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Partial densities of states of ordered Cu_3Au

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A comparison of photoemission data and linear augmented-plane-wave results for Cu_3Au serves to elucidate the Au partial density of states.

INTRODUCTION

The determination of the partial electronic densities of states (DOS) of Cu_3Au, an intermetallic compound with a fcc space lattice like those of Cu and Au, provides an interesting challenge because the *d* states of both elements fall in the same energy range. Early soft-x-ray data indicated that the partial Cu and Au densities of states are like those of the pure elemental metals.[1] More recently, it was concluded from ultraviolet-photoelectron-spectroscopy (UPS) measurements that the DOS of the gold is reduced to a spin-orbit doublet,[2] while that of the Cu remains largely like that of the pure metal. Elementary arguments do little to clarify this issue, other than to confirm that the Au partial DOS in Cu_3Au should differ more significantly from that of the elemental metal than that of Cu. In the Cu_3Au structure, Au atoms have twelve Cu near neighbors and six Au next-near neighbors, making it unlikely that the Au partial DOS resembles that of Au itself. Cu atoms have eight Cu and four Au near neighbors and six Cu next-near neighbors, making it more likely that the Cu partial DOS resembles that of elemental Cu.

Some aspects of the Cu partial density of states are readily determined by photoemission, because the cross section of the Au 5*d* states drop to 0.1 Mb for photon energies above 200 eV (at the Copper minimum), where the cross section of the Cu 3*d* states is 2.5 Mb.[3] Considering the 3:1 [Cu][Au] composition ratio, the Au signal then contributes only 1.3% of the total response in the region of the *d* band. The Au partial density of states is, however, not readily isolated, because at low photon energy the Au cross section[3] exceeds that of Cu by at most a factor of 4, so that the valence-band region between 2 and 5 eV is still dominated by the Cu signal. In this assessment, we have used the theoretical atomic photoionization cross sections of Yeh and Lindau[3] rather than the experimental values,[4,5] because the latter, which predict a much greater attenuation of the Cu signal at low photon energy,[6] are incompatible with certain aspects of the data for Cu_3Au. For example, they indicate equal Cu and Au response at 125 eV, where the Au signal is very weak, and a much weaker Cu signal at photon energies below 50 eV than is observed. The calculated cross sections[3] are equal at a photon energy of 65 eV, where valence-band data indeed correspond quite well to the calculated total density of states.

The band structure of Cu_3Au has been discussed by Skriver and Lengkeek,[7] who qualitatively illustrate the effects of various approximations on the Cu and Au *d* contributions to the valence band. However, partial densities of states were not presented. In this report we make a comparison between photoemission data for ordered Cu_3Au and the results of self-consistent linear augmented-plane-wave (LAPW) calculations for both Cu_3Au and its elemental constituents.

TECHNICAL DETAILS

A sample of Cu_3Au that had been used in earlier studies[8,9] was cleaned by Ar-ion sputtering and annealed to $\approx 750\,^\circ\mathrm{C}$ in a preparation chamber on the Bell Laboratories 6-m toroidal-grating-monochromator (TGM) beam line at the National Synchrotron Light Source at Brookhaven National Laboratory (Upton, NY). Surface contamination was monitored by Auger spectroscopy. Data were taken with a 100-mm hemispherical analyzer with 5° angular resolution at 45° to the surface normal of the (100) surface.

The present self-consistent energy-band results for fcc Cu and Au and simple-cubic (sc) Cu_3Au have been calculated with the use of a scalar-relativistic version of the LAPW method.[10] The observed room-temperature values[11] for the Cu ($a = 3.615$ Å), Au ($a = 4.078$ Å), and Cu_3Au ($a = 3.748$ Å) lattice parameters have been utilized. The radii of the Cu [$R(\mathrm{Cu}) \approx 1.24$ Å] and Au [$R(\mathrm{Au}) \approx 1.40$ Å] muffin-tin spheres were chosen so that they were nearly touching along the nearest-neighbor bond directions of the fcc structure. These same radii were also used in the Cu_3Au calculations, where now the Cu-Au spheres nearly touched along the four nearest-neighbor Cu—Au bond directions.

