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Author

Dabbousi, O. B.

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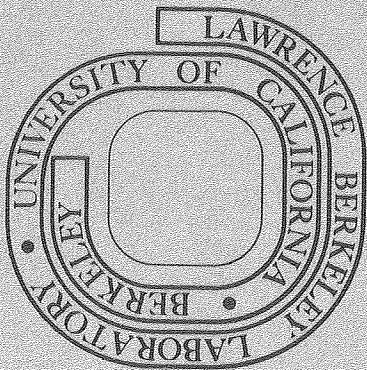
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TEMPERATURE INDEPENDENCE OF THE ANGLE-RESOLVED X-RAY
PHOTOEMISSION SPECTRA OF GOLD AND PLATINUM VALENCE BANDS*O. B. Dabbousi,[†] P. S. Wehner, and D. A. ShirleyMaterials and Molecular Research Division
Lawrence Berkeley Laboratoryand
Department of Chemistry
University of California
Berkeley, California 94720

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ABSTRACT

Angle-resolved valence-band x-ray photoemission spectra were taken along the [111] and [100] directions of gold single crystals and along the [100] direction of a platinum single crystal at room temperature (293K) and on a probe cooled nearly to liquid nitrogen temperature (77K). No change was detected on cooling the samples, in contrast to expectations based on a simple direct-transition model. A simple "matrix-element" model appears to predict spectra well even at low temperatures, perhaps because the complexity of the high-energy final-state bands permits sampling effectively throughout the zone.

Strong angular variations have been reported in the valence-band angle-resolved x-ray photoemission (ARXPS) spectra of copper and gold single crystals.¹⁻⁵ Two models were proposed to explain the observed behavior. A direct-transition model^{1,2} predicted that ARXPS would sample only a small volume in the first Brillouin Zone, while a "matrix-element" model³⁻⁵ interpreted ARXPS as sampling the valence bands widely throughout the Zone. A detailed comparison of both models with experiment showed⁵ that the matrix-element model gave good agreement, while the direct-transition model failed. Recently, a compelling reason for breakdown of the direct-transition model – namely, thermal diffuse scattering – has been suggested by Shevchik⁶ and confirmed experimentally at intermediate energy (45 eV) for copper.⁷ If thermal diffuse scattering were the only reason for the failure of the direct-transition model to predict ARXPS spectra, then (as discussed below) the direct-transition processes should be substantially restored by cooling the sample to liquid nitrogen temperatures. In this Communication we report low-temperature ARXPS studies on gold and platinum that were designed to test this question.

With thermal diffuse scattering taken into account, the angle-resolved photoemission cross-section is given as the sum of two terms: a k-conserving direct transition term and an atomic term.^{6,7} The relative contributions of these two terms are related to the Debye-Waller factor, which can be expressed as

$$f = \exp[-\langle (\vec{q} \cdot \Delta \vec{r}_T)^2 \rangle] \quad , \quad (1)$$

where $\Delta \vec{r}_T$ is the instantaneous thermal displacement of an atom in the lattice, and $\vec{q} = \vec{k}_f - \vec{k}_i - \vec{k}_{h\nu}$, where \vec{k}_f and \vec{k}_i are the final and initial electron wavevectors, respectively and $\vec{k}_{h\nu}$ is the photon wavevector. The energy distribution curve (EDC) for photoelectrons inside the crystal is given by⁷

$$N(E_f, \vec{k}_f, h\nu) \propto \int_{\text{BZ}} d^3k_i \sum_{\substack{E_j < E_F \\ E_j(\vec{k}_i)}} |\langle E_f(\vec{k}_f) | \vec{A} \cdot \vec{p} | E_j(\vec{k}_i) \rangle|^2 \delta[E_f(\vec{k}_f) - E_j(\vec{k}_i) - h\nu] . \quad (2)$$

The sum integral are taken over all the occupied bands in the first Brillouin Zone (BZ). If photoelectron transport and surface transmission do not alter N significantly, the EDC can be obtained by summing over final energy and momentum states. If tight-binding initial states and plane wave final states are assumed, the matrix element of Eq. (2) demonstrates a temperature dependence similar to x-ray diffuse scattering theory;⁸ i.e.,

$$|\langle \exp(i\vec{k}_f \cdot \vec{r}) | \vec{A} \cdot \vec{p} | E_j(\vec{k}_i) \rangle|^2 \propto \left\{ \cos^2 \gamma f \sigma_{ij}(\vec{k}_f) \left[\delta(\vec{q} - \vec{G}) + [1 - \delta(\vec{q} - \vec{G})] [k_B T (|\vec{q}|^2 / |\vec{q} - \vec{G}|^2) \phi_1 + (k_B T)^2 |\vec{q}|^4 \phi_2 + \dots] \right] \right\} . \quad (3)$$

