Angular Dependence of X-Ray-Photoemitted Valence-Electron Spectra from Single-Crystal Gold*

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High-resolution x-ray-photoemitted valence-electron spectra from a gold single crystal are found to exhibit significant differences for electron emission along various low-index directions, with $\langle 100 \rangle$ and $\langle 111 \rangle$ showing the most pronounced dissimilarities. Direct-transition-model calculations predict that such spectra result from initial wave vectors in different well-defined regions of the Brillouin zone. Densities of states in these regions agree very well with the qualitative differences observed between $\langle 100 \rangle$ and $\langle 111 \rangle$ spectra.

We have recently noted[1] that significant changes occur in valence-level x-ray-photoelectron (XPS) spectra when electron emission is varied from one low-index direction to another in a single crystal, with large differences being observed between Au valence-electron spectra obtained along $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. These results have subsequently been confirmed at somewhat lower resolution,[2] and similar effects have been noted in recent preliminary studies of Ag,[2] Cu,[3] Pt,[3] and Si.[4] In this Letter, we report more detailed observations of such effects in Au, including high-resolution spectra obtained along several directions, and also propose a theoretical explanation for such phenomena in terms of a direct-transition model.

The spectrometer utilized was a Hewlett Packard 5950A with monochromatized Al $K\alpha$ radiation source (1486.6 eV) modified to permit azimuthal and polar specimen rotations *in situ*.[5,6] Polar rotations were about an axis perpendicular to the plane containing the fixed x-ray-incidence and electron-exit directions (separated by an angle of $108°$). Resolution loss for operation at polar angles other than that permitting dispersion compensation[7] was minimized by operating the electron lens in two different modes.[5] All spectra were obtained under conditions such that the Au $4f_{7/2}$ full width at half-maximum (FWHM) intensity was between 0.8 and 1.2 eV. (Single-mode operation yields Au $4f_{7/2}$ FWHM intensities of up to 2.3 eV.[5]) All measurements were performed at room temperature and at pressures of $(2-4) \times 10^{-9}$ Torr.

A gold single crystal was mechanically polished with the surface normal tilted $8 \pm 1°$ away from [001] in a direction toward $[\bar{1}\bar{1}1]$ and etched in aqua regia to reduce surface disorder. This orientation enabled spectra to be obtained along several different $\langle 100 \rangle$ and $\langle 110 \rangle$ directions with reasonable intensity, as the photoelectron current becomes zero for grazing exit angles.[5,6] The only surface contaminant noted was carbon, with C $1s$ to Au $4f$ ratios lying in the range 0.03–0.04 (corresponding to $\sim 1-2$ monolayers coverage[8]). Relative photoelectric cross sections[9] thus indicate that the contaminant valence photoelectron intensity was negligible with respect to that of gold. When placed in a separate low-energy-electron-diffraction (LEED) system and subjected to only light ion bombardment so as to remove the carbon present, this crystal gave a LEED pattern characteristic of the basic (001) symmetry. This pattern did not change with annealing. Kikuchi-band–like features in the energy-integrated XPS core- and valence-electron peak intensities[10,11] were used to verify the orientation of the crystal to within $\pm 1°$.

Valence-electron spectra obtained along ten different directions in the crystal are shown in Fig. 1. No correction for inelastic scattering has been made. Although the basic two-component peak associated with the Au $5d$ bands[12] is preserved in all spectra, clear differences in the relative intensities of these two peaks are seen, together with changes in fine structure. Effects primarily associated with the bulk symmetry of the crystal are indicated by the fact that directions fully equivalent with respect to the crystal orientation in the spectrometer geometry (including its relationship to both x-ray-incidence and electron-exit directions) give essentially identical spectra; examples of this are [001] and [100], but not [102] and [201] or [101] and [110] (which do show slightly different spectra). The largest changes are observed between the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, for which more detailed spectra are shown in Fig. 2 in comparison to a spectrum from a polycrystal-
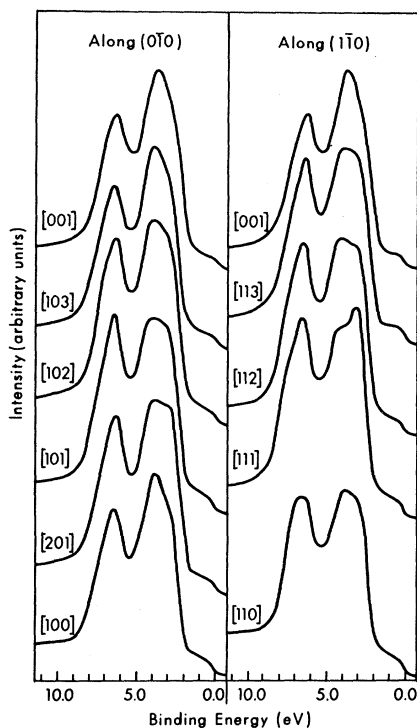
FIG. 1. XPS valence-electron spectra for electron emission along various low-index directions from a gold single crystal with approximately [001] orientation. The two sets of spectra were obtained by sweeping the emission direction in a (0$\bar{1}$0) plane and a (1$\bar{1}$0) plane.
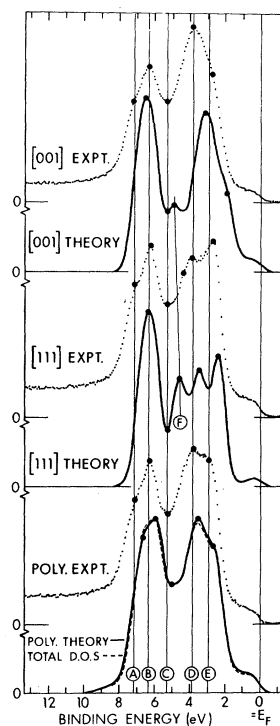

