.<sup>3</sup> Even the binding energy relative to  $E_F$  is identical to the data for the isolated atoms.<sup>3</sup>

Our observed spin-orbit splitting of the  $d$  bands (1.3 eV) is actually smaller than that of Au atoms (1.522 eV, Ref. 6) but can be explained by the repulsion between the Cu and Au  $d$  bands, as originally discussed by Moruzzi, Williams, and Janak.<sup>7</sup> In an alloy of two  $d$ -band metals, even with no

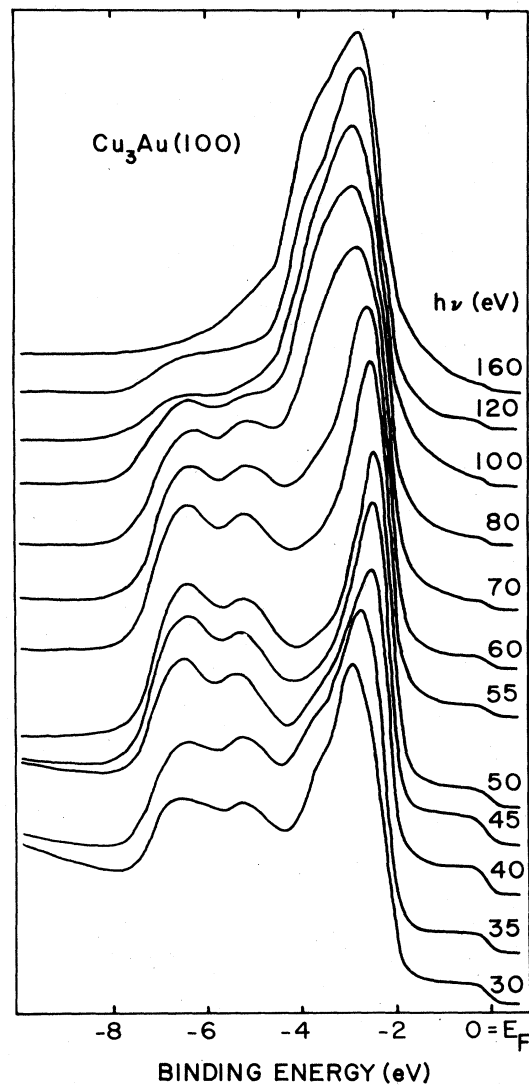


FIG. 1. Angle-integrated electron distribution curves of the valence band of  $\text{Cu}_3\text{Au}\{100\}$ .

direct energy overlap, there is a repulsion between the two sets of  $d$  bands, which actually reduces the bandwidth or apparent spin-orbit splitting of either subsystem since the repulsion depends on the energy separation of the noninteracting system.

In view of the surface core-level shift discussed later it is important to note that Graham<sup>8</sup> has measured the two-dimensional band structure of a  $c(2 \times 2)$  layer of Au evaporated onto a Cu(100) surface. The observed bands have very little dispersion (0.25 eV) and are centered at 5.1 and 6.2 eV below  $E_F$ . Graham<sup>8</sup> suggests that the evaporated Au actually substitutes Cu atoms in the top layer of the crystal, thus forming a surface identical in the top two layers to our alloy crystal {100} surface, but with a reduced lattice spacing.

The drastic reduction in dispersion shows that the  $d$  orbitals are, even in the solid, very localized. The average distance between nearest-neighbor Au atoms changes from 2.88 Å in pure Au to 3.75 Å in the  $c(2 \times 2)$  top layer of Cu<sub>3</sub>Au(100). This 30% increase in distance causes the dispersion of the Au  $d$  band to change from 1.4 to about 0.2 eV. The concentration of the Au atoms in the bulk of Cu<sub>3</sub>Au is smaller by a factor of 2 compared with the {100} surface and the Au and Cu  $d$  bands are separated in energy, thus the Cu  $d$  electrons do not mediate an overlap between the dispersed bulk Au atoms. With respect to the  $d$  electrons the bulk Au atoms thus resemble single-dispersed Au atoms imbedded in a Cu matrix. On the other hand the  $s$ - $p$  electrons will most likely still have an overlap.