The basis size for each calculation was set using a plane-wave energy cutoff of 10 Ry, yielding approximately 60, 80, and 250 LAPW's for Cu, Au, and Cu_3Au, respectively. The lattice-harmonic expansion of the nonspherical contributions to the charge density and potential within the muffin-tin spheres included all terms through $l = 6$. The corresponding Fourier expansions in the interstitial regions included from 1100 to 5000 plane waves. The Brillouin-zone sampling involved 10 uniformly distributed *k* points in the appropriate $\frac{1}{48}$ irreducible wedge of the full fcc and sc zones. Exchange and correlation effects have been introduced with the use of the Wigner interpolation formula.[12]

The DOS curves have been calculated using tetrahedral interpolation on a mesh of 44 and 84 k points within the irreducible Brillouin-zone wedges for the fcc and sc structures, respectively. The projected Cu and Au contributions to the total DOS are evaluated by weighting the total DOS by the integrated charge within the Cu and Au muffin-tin spheres. Although this weighting includes s-p as well as d components, the latter determine the principal DOS features below E_F in these materials.[13] Thus in the following discussion, the projected Cu and Au DOS results will be described simply as the Cu $3d$ and Au $5d$ components.

RESULTS AND DISCUSSION

Core-level binding-energy shifts

We begin with a discussion of the Au $4f$ core-level "chemical" and surface-atom shifts in Cu_3Au. The Au $4f$ core-level data in Fig. 1 yield results in good agreement with those reported earlier.[2,9] The large intensity of the surface signal is due to the fact that the surface layer of ordered Cu_3Au contains an equal number of Au and Cu atoms.[8] We find a Au $4f$ bulk binding energy of 84.55 eV, corresponding to a shift of 0.55 eV from that of bulk Au, and a surface-atom core-level shift of -0.46 eV. The corresponding values obtained by x-ray photoelectron spectroscopy (XPS) (Ref. 9) were 84.55 and -0.50 eV, while those from ultraviolet photoelectron spectroscopy (UPS) (Ref. 2) were 84.40 and -0.41 eV. In this connection it is interesting to make a comparison with the core-electron binding energies of Au atoms incorporated into the first atomic layer of Cu(100). At 0.5 monolayer coverage these form an ordered two-dimensional layer, which is structurally like the first atomic layer of the annealed (100) surface of Cu_3Au.[14] In both cases the second layer contains only Cu atoms. The lattice constant of Cu_3Au is only slightly larger than that of Cu and in good accord with Vegard's law. In Cu(100)-$c(2\times2)$Au, the Au $4f$ binding energy was found to be 84.0 eV,[15] i.e., essentially equal to that of Au in the morphologically similar first atomic layer of Cu_3Au, 84.09 eV according to the data in Fig. 1.

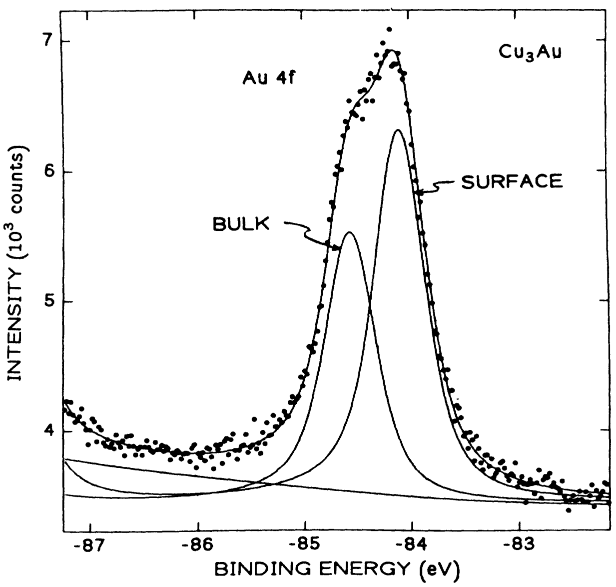

FIG. 1. Au $4f_{7/2}$ photoemission spectrum from the (100) surface of ordered Cu_3Au, taken with 170-eV photons. The data have been fitted by two Doniach-Šunjić lines of identical shape, representing emission from atoms in the bulk and the surface.

If we assume that the Cu_3Au was fully ordered, i.e., with only Cu atoms in the even layers and equal numbers of Cu and Au atoms in the odd layers, then the escape depth can be obtained from the relative intensities of the bulk and surface signal in Fig. 1. Considering the takeoff angle of 45°, we deduce an escape depth of 6.0 Å at a kinetic energy of 82 eV. This value is in good accord with the so-called "universal curve" and with determinations for Cu,[16] which should have similar properties.

