

## Partial densities of states of alloys: $\text{Cu}_3\text{Au}$

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The photon-energy dependence of the photoelectric cross section of the  $4d$  and  $5d$  elements is sufficiently strong to allow the isolation of the partial densities of states of many alloys and intermetallic compounds. For photon energies above 150 eV the valence-band spectra of  $\text{Cu}_3\text{Au}$  are dominated by bulk and surface Cu  $3d$  states. At photon energies below 50 eV the spectra correspond very closely to the  $d$ -band density of states of the surface Au atoms. X-ray photoelectron spectra at normal takeoff angle contain approximately equal contributions from bulk Au and Cu  $d$  states.

The band structure of alloys continues to present a significant challenge to both theory and experiment. A good agreement between the two has been obtained only for dilute alloys for which the coherent-potential approximation gives results entirely compatible with photoemission experiments, especially for split-band systems like the Ag-Pd alloys. For concentrated alloys with overlapping bands photoemission is generally assumed to be a poor source of information about the partial densities of states of the constituents. Soft-x-ray emission can make a significant contribution here, but is limited by self-absorption and by the properties of the shallow core-hole initial state of the x-ray transition. Angle-resolved photoemission can map the bands of ordered intermetallic compounds, but does not identify their "parentage."

A lack of information regarding the partial densities of states of  $\text{Cu}_3\text{Au}$  recently led to the suggestion<sup>1</sup> that the two peaks near 6 eV in the 40-eV valence-band spectrum of Fig. 1 represent the spin-orbit-split Au  $5d$  state, and constitute the entire contribution of the Au  $d$  states to the spectrum. On the basis of the insensitivity of these peaks to changes in photon energy it was concluded<sup>1</sup> that there is no discernible difference between the  $d$  states of Au in the bulk and at the surface. This led to the conclusion<sup>1</sup> that the surface-atom core-level shift must have a unique origin in this material. Subsequent work,<sup>2</sup> using takeoff-angle-dependent x-ray photoelectron spectroscopy (XPS), was able to prove that the Au contribution to the surface density of states is narrowed at the bottom of the band, just like in the bulk metal, indicating that the same mechanism can explain the surface-atom core-level shift in both materials. However, in the latter work the entire Au  $5d$  partial density of states could not be obtained, because it is impossible both to remove the Cu contributions and to separate the bulk and surface contributions of the Au by a linear combination of two spectra. Such partial densities of states would not only be of use in the interpretation of surface-atom core-level shifts, but would also provide constraints on band-structure calculations.<sup>3-5</sup>

My purpose here is to point out that this information is, in fact, readily obtained from the photon-energy dependence of the valence-band spectra of alloys, espe-

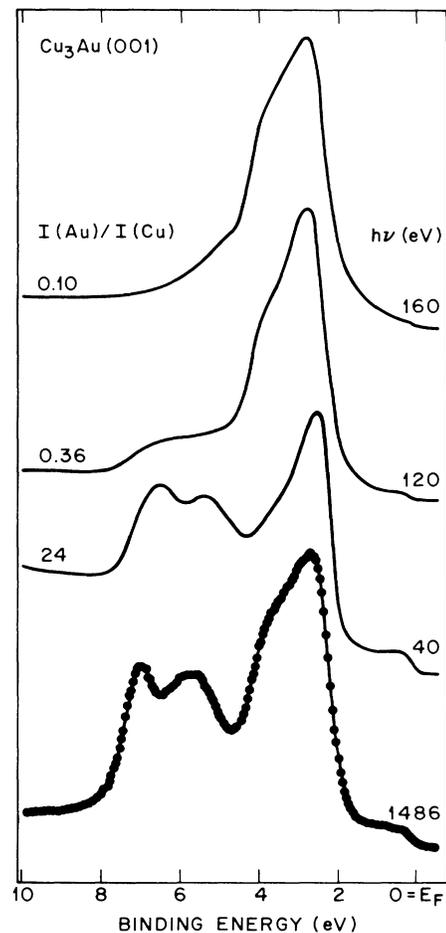


FIG. 1. Valence-band photoemission data for  $\text{Cu}_3\text{Au}(001)$  obtained with photon energies of 40, 120, and 160 eV, taken from Ref. 1. Also shown are Al  $K\alpha$  XPS data at normal takeoff angle, from Ref. 2. The Au to Cu  $d$ -band intensity ratios  $I(\text{Au})/I(\text{Cu})$  expected on the basis of the data of Ref. 6 are shown for the synchrotron data.

cially those involving  $4d$  and  $5d$  group elements. It relies on the fact that the  $4d$  and  $5d$  cross sections decrease by factors of 100 as the Cooper minimum is approached from low photon energy.<sup>6,7</sup> Under those circumstances, angle-integrated spectra taken at two selected photon energies suffice to isolate the partial densities of states. In some cases the selectivity is so extreme that spectra corresponding to almost pure partial densities of states are directly obtained. This method should have quite general utility in the study of alloys and compounds.

