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D. A. Shirley

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d-ORBITAL DIRECTED PHOTOEMISSION FROM SILVER AND GOLD*

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ABSTRACT

An angular dependence in the photoemission spectrum from d bands, heretofore unappreciated, has been predicted and observed in single crystals of silver and gold. It is a symmetry effect, and is predicted to be observable widely in d shells of transition metals and their compounds independent of photon energy.

In this letter we report the theoretical prediction and experimental observation of an angular dependence in the valence-band X-ray photoemission spectrum of the noble metals silver and gold. The effect reported here should be ubiquitous in valence-level d shells, as it is an essential consequence of the breakup of the d shell into two distinct irreducible representations, $t_{2g}(\Gamma_{25'})$ and $e_g(\Gamma_{12})$ in a field of cubic symmetry. Because it is a symmetry effect, we expect it to be essentially independent of photon energy, provided only that the energy is above the region where final-state effects become important.

High-purity single crystals of silver and gold were cut to produce a (100) surface orientation, polished to 1 micron smoothness and etched repeatedly, in aqua regia for gold and a 1:1 solution of $NH_4OH:H_2O_2$ for silver, to remove the damage layer formed by polishing. Back-reflection Laue patterns taken to orient the crystals after this process showed sharp diffraction features, indicating the absence of a deep damage layer.

The crystals were spot-welded to rotatable platens and inserted into a Hewlett-Packard 5950A electron spectrometer, modified for ultra-high vacuum operation. The sample preparation chamber was then baked to achieve a base pressure of $\sim 8 \times 10^{-10}$ torr, and the surfaces were cleaned by argon ion bombardment. After this cleaning procedure the C1s intensity indicated less than 0.1 of a monolayer. The oxygen 1s peak was undetectable. The crystals were then heated to ~800°C for 1 hr. to anneal out surface damage introduced by ion bombardment. Valence-band spectra taken on annealed and unannealed samples showed definite reproducible differences[1-3]. Numerous spectra were run with both elements,

analyzing electrons emitted along the [100], [111] and [110] directions. These directions were selected by tilting and azimuthally rotating the crystals. The orientation was adjusted optically to a precision of ±½ degree. We estimate the total angular accuracy of ±2 degrees or less, with a spectrometer solid angle of acceptance of ±3 degrees. The take-off angles were high in each case (90°, 35.3°, and 45°, respectively). Although we studied both annealed and unannealed ("amorphous") single crystals, we shall for brevity present and discuss only those spectra taken with photoelectrons propagating along the [100] and [111] directions from well-annealed samples, as these directions show the largest effects and are the simplest to interpret.

Figures 1a,b and 2a,b show the photoemission spectra obtained for photoelectrons propagating along the [100] and [111] axes for silver and gold. The spectra are distinctively different, the major differences being the change of the peak height ratios for the high- and low-binding-energy d-band peaks, and the change in the shape of the leading edge of the d-band peak.

To develop a physical understanding of the effect, consider photoemission from the point Γ ($\vec{k} = 0$) in the Brillouin zone (BZ). This is the ligand field theory case. In the absence of spin-orbit splitting, the five degenerate d states are split into $t_{2g}(\Gamma_{25'})$ and $e_g(\Gamma_{12})$ levels. Photoemission from the t_{2g} orbitals in [100]-type directions is forbidden because matrix elements of the form

$$\langle e^{iq_x x} \mid \vec{p} \mid d_{xy},\ d_{yz} \text{ or } d_{xz} \rangle \qquad (1)$$

are forbidden by symmetry, while photoemission from t_{2g} states is allowed along the [111] axes. The exact reverse is true for the e_g states. Thus by selecting photoelectrons emitted in the [100] or [111] directions one could observe a t_{2g} peak or an e_g peak alone. Spin-orbit coupling would reduce the anisotropy effect by mixing the t_{2g} and e_g states and splitting the t_{2g} level into Γ_8 and Γ_7 states; however, even for Au, the crystal field is still dominant, and the t_{2g}-e_g mixing is only 15 percent.