The 0.55-eV increase in Au $4f$ core-electron binding energy in Cu_3Au relative to bulk gold is opposite to what is expected on the basis of the electronegativity difference, but this does not negate the possibility of charge transfer to the gold, since other effects may predominate. The Born-Haber cycle expression for the core-electron binding-energy shift[17] contains four cohesive energies, those of Au and Hg (the element with next-higher atomic number) in Au and Cu_3Au:

$$\Delta E_B = E^{\mathrm{Au}}_{\mathrm{Cu_3Au}} - E^{\mathrm{Au}}_{\mathrm{gold}} - E^{\mathrm{Hg}}_{\mathrm{Cu_3Au}} + E^{\mathrm{Hg}}_{\mathrm{gold}} , \qquad (1)$$

where the superscript refers to the solute and the subscript to the solvent. The contribution of the first two terms is readily estimated from the thermodynamic properties of Cu-Au alloys.[18] The partial molar enthalpy of mixing for Au in the disordered state at 800 °C is -0.14 eV/atom. The sign indicates that the Au is more strongly bound in the alloy, making the contribution of the first two terms in Eq. (1) positive. This is, however, an underestimate the value for the ordered state. For that state Ref. 18 provides only the partial molar free energy, -0.22 eV/atom. The partial molar enthalpy is greater by the $T\,\Delta S$ entropy term, which is also inherently negative. The first two terms of Eq. (1) consequently account for at least 40% of the measured shift. The contribution of the second two terms is also positive since Hg is soluble in Au but not in Cu.[19] It is therefore likely that a large part of the shift arises from the properties of the Hg atom, which represents the hole-state Au atom in the final state.

We next attempt to relate the observed core-level shift to the calculated band-structure results, relying on the observation[20] that noble-metal d bands have shifts comparable to those of the core levels. The calculated total and projected Cu and Au d densities of states for Cu_3Au and the elemental metals are compared in Figs. 2 and 3. Between -3.5 eV and E_F the Cu d DOS results in Fig. 2 are very similar, but below -3.5 eV structure of the Cu component of the Cu_2Au DOS is spread out, with the last major peak at -6 eV. For the Au $5d$ DOS results, Fig. 3 shows that the contribution of the Au to the DOS of Cu_3Au is more strongly perturbed, with some of the state

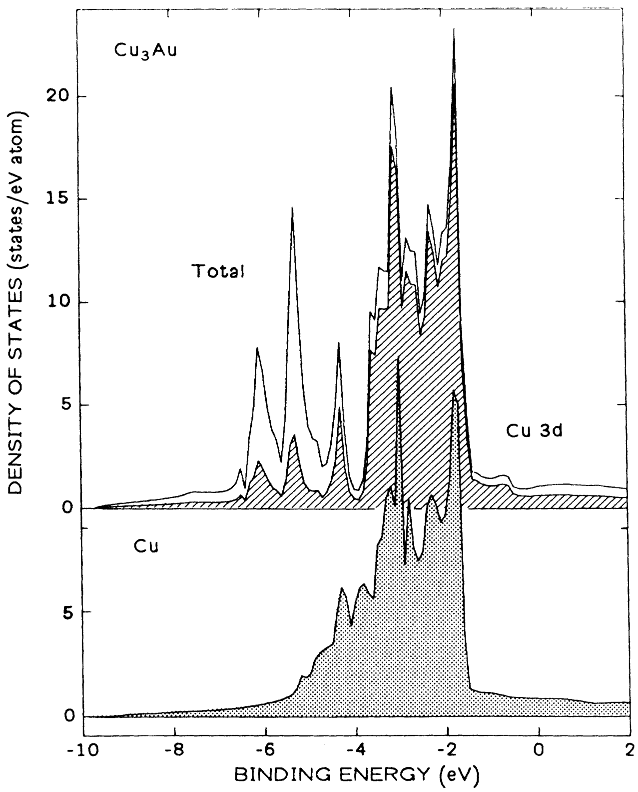

FIG. 2. Comparison of the calculated total and d-band densities of states for Cu$_3$Au and Cu. The Cu 3d contributions are shaded.

