Core-Level Binding Energy and Density of States from the Surface Atoms of Gold

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X-ray photoemission spectra of 4*f* and valence electrons in surface atoms of gold have been obtained. The surface-atom 4*f* level is shifted 0.40 ± 0.01 eV to lower binding energy relative to the bulk value. The surface density of states is narrowed by $(7.6 \pm 1.1)\%$ and its center of gravity is shifted to lower binding energy by 0.51 ± 0.08 eV. A model is proposed to account for the core-level shift in terms of the modified surface density of states.

It is well recognized that because electron escape depths at < 1.5 keV are so small, ~ 20 Å, x-ray photoemission experiments must necessarily contain appreciable contributions from the surface layer. In spite of this, attempts to measure differences between bulk and surface atoms, either in the form of surface-atom d-band narrowing or surface-atom core-level shifts, have led to conflicting or negative observations. Houston. Park, and Laramore¹ claimed to have observed surface core-level shifts in Ti, Cr, and Ni using appearance-potential spectroscopy, while subsequent measurements by Webb and Williams² disputed those results. Mehta and Fadley³ have reported *d*-band narrowing in Cu, while Chye $et \ al.^4$ found no such effect in Au. No surface-atom corelevel shift (SCS) has ever been found in x-ray photoemission, either in Cu,³ or in Au,⁵ or in Al, Ni, or In.⁶ In this Letter we report the unambiguous measurement of such a shift in Au. We also measure a narrowed and shifted surface density of states (DOS) for that material. A model is proposed which relates this modification of the band structure at the surface to the sign and magnitude of the SCS. It also elucidates its chemical behavior in other systems.

Ultrapure Au, Ag, and Cu were evaporated onto cooled (~10°C) optically flat glass substrates at a base pressure of ~1×10⁻¹¹ Torr, forming random polycrystallites $\leq 1 \ \mu m$ grain size⁷ in films >1000 Å thick. X-ray photoemission spectra were recorded with a modified AEI instrument using monochromatized Al K α radiation⁸ and a total instrumental resolution of 0.25 eV.⁹ Core- and valence-level spectra were taken as a function of takeoff angle, θ , measured from the surface normal and accurate to $\pm 2^{\circ}$.

Figure 1 shows the raw x-ray photoemission spectra of the narrowest core levels in Au, Ag,

and Cu recorded at different values of θ and normalized in peak height. A monotonically increasing shoulder on the low-binding- (high-kinetic-) energy side of the peak with increasing θ is obvious for the Au $4f_{7/2}$ level and less apparent for the shorter-lived Cu $2p_{3/2}$ and longer-lived Ag $3d_{5/2}$ levels. On the basis of the increasing intensity of the shoulder with increasing surface sensitivity (increasing θ) and its essential absence in the narrow Ag 3d spectra (indicating that it is not an instrumental artifact), we assign the shoulder to photoemission from a surface layer. Because the SCS is most clearly observable in Au, we restrict our discussion here to that metal.

Inspection of the Au 4f data suggests the hypothesis that they contain only two components, corresponding to emission from bulk and surface atoms. If that is true, then linear combinations of spectra recorded at different takeoff angles can be used to separate the individual bulk and surface contributions. We illustrate the procedure in Fig. 2. The following criteria are used to determine the appropriate weighting coefficients β and γ for the two (nonnormalized) spectra.



FIG. 1. Normalized x-ray photoemission spectra from Au, Ag, and Cu as a function of increasing surface sensitivity (increasing θ).



FIG. 2. Isolation of bulk and surface components from the difference of 0° and 80° spectra. β and γ are weighting coefficients. The solid line is the Doniach-Šunjić line shape.

The line shape on the low-binding-energy side of the surface line must be a Lorentzian convoluted with the instrumental response function.⁹ Since the 4f hole lifetime is dominated by intra-atomic Auger processes, we require that the low-binding-energy side of the bulk line be the same. The resulting bulk line is then found to be very well represented by a Doniach-Šunjić (DS) line shape.^{9,10} For the surface line we require only that its high-binding-energy side have a physically reasonable shape. We then find that it too is well represented by a DS line shape, and one that is the same as that of the bulk within experimental error. Note that this surface-bulk separation procedure is carried out without prior knowledge of any details of the line shape beyond those mentioned above.

