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Au surface density of states and surface core-level shifts in $Cu_3Au(001)$

S. B. DiCenzo, P. H. Citrin, E. H. Hartford, Jr., and G. K. Wertheim
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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We have separated the Au surface density of states in $Cu_3Au(001)$ from the Au bulk states and find that the bottom of the Au $5d$ band is shifted up to lower binding energy, similar to the $5d$-band shift previously observed at the surface of pure Au. This suggests a similar origin in Cu_3Au and in Au for the Au surface-atom core-level shifts, which have the same sign and comparable magnitude in both materials.

It is well known that the core electrons of atoms at the surface of a metal have different binding energies from those of the bulk.[1-3] This surface-atom core-level shift (SCS) has its origin in the valence band, which is narrowed at the surface as a result of the reduced coordination number of the surface atoms. When such narrowing affects nonbonding or antibonding d states of surface atoms, as is the case for transition metals with more than half-filled bands, there is a net loss of bonding and consequently a decrease in the surface-atom core electron binding energy. This negative SCS is also found in noble metals, even though their d bands are nominally filled, because it is the s-hybridized part of the d band that is affected.

Citrin, Wertheim, and Baer[1] have isolated the surface valence bands of polycrystalline Au by using the surface/bulk intensity ratios determined from the core-level photoemission spectra. Other studies[4,5] using x-ray photoelectron spectroscopy (XPS) have shown that the surface density of states (DOS) differs from the bulk DOS, although in that work the two components were not separated. Recently, Eberhardt *et al.*[6] have used synchrotron radiation to study the (001) surface of Cu_3Au. They found a well-defined SCS for Au, but failing to observe any apparent difference between their bulk- and surface-sensitive valence-band spectra, they concluded that the SCS must be the result of some new mechanism.

In this work we report on XPS data from $Cu_3Au(001)$ in which a difference between the Au bulk and surface DOS is clearly demonstrated. We find that the bottom of the surface Au $5d$ band is shifted up to lower binding energy, an effect entirely consistent with the earlier understanding of the SCS.[1-3] While photoemission with synchrotron radiation can usually be made more surface-sensitive than XPS, our work highlights a particular virtue of the latter technique, namely, that the use of core-level spectra makes it possible to separate surface and bulk valence emission unambiguously.[1] The success of our procedures demonstrates the general feasibility of isolating the surface DOS in XPS from other single crystals.

An oriented and polished $Cu_3Au(001)$ crystal was cleaned by cycles of Ar^+ sputtering and annealing just below the ordering temperature of 390 °C. The sharp $c(2\times2)$ pattern observed in low-energy electron diffraction confirmed that the surface was well ordered. The annealing lasted for 15 h or more, and occurred in the spectrometer chamber where the pressure remained at $\sim1\times10^{-10}$ Torr throughout the annealing and data collection. The meaurements were made with an ESCALAB II analyzer equipped with a monochromated Al $K\alpha$ source ($h\nu = 1486.6$ eV). The valence-band data were taken with a pass energy of 10 eV, and the Au $4f$ spectra were taken with pass energies of 10 and 5 eV.

We first discuss the bulk valence-band spectrum of Cu_3Au (Ref. 7) shown in Fig. 1. An early x-ray emission study[8] suggests that the Cu_3Au valence band is well approximated by a superposition of Cu $3d$ and Au $5d$ bands, implying that the peaks at ~6.9 and ~5.6 eV are primarily of Au $5d$ character, but that the Au bands also extend into the broad peak at ~3 eV, which is dominated by the Cu $3d$ emission. Eberhardt *et al.*[6] suggest, on the other hand, that there is no overlap of the Cu and Au d bands, i.e., that the Au $5d$ emission is confined to the two peaks at 6.9 and 5.6 eV. They identify these two peaks as the Au $5d$ spin-orbit doublet, even though their splitting is actually smaller than the atomic value. (In fact, this splitting was taken as evidence for the atomiclike nature of the Au $5d$ band.[6]) In our data the intensity ratio between the Cu-dominated peak and the hypothetical Au doublet is ~1.5, whereas the XPS cross sections[9] of the Cu $3d$ and