FIG. 2. XPS valence-electron spectra for the [001] direction, the [111] direction, and a polycrystalline specimen are compared to densities of states calculated over $\vec{k}^i$ values allowed by the direct-transition model and to a theoretical total density of states.

line specimen deposited *in situ* on a glass substrate.

All three experimental spectra in Fig. 2 exhibit the same five labeled features $A-E$, but changes in both relative intensity and position occur. A more quantitative comparison yields these observations: (1) For all three cases, the following spectral parameters do not change: (a) the overall FWHM of the d-band peak, which is 5.3–5.4 eV; (b) the position of the spectrum minimum C, which is at 5.2–5.3 eV below the Fermi energy (E_F); (c) the positions of features A and B at 6.4 and 7.2 eV below E_F, respectively; and (d) the slope of the leading edge of the d-band peak between 1.5 and 2.3 eV below E_F. (2) The two main components within the d-band peak have different relative intensities; as judged by maximum peak heights, $A+B < D+E$ along [001], $A+B \approx D+E$ along [111], and $A+B \lesssim D+E$ in the polycrystalline case. (3) Peak D is more intense than peak E along [001], whereas the reverse is true along [111]. (4) For emission along [111] only, a minimum exists between peaks D and E. (5) Relative to the maximum peak height, the minimum at C along

[001] is deeper than that along [111]. (6) With respect to the polycrystalline spectrum, features D in the [001] and [111] spectra occur at essentially the same positions, whereas shoulder E in the [001] spectrum and peak E in the [111] spectrum are shifted to lower binding energies by approximately 0.3 eV (cf. also the [100] spectrum in Fig. 1).

These results can be explained in terms of a direct-transition model closely related to that utilized in interpreting angular-dependent ultraviolet-photoemission (UPS) data from single crystals of several materials,[13-15] including Au.[15] Wave-vector conservation in the photoemission process is assumed, so that $\vec{k}^i + \vec{g} + \vec{k}_{h\nu} = \vec{k}^f$, in which $\vec{k}^i$ is the initial-state wave vector in a reduced-zone representation, $\vec{g}$ is a reciprocal-lattice vector, $\vec{k}_{h\nu}$ is the photon wave vector, and $\vec{k}^f$ is the wave vector of the photoelectron. The high photon energy in the XPS experiment implies that (a) $\vec{k}_{h\nu}$ cannot be omitted from the conservation equation as it is in UPS. For example, for Al $K\alpha$ radiation, $k_{h\nu} = 0.49(2\pi/a)$, with $2\pi/a$ approximately the mean Au Brillouin zone radius. (The inclusion of

$\vec{k}_{h\nu}$ prevents [102] and [201], as well as [101] and [110], from being equivalent in Fig. 1.) (b) To a good approximation, $\vec{k}^f$ can be assumed to be associated with a pure free-electron state. Secondary bulk-[10,11,13] or surface-scattering[13] events are thus also neglected. (c) k^f changes very little in magnitude over the valence spectrum $[12.84(2\pi/a) \leqslant k^f \leqslant 12.88(2\pi/a)]$. (d) Electron refraction at the surface is negligible for the exit angles considered here.[6]