Here γ is the angle (\vec{A}, \vec{k}_f) , $\sigma_{ij}(\vec{k}_f)$ is the atomic cross-section, \vec{G} is a reciprocal lattice vector, and ϕ_1 and ϕ_2 represent sums over phonon modes.^{7,8}

Equation (3) implies that the direct transition component ($\delta(\vec{q} - \vec{G})$) should increase in importance, relative to the phonon-assisted component, as the temperature is lowered. For gold, using bulk mean-square displacement values derived from x-ray measurements,⁹ we calculated a

Debye-Waller factor of 0.063 for $T = 293^\circ\text{K}$ and 0.393 for $T = 93^\circ\text{K}$.¹⁰ For platinum, the Debye-Waller factor is approximately 0.23 for $T = 293^\circ\text{K}$ and 0.58 for $T = 93^\circ\text{K}$. Hence, a very substantial enhancement of the direct-transitions contribution to the spectrum would be expected upon cooling the samples to the liquid-nitrogen temperature range.

A gold single crystal was cut to produce two samples: one with a (111) surface orientation and the second with a (100) surface orientation. A platinum sample with a (111) surface orientation was also prepared. The samples were polished, etched, and checked for damage using back-reflection Laue patterns.^{3,11} The samples were placed on a specially-built low-temperature probe in a Hewlett-Packard 5950A ESCA spectrometer and irradiated with monochromatized $\text{AlK}\alpha$ radiation (1486.6 eV). The probe was rotated to allow analysis of electrons emitted along the [100] direction from the (111)-cut crystals and along the [111] direction from the (100)-cut crystal.

In each configuration the lens voltages were optimized for the sample orientation and position. The resolution of the spectrometer was between 1.1 and 1.2 eV FWHM, measured on the $\text{Au } 4f_{3/2}$ line, throughout these measurements. The samples were repeatedly subjected to light argon-ion bombardments to control carbon and oxygen surface contamination, which built up over a few-hour run to levels such that the $\text{C } 1s/\text{Au } 4f_{7/2}$ intensity ratios would be ~ 0.02 - 0.05 . While the active-sample temperature was not monitored,¹⁰ there was little reduction in the $\text{N}(1s)$ signal over a 12-hour period when N_2 was deliberately adsorbed onto a cooled sample.

Our experimental results are compared with theory in Figs. 1-3. In each case the lowest (solid) curve is the experimental room-temperature result, and the top (dot-dashed) curve is a theoretical low-temperature curve, calculated based on the direct-transition model. Both Baird, et al.¹ and Wehner, et al.⁵ have calculated direct-transition model spectra for AlK α ARXPS of gold in the [100] and [111] directions. We have used the direct-transition curves of Wehner, et al., which were based on Smith's parameterization¹² of the Hodges, Ehrenreich, and Lang tight-binding interpolation scheme.¹³ To generate the theoretical low-temperature curves expected if the direct-transition model were partially restored at low temperatures, we first broadened the calculated direct-transition with Gaussian functions to simulate the effect of experimental resolution. Then these curves were weighted by 1/3 and added to the experimental room-temperature curves after the latter had been weighted by 2/3. These weighting factors are appropriate for the change in the Debye-Waller factor of gold on cooling. By using the experimental room-temperature curves in the calculation, and looking for any changes in the spectra on cooling in the direction of the calculated low-temperature spectra, we have a very sensitive experiment to detect partial restoration of the direct-transition model.

No changes were observed in the gold ARXPS spectra at low temperature. The middle (dashed) experimental low-temperature curves for gold in Figs. 1 and 2 are identical to within the accuracy of our measurements with the room-temperature curves. They are in marked disagreement with the predicted curves.

For platinum [100], which was run as a confirmatory experiment, the conclusion is exactly the same, although several experimental parameters are quite different from the gold case. The Debye-Waller factors are larger for Pt than for Au at both ambient and low temperatures. In addition, because of the different lattice constant, a different part of the Brillouin Zone would be sampled in the $AlK\alpha$ spectra of Pt, according to the direct-transition model. As Fig. 3 shows, there would be a very large change in the spectrum with temperature according to this model, whereas none whatever is observed. In this case the direct-transition calculation was convoluted with a Gaussian function of 0.87 eV FWHM, and again it was given a weighting factor of 1/3.