The effect persists throughout the BZ. Following Ehrenreich and Hodges[4] we can write the initial band state $|j>$ in the tight binding form

$$|j> \;=\; \psi_k^j(\vec{r}) \;=\; N^{-\frac{1}{2}} \sum_{\ell\mu} e^{i\vec{k}\cdot\vec{R}_\ell} \; \beta_\mu^j(\vec{k}) \; \Phi_\mu(\vec{r} - \vec{R}_\ell) \qquad (2)$$

Here $\Phi_\mu(\vec{r}) = R(r)\, d_\mu(\Theta_r, \phi_r)$ are atomic wavefunctions where the $d_\mu(\theta_r, \phi_r)$ are the e_g and t_{2g} functions given in Table 1 of reference 5. The coefficients $\beta_\mu^j(\vec{k})$ are obtained from the band structure calculation.[4,6] The transition strength at a general $\vec{k}$ point is given by

$$\sigma(\vec{k}, j, \vec{q}) \sim \frac{1}{q^2} \left| < e^{i\vec{q}\cdot\vec{r}} \, |\vec{p}| \, j > \right|^2 \qquad (3)$$

Here we have assumed a plane wave final state. We shall neglect the s-part of the initial state wavefunction since its transition matrix element is small. In any case it may be omitted in discussing angular effects since it contributes no anisotropy to the photoemission spectrum. Equation (3) may be evaluated to yield

$$\sigma(\vec{k}, j, \vec{q}) \sim \sum_{G} \left|\sum_{\mu} \beta_{\mu}^{j}(\vec{k})\ \Phi_{\mu}(\vec{q})\right|^{2} \delta(\vec{k} - \vec{q} - \vec{G}) \tag{4}$$

where $\Phi_{\mu}(\vec{q}) = f(q)\ d_{\mu}(\Theta_q, \phi_q)$ is the Fourier transform of the initial state wavefunction $\Phi_{\mu}(\vec{r})$ and $\vec{G}$ is a reciprocal lattice vector. For a given photon energy (and hence $|\vec{q}|$) equation (4) simplifies to

$$\sigma(\vec{k}, j, \vec{q}) \sim \sum_{G} \left|\sum_{\mu} \beta_{\mu}^{j}(\vec{k})\ d_{\mu}(\Theta_q, \phi_q)\right|^{2} \delta(\vec{k} - \vec{q} - \vec{G}) \tag{5}$$

In the XPS regime (Aℓ K_{α} excitation) the final state wavevectors $\vec{Q}$ are more than an order of magnitude larger than the maximum $\vec{k}$ in the first BZ. In this case, the angular averaging of ± 3° given by the analyzer allows us to sample the whole Brillouin Zone. In addition the direct transition requirement $\vec{k} - \vec{q} - \vec{G} = 0$ is always satisfied. Hence for XPS we can write

$$\sigma(\vec{k}, j, \vec{q}) \sim \left|\sum_{\mu} \beta_{\mu}^{j}(\vec{k})\ d_{\mu}(\Theta_q, \phi_q)\right|^{2} \tag{6}$$

and the angular intensity distribution may be discussed in terms of the functions $d_{\mu}(\theta_q, \phi_q)$. Let us illustrate this by considering the two cases $\vec{q} \parallel [100]$ and $\vec{q} \parallel [111]$. For $\vec{q} \parallel [100]$ we have $\theta_q = 90°$, $\phi_q = 0°$ and hence (compare Table 1 of reference 5) $d_{x^2-y^2} = \sqrt{3}\ d_{3z^2-r^2} \neq 0$ and d_{xy}, d_{yz}, $d_{xz} = 0$. Thus the cross-section given by equation (6) is just the e_g projection. Likewise for $\vec{q} \parallel [111]$ ($\theta_q = 54.7°$, $\phi_q = 45°$) we obtain $d_{x^2-y^2} = d_{3z^2-r^2} = 0$ and $d_{xy} = d_{yz} = d_{xz} \neq 0$. In this case the cross section is given by the t_{2g} projection.