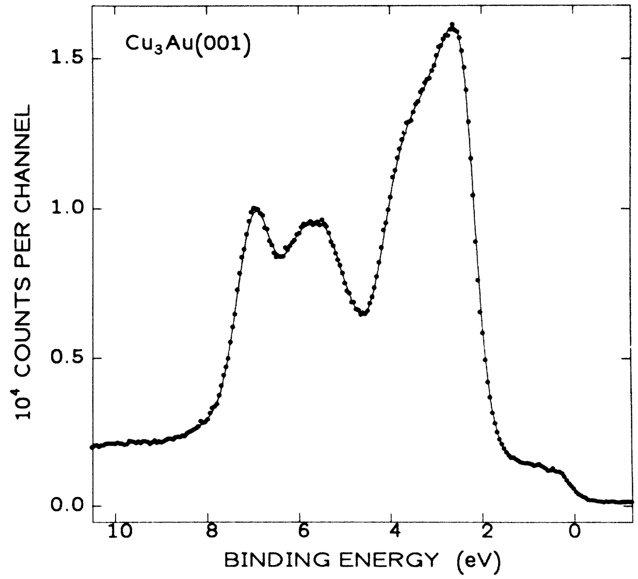

FIG. 1. XPS valence band spectrum of $Cu_3Au(001)$.

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Au $5d$ electrons and the composition and structure[10,11] of the sample predict Cu $3d$ and Au $5d$ bands whose intensities (i.e., areas) are very nearly equal. Therefore, our photoemission data do not support the view of Eberhardt *et al.*[6] but are instead consistent with the interpretation of the x-ray emission work.[8] Confirmation of the bandlike—not atomiclike—character of the Au d states and their overlap with the Cu d bands in Cu_3Au is provided by self-consistent linearized augmented plane wave (LAPW) calculations.[12]

Turning now to the core-level data, we remind the reader that on the scale of a typical surface-atom layer thickness d of ~ 2 Å, XPS is *not* particularly surface sensitive because 1-keV electrons in most solids have escape depths λ of ~ 20 Å. With a photon source of fixed energy, surface sensitivity is controlled by varying the take-off angle of the detected photoelectrons. The escape depth of electrons emitted from a sample tilted through an angle θ from the normal is decreased by a factor $\cos\theta$ relative to emission along the normal. This increases the surface-to-bulk intensity ratio from $(e^{d/\lambda}-1)$ to $(e^{d/\lambda\cos\theta}-1)$. As an example, for a monatomic crystal with $d = 2$ Å and $\lambda = 20$ Å tilted from $\theta = 0°$ (normal emission) to $\theta = 70°$ (grazing emission), the surface-to-bulk intensity ratio changes from 0.11 to 0.34. This ability to obtain data with varying degrees of surface sensitivity is crucial to the process of separating the surface and bulk DOS.

Fortunately, the structure[10,11] of Cu_3Au enhances the surface sensitivity of the XPS Au core-level spectra. This compound, like pure Cu and pure Au, has an fcc space lattice. The Au atoms may be thought of as occupying the corners of the cubes while the Cu atoms are at the face centers. In a well-ordered crystal, the first atomic layer at the (100) face contains 50% Au atoms while the second layer is composed of only Cu. This two-layer sequence then repeats into the bulk. The resulting surface-to-bulk ratio for Au photoelectrons is thus increased to $(e^{2d/\lambda\cos\theta}-1)$, more than twice the ratio for the pure metal. For photoemission from Cu atoms, the surface sensitivity is correspondingly decreased.