The direct-transition model as formulated by Wagner, et al.¹⁴ has had considerable success in the UPS energy regime. Shevchik's thermal diffuse scattering model⁷ also appears to describe the breakdown of the direct-transition model for large values of $\langle (\vec{q} \cdot \vec{\Delta}r)^2 \rangle$ in the UPS regime. However, the present results indicate that the converse is not true in the XPS energy regime; i.e., that lowering the temperature does not substantially restore the direct-transition model in angle-resolved XPS. Rather, the "matrix-element" model,³⁻⁵ which relies on the assumption that ARXPS samples the zone thoroughly enough that the spectra are predicted by integrating over the zone, appears to predict the low-temperature spectra as well. This integration implies that the [100] and [111] spectra are very nearly given by the e_g and t_{2g} projections, respectively,¹⁵ as has been found for

copper and gold.⁵ This may well also be true for platinum, although our data do not provide a critical test of this point.

We suggest that the complexity of the final states — i.e., band mixing combined with the very high density of final states — is responsible for the failure of the direct-transition model to be restored in ARXPS at low temperatures. As a reminder of how complex the final-state spectrum is at XPS energies, we have plotted in Fig. 4 the empty-band states for energies between 1420 eV and 1520 eV. We note that this plot is unrealistically favorable to the direct-transition model. Band mixing would remove any degeneracies (producing more bands) and would make many of the bands shown much flatter.

More sensitive experiments are needed to test this proposal. In the XPS energy range, future experiments could use better angular or energy resolution, lower temperatures, or different materials. While XPS studies might thus be made sensitive enough to detect some restoration of direct transitions, our results indicate that only a fractional restoration can be expected. A more promising approach would be to carry out angle-resolved temperature-dependent photoemission in the intermediate energy range, between e.g., 100 eV and 1000 eV. There must be a transition between ARUPS behavior, in which direct transitions are restored as f is increased,⁶ and ARXPS behavior, in which they are not. Correlation of the energy range and form of this transition with the complexity of the final states would help to answer one of the remaining questions about high-energy photoemission from ordered solids.

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†Permanent address: University of Petroleum and Minerals, Dhahran, Saudi Arabia.

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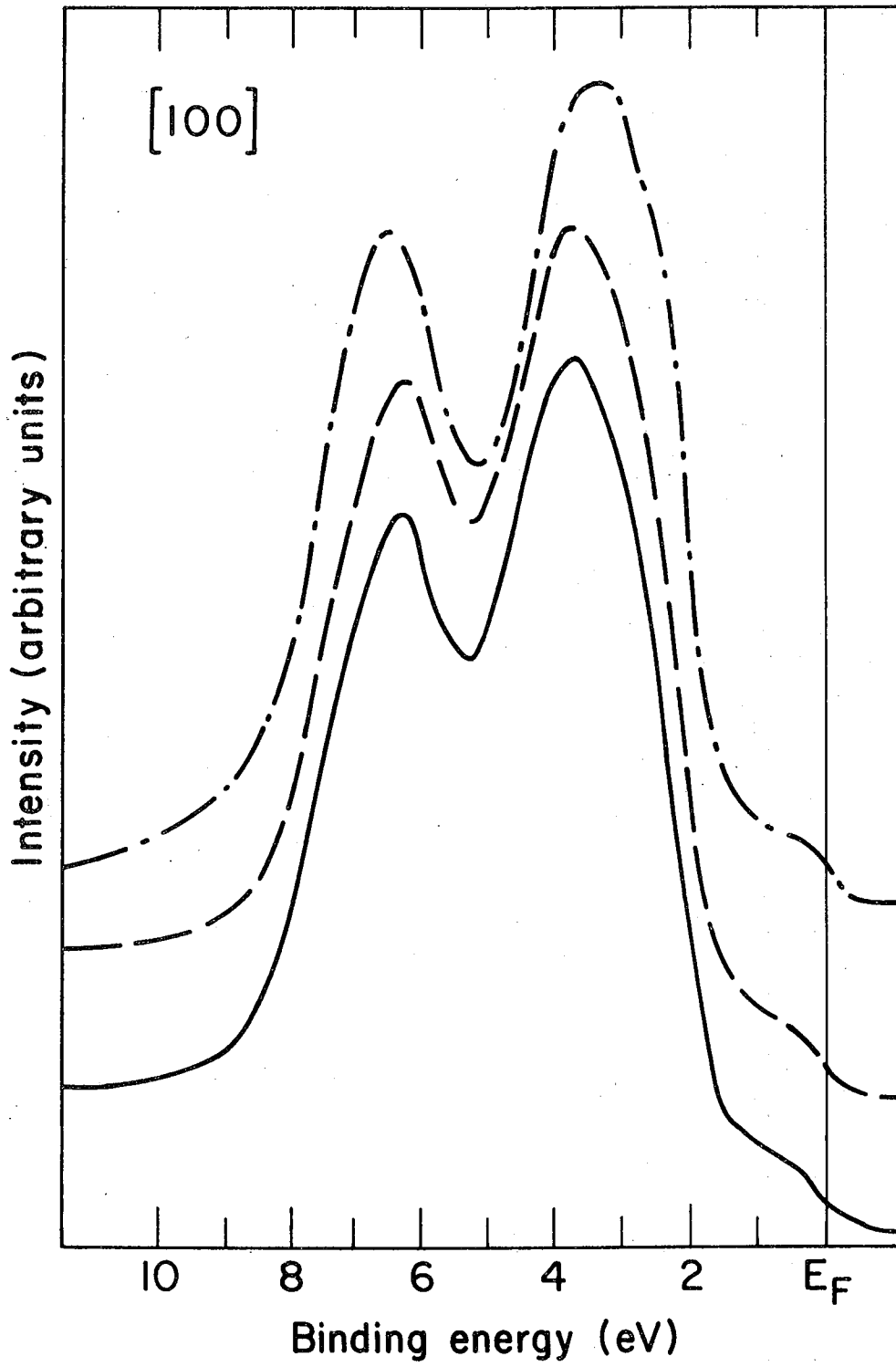