The anisotropy effects stand out most clearly in the gold spectra (Fig. 1). In the [100] spectrum the higher binding energy (E_B) peak is relatively less intense (in terms of peak heights; an area ratio measurement would be ambiguous), and the lower E_B peak has relatively less intensity on the low E_B side. Both effects are predicted in the calculations. The first arises because of a slightly lower density of e_g character in the bands that contribute to the high binding-energy peak. Those bands must be considered in detail to explain this effect quantitatively; qualitatively it can be attributed to a tendency for bonding to nearest neighbors at the "bottom" of the d band. The second effect can be identified readily with the top occupied band, which acquired predominantly t_{2g} character at L, K, and X in the BZ. This band is responsible for nearly all of the state density in the low E_B shoulder of the low-E_B peak, which is thus absent in the [100] spectrum.

Both of the above effects are also clearly present in silver (Fig. 2), although the narrower bandwidth precludes a detailed analysis. The peak height ratio in silver is 1.16(2) for [111] and 1.27(2) for [100]. The observation of this anisotropic angular distribution in two lattices and the close correspondence between theory and experiment appear to establish this effect unambiguously as arising from directed d orbitals.

d-orbital directed photoemission should be a rather general phenomenon. It should be present in the valence bands of other transition metals, and in some (e.g., platinum) it may be more pronounced than in silver or gold. Because it is a symmetry effect, it should be present at all photon energies. Remeasurement of XPS spectra of transition metals using oriented single crystals may therefore be expected to

yield useful new information about the valence bands. Even more distinctive effects should be present in transition-metal complexes, for which the t_{2g} and e_g orbitals are resolved in energy. There may also be diagnostic applications to orientational problems in absorbates on single crystals.

d-orbital directed photoemission has been observed before, but not explained. Eastman and Nilsson[7] studied photoemission from single crystal silver films, but did not use photon energies high enough to reach the d bands. Shirley[8] observed variations in the gold valence-band spectrum with crystal face, but gave no interpretation. These results can now be interpreted in terms of the electron propagation direction implied by the analyzer geometry; this interpretation is consistent with Fig. 1. We also note that indirect evidence for this effect has been available for some time in the different appearance of single-crystal[8] and polycrystalline[9] gold valence-band spectra. Recently Fadley[10] made the important step of correlating the spectrum variation with electron propagation direction, obtaining data very similar to the top two panels of Fig. 1. The above model appears to explain all of these earlier results.

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FOOTNOTES AND REFERENCES

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1. There were observable changes in the spectra on annealing. Evidence for differences in XPS valence-band spectra were reported for semiconductors by Ley, et al (Ref. 2) and for metals by Hüfner et al (Ref. 3).

2. L. Ley, S. Kowalczyk, R. A. Pollak, and D. A. Shirley, Phys. Rev. Letters 29, 1088 (1972).
3. S. Hüfner, G. K. Wertheim, and D. N. E. Buchanan, Solid State Commun. 14, 1173 (1974).
4. H. Ehrenreich and L. Hodges, Methods in Computational Physics, Vol. 8, p. 149 (1968).
5. J. W. Gadzuk, Phys. Rev. B10, 5030 (1974).
6. N. V. Smith, Phys. Rev. B3, 1862 (1971).
7. P. O. Nilsson and D. E. Eastman, Physica Scripta 8, 113 (1973).
8. D. A. Shirley, Phys. Rev. B5, 4709 (1972).
9. K. Siegbahn, D. Hammond, H. Fellner-Feldegg, and E. F. Barnett, Science 176, 245 (1972).
10. C. S. Fadley, in Faraday Discussion on Electron Spectroscopy of Solids and Surfaces, Vancouver, British Columbia, July 1975 (to be published), and private communication.