With this information we attempt to fit the corelevel data by a nonlinear least-squares procedure,⁹ the only constraints being that there are two components with the same DS line shape. The parameters determined from the four independent data sets are remarkably consistent and lead to significant conclusions. This mean Au $4f_{7/2}$ lifetime width is 0.317 ± 0.010 eV, where the quoted uncertainties are based on the standard deviations of the fitted parameters.⁹ The individual values all fall within these limits. The mean asymmetry parameter, α , is 0.052 ± 0.002 . The phonon broadening⁹ is negligible when added in quadrature to the Gaussian spectrometer function. With the assignment of the bulk Au $4f_{7/2}$ binding energy at $\theta = 0^{\circ}$ to be 84.000 eV, the corresponding values in the 60°, 70°, and 80° spectra are

 84.025 ± 0.015 , 84.010, ± 0.014 , and 84.014 ± 0.016 eV, respectively. The extremely small and nonsystematic variations of these values are direct evidence that a hypothetical third, "subsurface" component is not present in the data, thereby justifying our initial hypothesis of only two components.

The areas of the bulk and surface contributions from the fits provide a further check on the validity of our analysis and determine the effective thickness, D, of the surface layer. With the assumption of an ideally smooth surface, the fractional surface signal, f_{θ} , is equal to $1 - e^{-(D/\lambda \cos \theta)}$, where λ is the mean electron escape depth. From the fits, f_{θ} at 0°, 60°, 70°, and 80° is 0.115 ± 0.005 , 0.215 ± 0.004 , 0.267 ± 0.003 , and 0.313 \pm 0.003, respectively. The minimum D is the effective interlayer spacing for polycrystalline Au. We take this value to be the average of the d spacings of the most-stable surfaces in an fcc crystal, namely, the (100) and (111) surfaces, yielding D $= d_{\text{poly}} = 2.20 \pm 0.15$ Å. Solving for λ at the above angles we obtain 18.1 ± 2.1 , 18.4 ± 2.7 , 21.1 ± 3.7 , and 35.8±9.8 Å, where the quoted errors include all uncertainties in D, f_{θ} , and θ . The last λ value at $\theta = 80^{\circ}$ is undoubtedly in error because of surface-roughness effects. The first three consistent values are, however, in excellent agreement with the 19-Å value determined by Henke¹¹ and are in fair agreement with the 26 ± 3 -Å value of Klasson et al.¹² It follows from this agreement that the surface component comes from a laver one atom thick.

From the fits the surface-atom component is found to be shifted from the bulk to a lower mean binding energy by 0.399 ± 0.004 eV. The origin of its magnitude and sign is as follows: The reduced coordination number of atoms on the surface results in a narrowing of the valence band.¹³ In Au this narrowing is achieved by a combined reduction of d delocalization and s - d hybridization, giving an overall net increase in the localized dstates at the expense of the delocalized s and dstates (the total charge in the metal-atom surface layer is conserved, i.e., essentially equal to that of the bulk, because screening lengths are so small). This s - d charge redistribution decreases the energy between the center of the narrowed surface d band and the Fermi level. The Fermi level is fixed by the bulk, so that the surface DOS is pulled up to lower binding energy. Since most of the valence charge occupies tightly bound (i.e., atomiclike) states, the surface-atom core levels feel this change in potential and are therefore also shifted to lower binding energy. The result of these effects agrees with the intuitive notion that electron binding energies in surface atoms are intermediate between those in free and bulk atoms.

The prediction that core- and valence-electron shifts are intimately related suggests an obvious test of the model: Isolate the surface and bulk DOS and determine the difference between their d-band centers of gravity, $\langle \epsilon \rangle_s$ and $\langle \epsilon \rangle_{B}$. This is accomplished by using the same weighting coefficients which separate the core 4f spectra into bulk and surface components and applying them to the valence band spectra taken at the same angles. This procedure is valid because at these energies differences in escape depths between Au valence and 4f levels are negligible, and because angular variations of valence transition strengths^{14,15} are averaged out in the polycrystalline film. Note that there are no further adjustable parameters in the valence-band analysis.