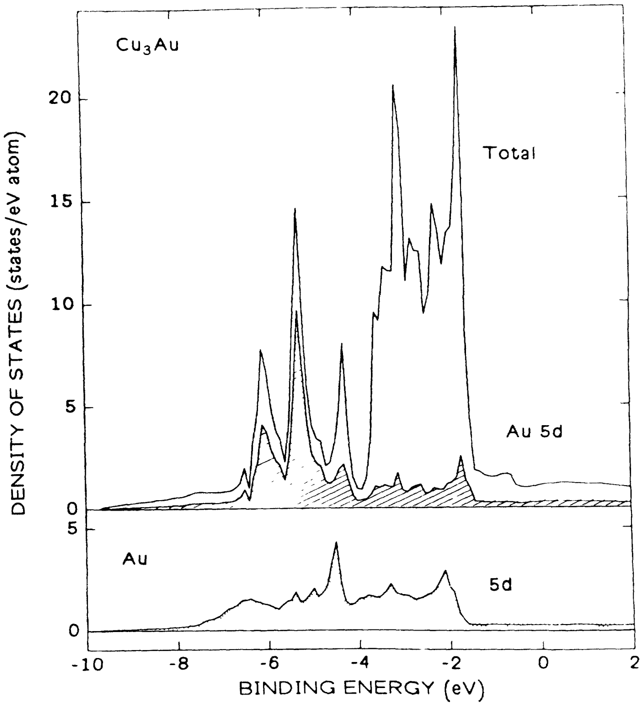

FIG. 3. Comparison of the calculated total and d-band densities of states for Cu$_3$Au and Au. The Au 5d contributions are shaded.

density displayed below that of the Cu bands. However, the Au DOS does extend over an energy range comparable to that in Au itself.

A comparison of these results with UPS data (see below) shows that the d-band binding energies are not accurately placed relative to the s-p bands, falling too close to E_F. This is in accord with the general experience with self-consistent calculations for these systems.[13] In terms of the d-band binding energies, the "experimental" Fermi level in the Au spectrum must be increased by 0.56 eV and that in the Cu$_3$Au spectrum by 0.65 eV. In both Au and Cu$_3$Au, the required shift adds 0.183 states/atom to the occupied DOS. It is also worth noting that the occupied Au integrated d density of states is 0.17 electrons greater in Cu$_3$Au than in Au, in accord with primitive expectations based on the electronegativity difference. The centroid of the Au d-band density of states of Cu$_3$Au falls at -5.32 eV, while that of Au falls -4.89 eV below E_F. Since the Fermi-level corrections made above are comparable, they contribute little to the d-band centroid shift. The shift from Au to Cu$_3$Au is $+0.43$ eV, which compares favorably with the measured core-level shift of $+0.55$ eV.

The surface-atom core-level shift in Cu$_3$Au has the same sign (negative) but is somewhat larger in magnitude than that in bulk gold.[20,21] The negative sign follows immediately from the Born-Haber cycle analysis in which the surface-atom shift is related to the decreased coordination number at the surface. A negative surface-atom shift requires only that the cohesive interaction of Au in Cu$_3$Au be greater than that of Hg in a Au site, a fact already mentioned above.

Valence-band spectra

Valence-band data, taken over a range of photon energies, are illustrated in Fig. 4. At the highest photon energy, the data are dominated by emission from Cu 3d states, at the intermediate energy the Cu and Au cross sections are comparable, and at the lowest energy the Au cross section is nominally 4 times that of Cu. For photon energies in the lower range, spectra that are (partially) angle resolved correspond to transitions between bands and do not provide an image of the occupied density of states. However, bands whose dispersion is small will always appear at approximately the same energy. This is true for the Cu d states between 2 and 3 eV and has also been established for Au states in Cu(100)-$c(2\times2)$Au.[15] It is therefore no surprise that certain peaks in the spectra of Fig. 4 can be identified at all photon energies. Intensities are, however, not simply proportional to densities of states.