Contrary to the Au-derived part of the valence bands the change in the Cu-derived parts is less obvious upon alloying. The angle-integrated  $d$ -band spectra show a similar position and width of the Cu  $d$  band in the alloy as observed for pure Cu. This is evident from the spectra taken around 160 eV where the Au  $5d$  emission is at its Cooper minimum and we essentially observe only the Cu  $3d$  features and the emission from the  $s$ - $p$  derived states. The subtle changes in the details of the alloy band structure as derived from an angle-resolved photoemission study will be discussed in a forthcoming publication.<sup>9</sup>

In our experiments the Au  $d$  bands show hardly any difference between bulk and surface atoms, yet the Au  $4f$  emission shows a large surface core-level shift. Figure 1 shows that there is essentially no shift of the Au  $5d$  bands (at 5.1 and 6.4 eV) when the photon energy varies from 35 eV (mostly surface sensitive) to 80 eV (more bulk sensitive). Figure 2 shows high-resolution EDC's of the Au  $4f_{7/2}$  core levels of Cu<sub>3</sub>Au{100} and of polycrystalline Au. The curves are taken at a photon energy of 120 eV to assure both good photon-energy resolution and high surface sensitivity. Clearly the core-level peaks have two components, one due to bulk emission and the other, at the lower binding-energy side, due to the Au atoms on the surface. A decomposition into two asymmetric Lorentzians obtained in a least-squares fit is shown. Comparison with the curves taken at 160-eV photon energy establishes the lower binding-energy component to originate from the surface. The detailed parameters obtained in the fit are listed in Table I. The fitting of the curves to two Lorentzians was done after subtraction of a background, which was approximated by a quadratic polynomial. The half-width in Table I includes the instrumental resolution. The overall instrumental-resolution function for monochromator and electron spectrometer was verified to be rather well

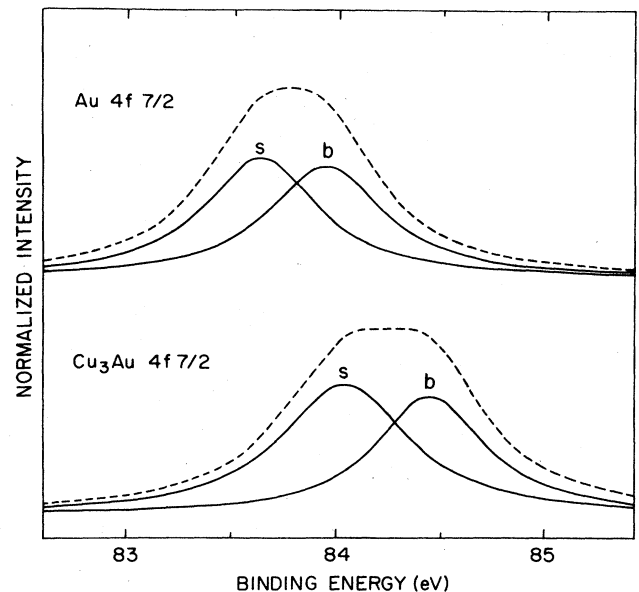


FIG. 2. Au  $4f_{7/2}$  core-level peaks for polycrystalline Au (top) and Cu<sub>3</sub>Au(100) (bottom). Dashed curves are experimental ( $h = 120$  eV), solid curves are surface ( $s$ ) and bulk ( $b$ ) components as indicated.

represented by a Lorentzian with a full width at half maximum of 370 meV by fitting the line shape of the Fermi level of the sample as measured under the same experimental conditions as the core levels. The surface to bulk intensity ratio of  $0.78 + 0.13$  is reasonable if one takes into account the average electron-collection geometry and escape depth.<sup>10</sup>

The increase of 0.48 eV in Au  $4f$  binding energy for the Au atoms in the bulk of the Cu<sub>3</sub>Au alloy is similar to the results of previous studies on Au-Ag alloys in the limit of low-Au concentration.<sup>11</sup> Watson, Hudis, and Perlman<sup>11</sup> did an extensive study of the electronic properties of Au alloys and found that there is a "rather substantial flow of  $s$ -like electron charge onto Au sites upon alloying, regardless of the atomic species of the alloy partner." For Au<sub>0.5</sub>Ag<sub>0.5</sub>, Watson, Hudis, and Perlman find the Au  $4f$  binding energy 0.3 eV larger than for pure Au. By itself, this suggests a small net flow of charge off, *not onto*, the Au sites. The combined results of XPS and Mössbauer isomer-shift stud-

TABLE I.  $E_B$  is binding energy of the Au  $4f_{7/2}$  level in the bulk of Au and Cu<sub>3</sub>Au{100}.  $\Gamma_B$  and  $\Gamma_S$  are the FWHM values of the bulk and surface peaks, respectively.  $\Delta E_S = E_B - E_S$ , with  $E_S$  denoting binding energy of the surface  $4f_{7/2}$  level.  $S/B$  is the ratio between surface and bulk peak areas.