In Fig. 3 we show two valence spectra taken at $\theta = 0^{\circ}$ and 70°, as well as the resulting surface and bulk DOS. For comparison we also show the calculated bulk DOS of Smith *et al.*¹⁶ The width of the surface (*d* band) DOS, evaluated from the second moment after background subtraction,¹⁷ is $(7.6 \pm 1.1)\%$ smaller than that of the bulk. The quoted error is almost solely due to the uncertainties in the weighting coefficients determined from the corresponding *core*-level spectra. The center-of-gravity shift between the surface and bulk DOS, $\langle \epsilon \rangle_{S} - \langle \epsilon \rangle_{B}$, is 0.51 ± 0.08 eV. The quoted error includes the same systematics as in the width determination.

It is interesting to note that because of the center-of-gravity shift, the observed (bulk plus surface) DOS is actually broader at increased surface sensitivity that that of the bulk alone. This may have a bearing on the interpretation of previous experiments on surface *d*-band narrowing.^{3,4} The magnitude of the narrowing in this study is significantly less than the $1 - \sqrt{Z}_S/Z_B$ value predicted by a strictly tight-binding *s*-band model,¹³ where Z_S is the coordination number of the surface atom. For a realistic *d*-band metal this prediction is known to be only approximate,^{13,18} a fact again shown in the recent self-consistent calculations for the surface DOS of Cu(111)¹⁹ and Pd(111).²⁰

The similarity in sign and magnitude between the SCS of 0.4 eV and the center-of-gravity shift of 0.5 eV provides firm support that the two effects are very closely related. This result is al-



FIG. 3. Separation of bulk and surface DOS from the difference of 0° and 70° spectra (note scale assignments). The weighting factors were determined from the corresponding 0° and 70° core-level spectra as in Fig. 2. The bulk theory is from Ref. 16.

so consistent with the calculations of Ref. 19 for Cu. In general, then, our model predicts that for an SCS to be experimentally observable there must be a measurable center-of-gravity shift between the bulk and surface DOS. Metals in which this criterion should be most readily met are those undergoing a redistribution of surface valence charge at the Fermi level that can be felt by the core levels. This would tend to rule out metals with free-electron-like (s, p) bands because of the large number of unfilled and highly delocalized states that are available for rehybridization upon charge redistribution.²¹ In a tight-binding metal, however, the unfilled states are considerably reduced in number and are more localized. A key element of our model is that the Fermi level lies within the hybridized portion of

a tight-binding valence band. It clearly predicts no SCS in metals with tight-binding bands that do not participate in the bonding, e.g., Zn, Cd, and Hg. The noble metals Au and Cu represent perhaps ideal cases in which the almost-filled dstates are involved in the bonding largely because of *s*-*d* hybridization. In Ag, on the other hand, such hybridization is reduced, and it is for this reason that we believe that its SCS is smaller than that in Au and Cu (note that because the Cu $2p_{3/2}$ level is much broader than the Ag $3d_{5/2}$ level its SCS is actually larger than it appears in Fig. 1).

We are quick to note that our simple, strictly initial-state²² model should be taken only as a qualitative guide. It does serve to aid our understanding of the SCS effect and lends itself to more careful scrutiny in other polycrystalline and single-crystal metals.

The authors gratefully acknowledge skillful assistance in the photoemission measurements by P. Cohn and stimulating discussions with D. R. Hamann.

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²¹Angle-dependent measurements by us for the Al 2p level show no SCS, in agreement with our model.

²²The similarity of the bulk and surface line shapes suggests that final-state relaxation (screening) processes are not substantially different.

ERRATUM

COEXISTENCE OF ANTIFERROMAGNETISM AND SUPERCONDUCTIVITY: A NEUTRON DIF-FRACTION STUDY OF $DyMo_6S_8$. D. E. Moncton, G. Shirane, W. Thomlinson, M. Ishikawa, and Ø. Fischer [Phys. Rev. Lett. 41, 1133 (1978)].

The illustrations for Figs. 2 and 3 should be reversed. The figure captions and references to the figures in the text are correct.

The final two sentences should read, "Although this correlation clearly shows that the H_{c2} anoma-

ly is due to magnetic ordering, the apparent relation to the order parameter is surprising since the H_{c2} measurements were done in a magnetic field strong enough to polarize the magnetic moments nearly completely.¹¹ This behavior suggests that the reduction in H_{c2} in the magnetic state is produced by an additional, nearly-fieldindependent, pair-breaking parameter which varies as the magnetic-order parameter."

Finally, the introductory sentence to the first paragraph beginning on page 1134 should read, "In the case of $ErMo_8Se_8...$ "