There is a second important difference between these experimental spectra and theoretical calculations for bulk solids. As demonstrated by the core-level data in Fig. 1, more than half of the Au signal comes from atoms in the first atomic layer when the escape depth is of the order of 6 Å. The valence-band data were also taken under this condition, so that Au surface atoms provide more than half of the Au 5d signal. XPS measurements[9] have already shown that the surface DOS of Cu$_3$Au is contracted at the bottom relative to that of the bulk. The nature of the Au 5*d* spectrum of the surface atoms emerges most clearly from the work of Graham.[15] He finds two weakly dispersing Au-derived peaks, at 5.2 and 6.3 eV, in Cu(100)-*c*(2×2)Au, while in Cu_3Au three peaks appear in this region, with the outer one at 7.0 eV. This is especially clear in data taken with He I radiation where the escape depth is larger, making the data more bulk sensitive. The location of the lowest bulk and surface peaks is in good agreement with those determined for the bulk and surface DOS of Cu_3Au by XPS, 6.9 and 6.3 eV (see Fig. 3 in Ref. 9). This is further evidence that the first atomic layer of Cu_3Au is electronically very similar to that of Cu(100)-*c*(2×2)Au. These bulk and surface peaks can also be discerned in the 75-eV data in Fig. 4.

In spite of the strong surface signal in the data, is seems worthwhile to make a more detailed comparison between theory and experiment. In order to carry this out we have introduced the expected binding-energy-dependent lifetime broadening into the calculated DOS. The lifetime width was assumed to vary as the square of the energy below E_F, and the magnitude of the broadening was adjusted to make the shape at the bottom of the band resemble that in the data. The requisite Lorentzian has a full width at half maximum (FWHM) of 0.47 eV at that point. A Gaussian instrumental function with a 0.2-eV FWHM was also folded into the DOS. It affects mainly the cutoff at E_F and some of the peaks at the top of the *d* band.

The resulting simulation of an experimental DOS, Fig. 5, is in satisfactory agreement with the major features seen in the data, except, of course, for the surface-related peaks. On the other hand, a simple weighed sum of the *d*-band DOS of elemental Cu and Au fails to reproduce the structure in the lower half of the band. Many of the peaks in Fig. 5 can also be identified in the spectra at other photon energies. The data at 150 eV compare quite favorably with the projected Cu 3*d* density of states, although the detailed structure above 4 eV is again washed out by the surface-atom shift. It seems clear from this comparison that the LAPW results present an accurate picture of the total and partial densities of states of Cu_3Au.

The order-disorder transition

A limited investigation of the order-disorder transition at 390 °C confirms that features associated with Au are broadened to a much greater extent than those due to Cu (see Fig. 6). For example, the rise at the top of the *d* band, which is dominated by Cu states, remains sharp, while the dip at 4 eV and other structure throughout the band tends to wash out. In early XPS work[22] the broadening of the lower Au-dominated part of the band was also readily observed. The changes in this part of the *d* band were seen most clearly by Jordan *et al.*[23] in UPS experiments with He I radiation and also reproduced in

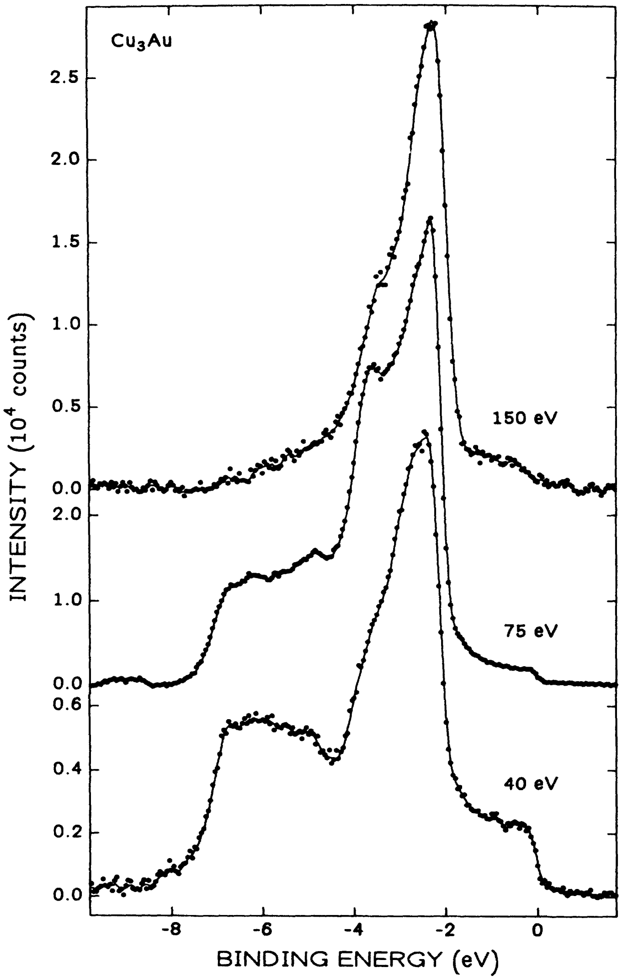

FIG. 4. Valence-band photoemission spectra from the (100) surface of ordered Cu_3Au at three selected photon energies.