	Au foil	Cu <sub>3</sub> Au{100}
$E_B$ (eV)	83.92	84.40 ± 0.014
$\Gamma_S$ (meV)	640	740 ± 25
$\Delta E_S$ (meV)	320	410 ± 10
$\Gamma_B$ (meV)	630	650 ± 30
$S/B$	0.93	0.78 ± 0.13

ies, however, indicate that the primary effect of alloying Au is not the motion of charge onto or off an Au site, but instead a depletion of  $d$  and a very nearly matching increase in  $s$  (or free-electron-like) conduction-electron character at an Au site. The ratio of  $d$  depletion to  $s$ -like conduction-electron gain is  $0.6 \pm 0.2$  for  $\text{Au}_{0.5}\text{Ag}_{0.5}$  and similar behavior is encountered in other Au alloys. We note that since the  $d$  electrons are more localized any change in  $d$  charge has a stronger influence on the core-level binding energy than a change in the  $s$  electron count. Therefore the increase in  $s$  electron charge at the Au atom, which by itself would cause the  $4f$  binding energy to be lower, is overcompensated by the  $d$ -hybridization loss, resulting in an actual increase of the core-level binding energy. Because the electronegativities of Ag and Cu are about equal we think the situation in  $\text{Cu}_3\text{Au}$  might be similar as in the Au-Ag alloys. Even though we are not aware of any Mössbauer studies of  $\text{Cu}_3\text{Au}$  we are inclined to attribute the 0.48 eV binding-energy increases in the bulk Au  $4f$  levels of  $\text{Cu}_3\text{Au}$  compared with pure Au to an initial-state shift, reflecting the net charge transfer and rehybridization just as in the Au-Ag alloys. At this point in time we have no reason to assume that the difference in final-state screening between  $\text{Cu}_3\text{Au}$  and pure Au is large enough to cause a shift of 0.48 eV in the Au  $4f$  emission.

Much more interesting than the shift of the bulk Au core levels between the alloy and pure Au is the fact that we do see a surface core-level shift even though the  $d$  levels of the surface are essentially degenerate with the bulk Au  $d$  levels, as discussed above. A surface core-level shift without a shift in the  $d$  valence orbitals is contrary to the general model for surface core-level shifts. We recall that this model establishes the link between the narrowing of the surface valence density of states, due to the lower coordination number, and the core-level shift by enforcing charge

neutrality of the layers.<sup>12</sup> In our experiments, we see no difference in the energy of the  $5d$  valence orbitals of Au in  $\text{Cu}_3\text{Au}$  between surface and bulk; hence the above model of surface core-level shifts cannot be invoked. We believe the explanation of the Au  $4f$  surface core-level shift lies in the fact that the surface atoms contain a greater fraction of  $d$  states than the bulk atoms.

In conclusion, we summarize the main points of the present study. The surface core-level shift of 0.4 eV, which we observe for  $\text{Cu}_3\text{Au}$ , is as large or larger than that previously observed for Au single crystals<sup>11</sup> (0.28–0.38 eV depending on the surface orientation and reconstruction). We rule out final-state effects as a major cause of our observed surface core-level shifts. Recent theoretical calculations for  $\text{Cu}\{100\}$ <sup>13</sup> indicate that final-state screening might be reduced at the surface, causing the core levels to shift to higher binding energy, which would be in the opposite direction of our observed shifts. Our explanation for the surface core-level shift is a different  $s$ - $d$  hybridization in the bulk than on the surface. This effectively would change the  $d$  count for surface atoms without necessarily causing a directly observable shift in the valence  $d$  states of the surface atoms. Rehybridization of the surface electronic states was previously only thought to play a role for non-noble-metals. Our observations demonstrate the need for calculations of the surface electronic structure including core levels in order to understand the effects relevant to surface core-level shifts. The usually applied simple model of surface-band narrowing and a shift of the surface density of valence states is deficient in explaining our results and needs to be replaced by more sophisticated models.

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