FIGURE CAPTIONS

Fig. 1. X-ray photoemission spectra along [100] and [111] axes, partial E_g and T_{2g} state densities, and band structure of gold metal. Note changes in relative peak heights from [100] (E_g) to [111] T_{2g}, and absence of T_{2g} shoulder at 2-3 eV in [100] spectrum.

Fig. 2. X-ray photoemission spectra along [100] and [111] axes, partial E_g and T_{2g} state densities, and band structure of silver metal. As in gold the peak height ratios change with E_g/T_{2g} character, and the low-E_B edge of the d-band peak is steeper in the [111] case.

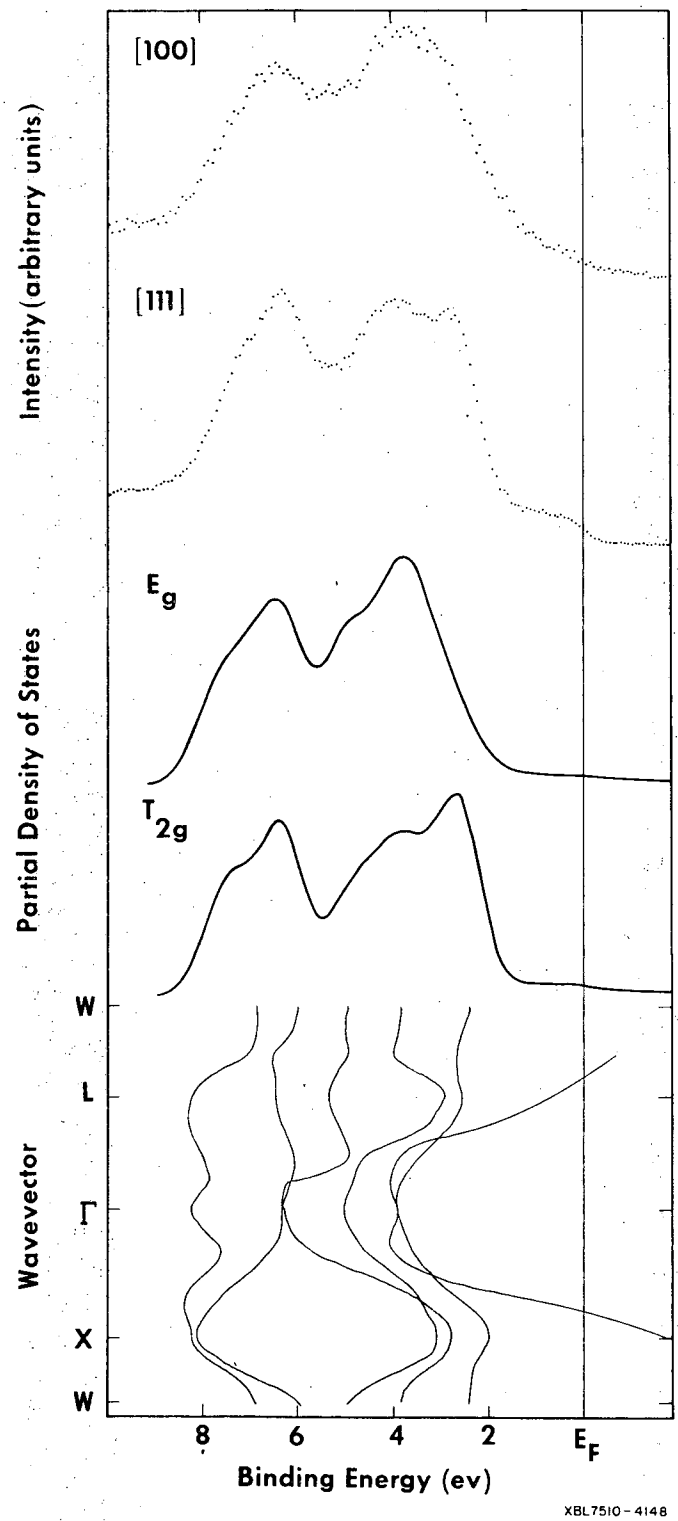
[100]
[111]
Intensity (arbitrary units)
E_g
T_{2g}
Partial Density of States
W
L
Γ
X
W
Wavevector
8
6
4
2
E_F
Binding Energy (ev)
XBL7510-4148