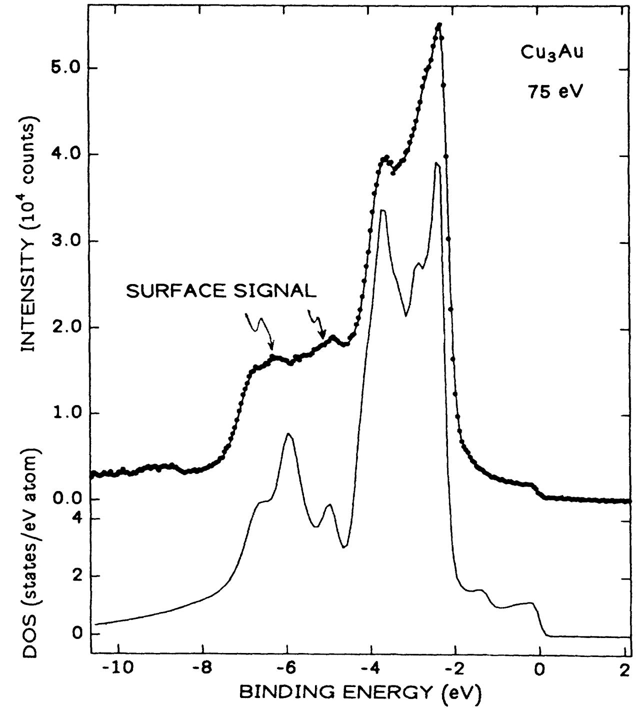

FIG. 5. Comparison of the 75-eV data with a smoothed, calculated total density of states for Cu_3Au (see text).

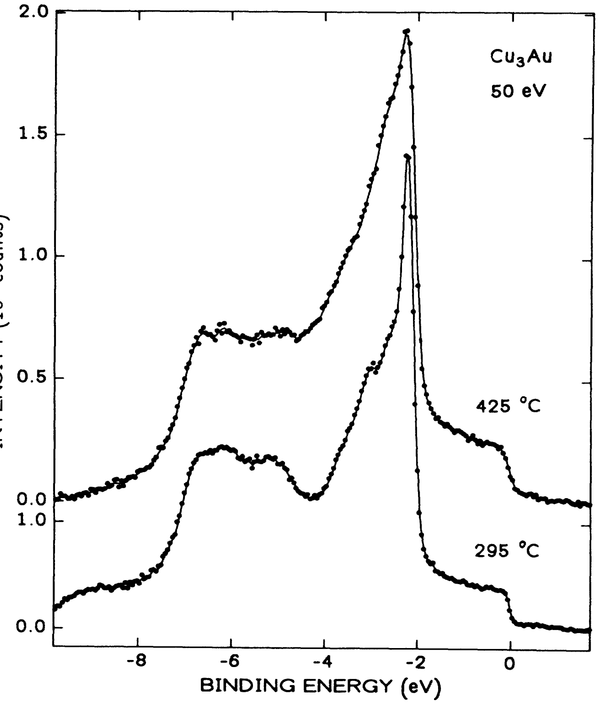

FIG. 6. Effect of disorder on the valence-band spectrum of Cu_3Au at 55-eV photon energy.

their random-alloy calculations. These changes presumably reflect the fact that the near-neighbor environment of the Au is much more strongly perturbed by disorder than that of the Cu. Recall that in the ordered state Au has twelve Cu neighbors and Cu has four Au and eight Cu neighbors, while in the disordered state all atoms will on the average have three Au and nine Cu neighbors. The evidence that the order-disorder transition produces changes throughout the region of the *d* band and not just in the region below 4 eV is an additional indication that the Au partial density of states extends over the entire *d*-band region.