Fig. 2

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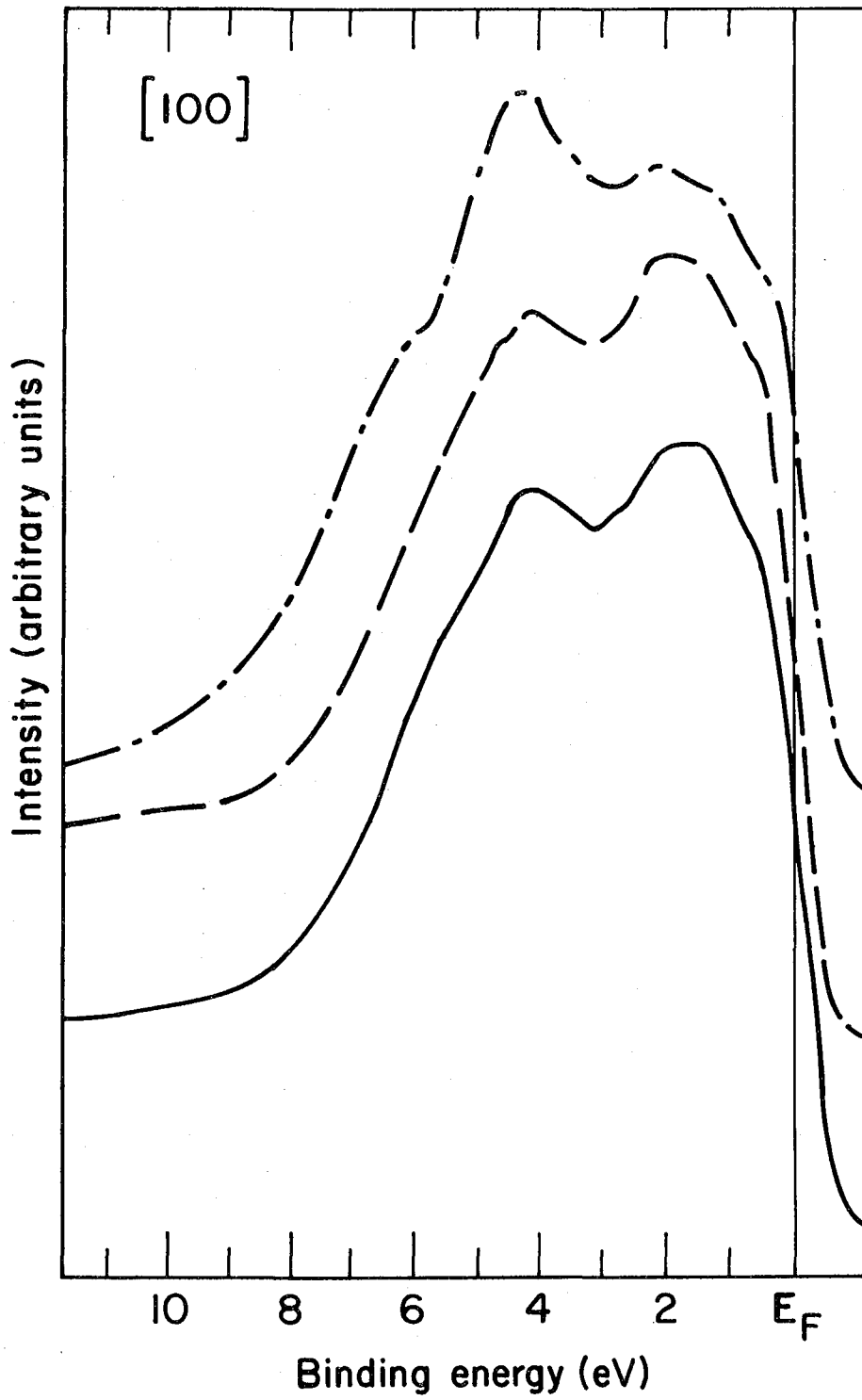
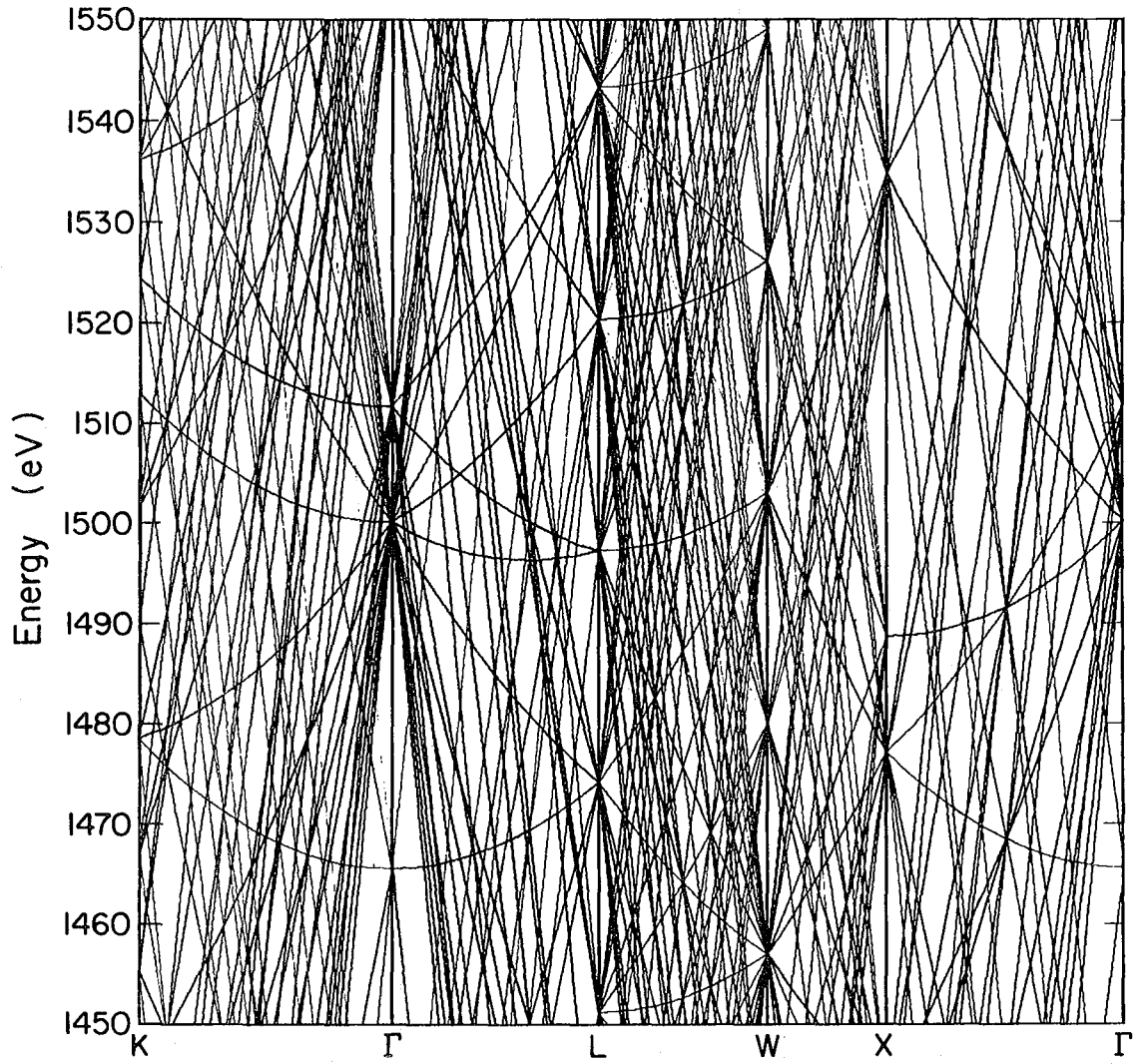


Fig. 3

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Fig. 4

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