The finite acceptance solid angle of the spectrometer (a cone of 3.5° half-angle) distributes the observed k^f values over an essentially planar, circular disk of radius $0.78(2\pi/a)$. The projection of this disk into the reduced zone with appropriate $\vec{g}+\vec{k}_{h\nu}$ values specifies the set of $\vec{k}_i$'s contributing to photoemission. If matrix-element variations over these $\vec{k}^i$ values are assumed small, the photoelectron spectrum will be proportional to the density of states on the projected disk. Utilizing the relativistic augmented-plane-wave Au band structure of Christensen and Seraphin,[16] we have calculated such densities of states for emission along [001] and [111] directions. In addition, the density of states appropriate to an experiment on a polycrystalline specimen was calculated by permitting $\vec{k}^f$ to have all directions with respect to the crystal axes. Finally, the total density of states as integrated over the complete zone was determined.

The results of these calculations (convoluted with a Gaussian of 0.80-eV FWHM to simulate minimum instrumental broadening) are shown in Fig. 2 together with the relevant experimental spectra. The experimental similarities and differences noted previously in items (1)–(6) are all qualitatively predicted by theory. The theoretical curves are completely consistent with observations (1), (3), and (5), as well as with the direction of the relative intensity change between [001] and [111] noted in item (2). The minimum between peaks D and E along [111] [item (4)] is also predicted by theory, although an additional lower-intensity peak F is also found in both the [001] and [111] curves. However, peaks F and D may be highly overlapping in the [111] experimental spectrum, and in fact a slight shoulder is observed near the predicted location for peak F. The relative energy shifts of features D and E in the [111] spectrum [item (6)] are also predicted to be in the correct directions and of approximately the correct magnitudes if it is assumed that peaks F and D are overlapping. The direction of the shift of shoulder E in the [001] spectrum is also correctly indicated. The only minor point of disagreement is that the theoretical [001] curve indicates a shift of peak D to lower energy that is not found experimentally.

The polycrystalline theoretical curve differs very little from the total density of states. This result is consistent with prior XPS studies in which polycrystalline spectra have been compared to total densities of states,[12] but it also indicates for the first time that such comparisons are possible in the limit of rigorous $\vec{k}$ conservation. Comparing experiment and theory for the polycrystalline specimen indicates that the $A+B$ component is too intense relative to $D+E$ in the theoretical curves, a discrepancy which has been noted in prior comparisons for gold,[12] and which is also qualitatively found in our results for both the [001] and [111] directions. Features A and B are also not as widely separated in the theoretical curves as they are in the experimental spectra, an effect which could be due to the particular band-structure calculation utilized.[12] Because we are concerned primarily with predicting similarities or differences between spectra, neither of these discrepancies affects the previous discussion.

Additional factors which must be considered in making a more quantitative comparison of theory and experiment are (a) crystal alignment errors in the experimental system—the fine structure in the theoretical curves is found to be weakly sensitive to changes of $\sim\pm 2°$ in the orientation of $\vec{k}^f$ with respect to the crystal directions, although the basic shapes of the curves are preserved in such changes. (b) Effects due to secondary scattering—these effects[10, 11, 13] would tend to make the experimental spectrum reflect more of a zone-averaged behavior, and may account for the fact that the differences between experimental spectra are in general less than those predicted by theory. The presence of Kikuchi-band–like fine structure in the angular distribution of integrated valence-electron intensity which is essentially identical to that for high-lying core levels[10, 11] also suggests that secondary scattering is not completely negligible. (c) Neglect of matrix-element variations—McFeely et al.[2] have recently proposed an alternative explanation for such angular-dependent XPS valence-electron spectra that considers only zone-averaged matrix elements for tight-binding d orbitals. It was predicted that only e_g character can be active along $\langle 100 \rangle$ and only t_{2g} along $\langle 111 \rangle$, and partial densities of states for e_g and t_{2g} were compared re-

spectively with a Au [001] spectrum obtained at much lower resolution than those shown in Figs. 1 and 2 (Au $4f_{7/2} \approx 2.0$ eV FWHM), and with a [111] spectrum in good agreement with the present data. The theoretical results are in qualitative agreement with our observations (1b), (1c), (2), and (4), but significantly disagree with (1a), (1d), (3), (5), and (6). Thus, although some type of matrix-element anisotropy certainly may play a role in producing such angular-dependent spectra, the wave-vector selectivity of the direct-transition model is by itself much better able to account for all of the experimental observations for gold.

In conclusion, the angular-dependent changes noted in XPS valence-electron spectra from single-crystal gold are qualitatively very well explained in terms of a straightforward extension of the direct-transition model. Such studies thus should provide another method for mapping energy-band characteristics throughout the Brillouin zone.

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