The data in Fig. 6 give little indication that the surface-related Au peaks at 5.2 and 6.3 eV are significantly attenuated in the disordered state. In a fully disordered state the number of Au atoms in the first atomic layer would be reduced by a factor of 2. This confirms that in the vicinity of the critical temperature of the surface segregation of the Au does not depend strongly on the long-range order of the bulk or surface.[8] The surface disorder seen in LEED above 390 °C must then be intraplanar.[8]

CONCLUSIONS

The good agreement between the LAPW results and the UPS data gives us confidence in identifying the Au partial density of states, which could not be directly observed in the region between 3.5 eV and E_F. The close correspondence between the Au 5*d* centroid shift and the Au 4*f* core-level shift also supports this conclusion. The broadening observed above the order-disorder transition extends over the entire *d*-band regin, but has little effect on features associated with Cu.

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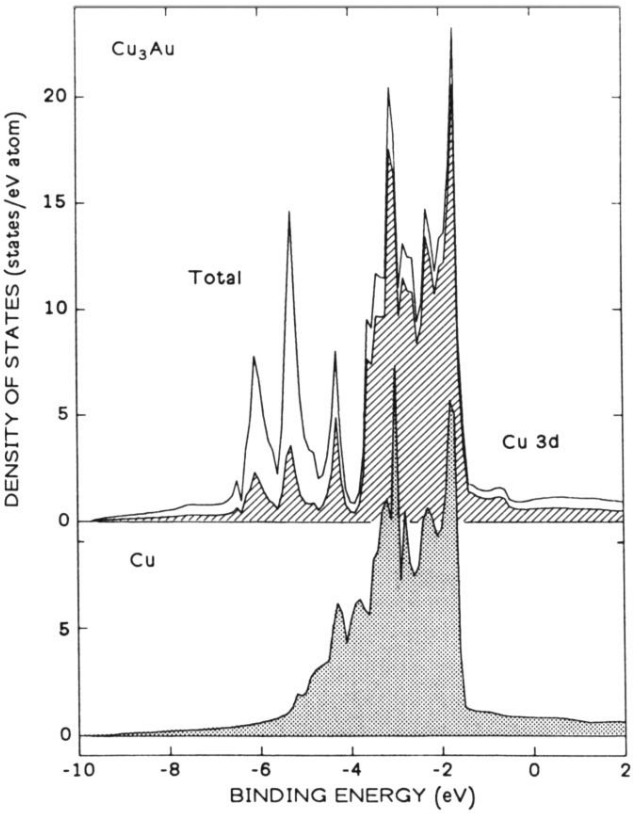

FIG. 2. Comparison of the calculated total and *d*-band densities of states for Cu_3Au and Cu. The Cu 3*d* contributions are shaded.

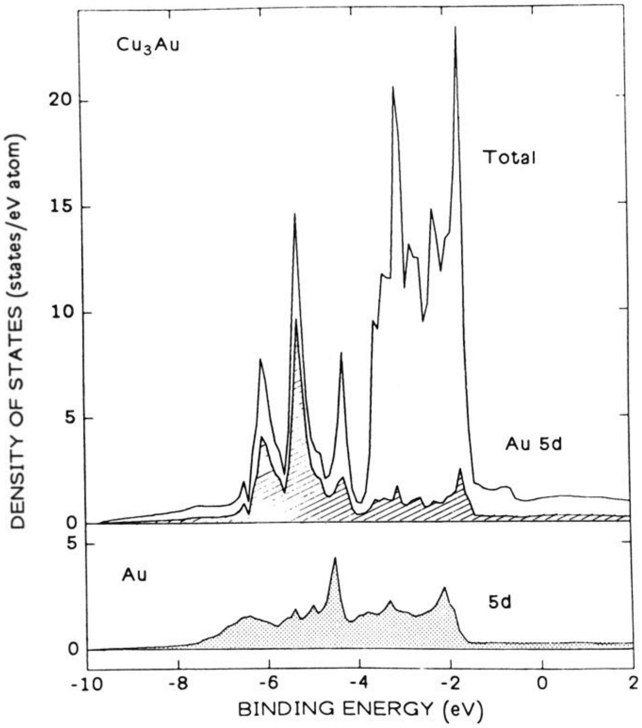

FIG. 3. Comparison of the calculated total and d-band densities of states for Cu$_3$Au and Au. The Au 5d contributions are shaded.