As a case in point consider the data for  $\text{Cu}_3\text{Au}$  in Fig. 1. Shown next to each spectrum is the Au to Cu  $d$ -band intensity ratio  $I(\text{Au})/I(\text{Cu})$ , expected on the basis of the data of Wehner *et al.*<sup>6</sup> These experimental, photon-energy-dependent photoemission intensities obtained from *metals* seem more appropriate for this analysis than the calculated *atomic* photoionization cross sections in Ref. 7. The two agree fairly well for Au  $5d$ , but for Cu  $3d$  the experimental intensities reach a maximum at a photon energy of 135 eV, while the atomic calculations show a maximum cross section at 50 eV.

The fact that the 160-eV spectrum of  $\text{Cu}_3\text{Au}$  is dominated by Cu emission was already recognized by Eberhardt *et al.*,<sup>1</sup> but no quantitative estimate of the selectivity was given. According to the data of Wehner *et al.*<sup>6</sup> the Cu  $3d$  bands should contribute more than 90% of the measured intensity in this spectrum. (The value obtained using the atomic cross sections is 98%.) The absence of an appreciable Au signal at 6.3 eV is in accord with these estimates. For photon energies below 50 eV, the selectivity favors the Au. The atomic cross sections<sup>7</sup> indicate an increase from 39% to 55% in the Cu signal as the photon energy is increased from 30 to 60 eV. This would manifest itself as a significant increase in the height of the narrow peak at 2.5 eV where the Cu  $3d$  density of states is concentrated. The data of Eberhardt *et al.*<sup>1</sup> are, however, largely independent of photon energy in this range. This is in better accord with the photoemission intensities,<sup>6</sup> which indicate that the Cu  $3d$  signal remains small compared to the Au  $5d$  signal in this range of photon energies. For the spectrum at 40 eV the Au contributes 96% of the spectral area according to Ref. 6. The Cu contribution is concentrated in the peak to 2.5 eV, but is much too weak to account for more than a small fraction of the observed intensity. This spectrum, with the peak slightly attenuated, then provides a reasonably accurate view of the Au  $5d$  partial density of states. It extends from 2 to 7 eV, and is not unlike that of bulk Au. At 120-eV photon energy the signals for Cu and Au  $d$  states are of approximately equal intensity, so that the photoemission spectrum gives a direct image of the total density of states. The development of the photon-energy-dependent spectra in Ref. 1 from 30 to 160 eV can be

understood in detail using the photon-energy-dependent signal intensities given by Wehner *et al.*<sup>6</sup>

The XPS data from Ref. 2, which are also shown in Fig. 1, agree well with the synchrotron data, when all factors are considered. They contain a Cu contribution which resembles the 160-eV data, in both width and position. It follows that the bulk and surface Cu  $d$  bands are quite similar. The Au contribution is greatly enhanced relative to the total density of states. The calculations of Scofield<sup>8</sup> yield an enhancement by a factor of 3, but the data suggest a value somewhat larger. Closer examination shows that the peak at 6.3 eV in the 40-eV data is shifted to 7.0 eV in the XPS data. This is a direct result of the fact that the normal-emission XPS data correspond largely to emission from Au in the *bulk*, while the synchrotron data contain mainly emission from the Au atom *surface*. It is confirmed by the fact that the corresponding peak in the Au *surface* spectrum extracted from takeoff-angle-dependent XPS data in Ref. 2, agrees well with the position of the peak in the low-photon-energy synchrotron data.<sup>1</sup>

In the range of photon energies from 40 to 160 eV the kinetic energy of electrons from the  $d$  band ranges from  $\approx 30$  to  $\approx 150$  eV. For these energies the escape depth is near its minimum of 5 Å, and does not vary sufficiently to produce a significant change in surface to bulk ratio.<sup>6</sup> This is particularly important for the (001) surface of ordered  $\text{Cu}_3\text{Au}$  in which there are no Au atoms in the second atomic layer, so that the Au uv photoemission spectrum is almost entirely a surface-atom spectrum. For confirmation note that there is little if any intensity attributable to the 7.0-eV bulk peak in the spectrum at 40-eV photon energy. In a material with smaller lattice constant such spectra would contain both bulk and surface contributions. These could then be separated by taking spectra at different takeoff angles, just as was done in XPS.

The most interesting result obtained here is that the bulk and surface Au  $5d$  partial densities of states in  $\text{Cu}_3\text{Au}$  extend over the entire  $d$  band of the alloy, and are hardly narrowed relative to those of Au itself.<sup>9</sup> This is quite different from the behavior of the Au  $d$  states in intermetallic compounds like Au Zn and Au Mg, which have the same space lattice, but show very significant narrowing of the  $5d$  band,<sup>10</sup> even though the Au concentration is twice as great. Other compounds, e.g.,  $\text{AuX}_2$ , where X may be Al, Ga, or In, also have greatly narrowed  $d$  bands.<sup>11</sup> This points to the importance of  $3d$ - $5d$  mixing in maintaining the width of the  $d$  band, and gives no support to arguments based on  $d$ - $d$  repulsion.<sup>12</sup> In this connection it is worth noting that Ag-Au alloys, which do have substantial  $4d$ - $5d$  overlap, behave like  $\text{Cu}_3\text{Au}$ , in that the Au  $5d$  band narrows little upon dilution by silver.<sup>13</sup>

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