Fig. 1

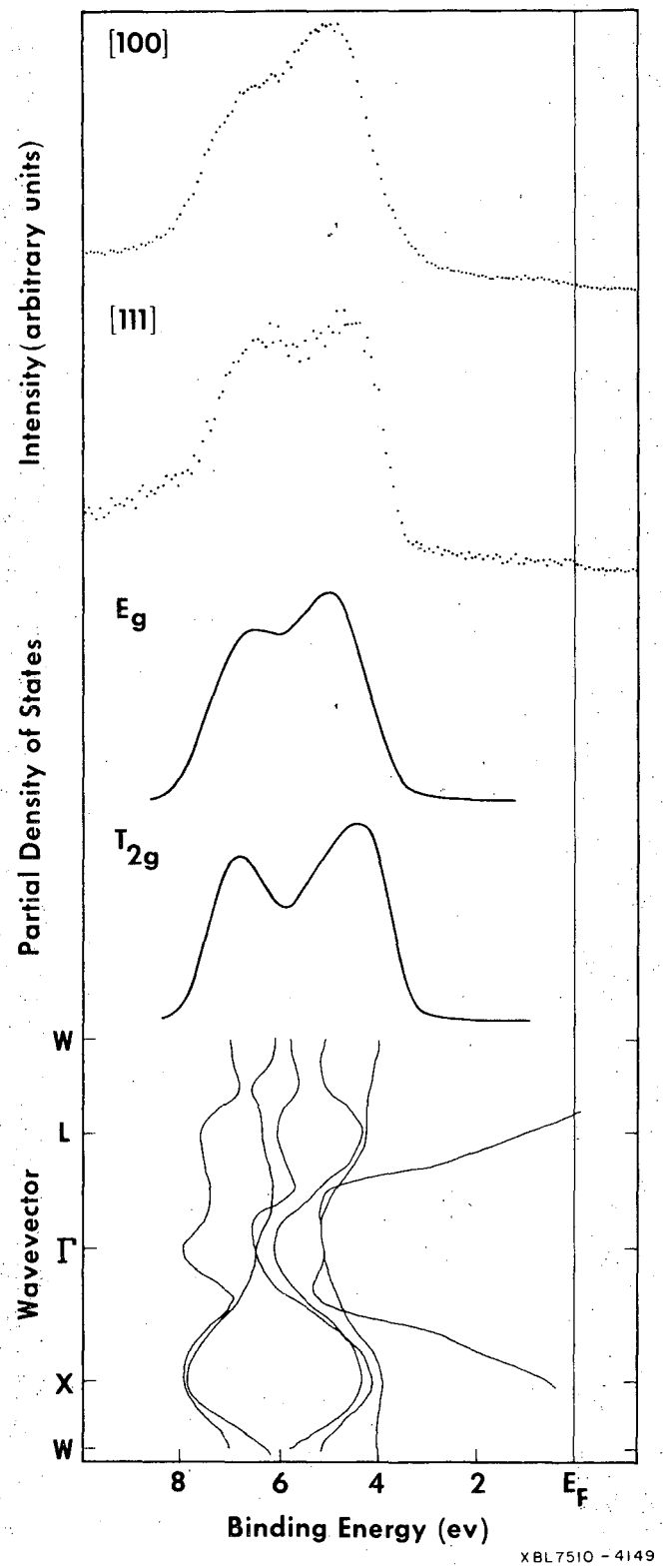
[100]
[111]
Intensity (arbitrary units)
E_g
T_{2g}
Partial Density of States
W
L
Γ
X
W
Wavevector
8
6
4
2
E_F
Binding Energy (ev)
XBL7510 - 4149

Fig. 2

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