Figure 2 shows the Au $4f_{7/2}$ peak for emission at $\theta = 0$ and 70°. The enhanced surface component is obvious in the latter spectrum and appears at lower binding energy than the bulk peak. The sign of the surface shift is the same as in pure Au,[1] as expected from a Born-Haber analysis of the surface effect.[13] The solid curve is the function fitted to the data by a least-squares method[14] and represents the sum of the two components shown. Each component consists of a convolution of a Gaussian with a Doniach-Šunjić line shape,[15] which itself contains the Lorentzian lifetime width and the metallic singularity index. By fitting the two spectra in Fig. 2 simultaneously and requiring the surface shift to be the same in both, we obtain a value of 0.50 ± 0.05 eV for the Au SCS in Cu_3Au. The value reported by Eberhardt *et al.*[6] of 0.41 ± 0.01 eV is somewhat lower, as is their value of 84.40 ± 0.014 eV for the bulk component's binding energy, relative to ours of 84.55 ± 0.05 eV. Similarly, their SCS value of 0.32 eV in polycrystalline Au is smaller than that of 0.40 ± 0.02 eV found by Citrin *et al.*[1] These slight discrepancies may arise from their model functions or their method of background subtraction. Based on the surface-to-bulk intensity ratio for the normal-emission spectrum, we find an escape depth of 15 ± 2 Å for 1.4 keV electrons in Cu_3Au. The increased surface-to-bulk intensity ratio in the 70° data is consistent to within 1.5° of our nominal sample angle of 70°, providing firm support for the reliability of our analysis procedures. A similar analysis of the surface components for Cu could not be carried out because the Cu $2p$ peaks are intrinsically too broad.

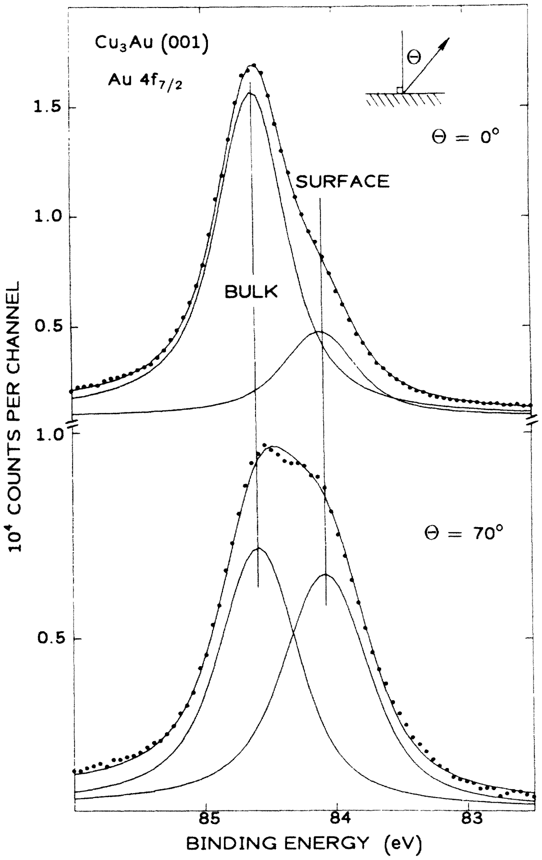

FIG. 2. The Au $4f_{7/2}$ peak in Cu_3Au bulk-sensitive spectrum (top) and surface-sensitive spectrum (bottom). The solid curves represent the results of a constrained, simultaneous fit to both spectra. The separation between the surface and bulk components is 0.50 eV.

We now turn our attention to the valence-band spectrum to extract information about the surface density of states. This is accomplished[1] using the results of our Au $4f$ core-level analysis, specifically, the ratio between the bulk photoemission intensities taken at $\theta = 0$ and 70°. Since the kinetic energies of the valence and Au $4f$ electrons are so close (~ 1480 and ~ 1400 eV), the bulk Au valence-band emission at those angles should have the same ratio. Figure 3 shows the valence-band spectrum obtained at each angle as well as the difference spectrum obtained by subtracting the $\theta = 0°$ (bulk-sensitive) data, appropriately normalized, from the $\theta = 70°$ (surface-sensitive) data. This subtraction process removes all the signal due to Au atoms in the Cu_3Au bulk, but it does not yield a pure surface valence spectrum. Rather, the differ-

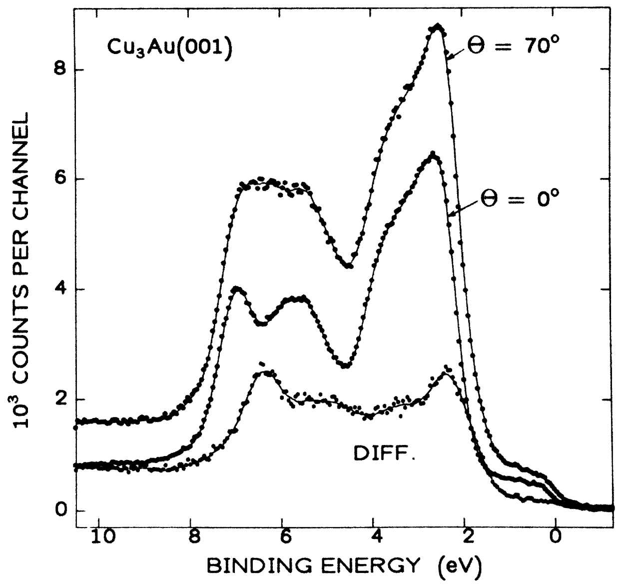

FIG. 3. Valence-band spectra from Cu_3Au. The lowest solid curve is the difference spectrum obtained by subtracting the bulk-sensitive data ($\theta = 0°$), shown correctly normalized, from the surface-sensitive data ($\theta = 70°$). The difference spectrum contains no contribution from bulk Au atoms.

ence spectrum consists of photoemission from equal numbers of Cu and Au surface atoms, together with a contribution from bulk Cu atoms. The bulk Cu signal is somewhat weaker than the surface Cu signal, and appears because Au and Cu have different surface-to-bulk intensity ratios. Actually, the difference spectrum is dominated by states of Au 5*d* character since the Au 5*d* cross section is three times that of Cu 3*d*. (It is, in principle, possible to eliminate the Cu bulk signal using a spectrum taken at a third polar angle, but small uncertainties in the normalizations used would result in unacceptably large errors in the final spectrum.) As in Ref. 1, the subtraction of the valence-band spectra presented here is parameter-free because the normalization is completely determined by the analysis of the core-level data.

Inspection of the difference spectrum in Fig. 3 shows that at the surface of $Cu_3Au(001)$ the bottom edge of the Au *d* band is shifted up to lower binding energy. A similar shift is observed at the surface of pure Au,[1] where it is associated with the narrowing of the *d* band and the attendant surface core-level shift. Our observation of similar surface effects in pure Au and in Cu_3Au suggests that the same mechanism is responsible for the Au SCS in both materials, contrary to the conclusions of Eberhardt *et al.*,[6] who failed to observe the surface-bulk variation in their valence-band spectra. Undoubtedly the reason for their failure is that the photon energy used to achieve surface sensitivity for the Au 4*f* data did not provide sufficient surface sensitivity for the valence bands.

One might be concerned whether the differences observed between our valence-band spectra are due not to differing amounts of surface contribution but rather to the angular dependence of *d*-band emission previously observed[16] for Au single crystals. We have tested that hypothesis by varying the azimuthal orientation of our sample and by taking data at intermediate polar angles. As expected, some slight variations in the spectra were observed for data taken along different crystal axes, but they were much less important than those due to surface-versus-bulk effects. The general features of the difference spectrum in Fig. 3 can therefore be taken as representative.

In summary, we have separated the Au surface DOS in $Cu_3Au(001)$ from the bulk Au DOS and find that the bottom of the Au 5*d* band is clearly shifted up to lower binding energy, as in pure Au. This indicates that the surface-atom core-level shift has similar origins in the compound and in the pure metal. Our work further demonstrates that, offsetting its limited surface sensitivity, there are advantages to using XPS to determine the surface DOS. The Au core-level spectra are obtained under exactly the same conditions of photon intensity, resolution, and collection efficiency, and nearly the same kinetic energy, as those of the valence-band spectra. The core-level analysis thus completely determines the normalization required to remove the bulk Au component from the valence-band spectrum. The difficulty of obtaining a pure surface valence-band spectrum from a compound will not arise when angle-dependent XPS is applied to single crystals of pure metal.

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