Observation of f-band final-state structures in gold by ultraviolet photoemission spectroscopy*

J. Hermanson, J. Anderson, and G. Lapeyre
Montana State University, Bozeman, Montana 59715
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The availability of synchrotron radiation from storage rings makes possible a new technique for studying final-state structures in ultraviolet photoemission spectroscopy (UPS). By synchronously varying the photoelectron kinetic energy and the photon energy, constant initial-state-energy spectra were obtained for Au in the spectral range $8 < h\nu < 30$ eV; these data complement previous UPS and x-ray photoemission spectroscopy data which have been used to elucidate the properties of electron states near the Fermi energy, E_F. Pronounced structures attributed to $d \rightarrow f$ transitions near the center of the Brillouin zone were observed for final-state energies about 16 eV above E_F. The amplitude of these structures is a sensitive function of initial-state energy. Although a complete band-structure interpretation was not attempted, the data support the relativistic band calculation of Christensen and Seraphin, which places the f-band edge, Γ_6^-, at 15.6 eV above E_F. Thermoreflectance data on Au near 20 eV are reinterpreted in the light of this finding.

I. INTRODUCTION

The electronic structure of Au has been the subject of intensive spectroscopic and theoretical investigations. Until recently, optical[1] and photoemission[2,3] data tended to emphasize the properties of *occupied* d-band states and transitions in the vicinity of the Fermi surface. Although measurements of the optical constants[4] in the spectral region where $d \rightarrow f$ transitions are expected (on atomic grounds) have been available for about a decade, detailed interpretations were not attempted until recently. The utilization of synchrotron radiation as an intense windowless continuum in the vacuum ultraviolet has made possible high-resolution studies of *final*-state structures in Au, associated with atomic $5d \rightarrow 5f$ transitions. These structures are strong because both the orbital degeneracy and the electric-dipole matrix elements are large.

The first studies to probe $d \rightarrow f$ transitions in Au in the light of band-structure calculations were those of Olson, Piacentini, and Lynch.[5] These investigators obtained thermoreflectance (TR) data in the 6–35-eV region using synchrotron radiation from the storage ring at the University of Wisconsin Physical Sciences Laboratory (UWPSL). Their spectra, which resemble the second derivative of the reflectivity, contain five structures in the 18–26-eV region where the reflectivity contains an intense but almost featureless peak. Three of these structures were interpreted as d-band excitations near Γ in the Brillouin zone; by shifting the final-state (Γ_7^-) f-band energy upward by 1.3 eV, the band calculation of Connolly and Johnson[6] could be made consistent with this interpretation-experiment and theory agreed within 0.2 eV.

Another relativistic-band calculation is available for Au,[7] and has been used[8] without empirical adjustment to account for the major features in the photoemission energy-distribution curves (EDC's) below 13 eV. EDC structures were related, through the direct-transition model, to extended regions of k space not in general associated with critical points. We take the point of view that the consistency of computed and measured EDC's in this spectral range validates the calculated bands[7] to a high degree, at least in the valence-band region. This would imply that the d bands in Ref. 6 are about 0.5 eV too high, although the relative energy separations at Γ seem to be about right. Now TR data[5] do not contain unambiguous information on initial-state (or final-state) energies, only energy differences; hence a photoemission experiment seemed desirable. Previous experiments[2,3] have provided definitive information on occupied states, so we chose to do an experiment which emphasized *final*-state features in the region of the f bands. The experiment performed at UWPSL, is described in Sec. II and the results are presented and interpreted in Sec. III. The conclusions reached by us and summarized in Sec. IV yield a more complete picture of the energy bands in Au, especially near Γ in the Brillouin zone, where photoemission experiments below 13 eV have insufficient photon energy (d-band threshold ~ 19 eV); previous high-energy experiments[3] emphasized *initial*-state effects in this region.

II. EXPERIMENT

Au films were vacuum deposited by evaporation at the rate of approximately 10 Å/sec onto polished metallic substrates.[9] During deposition the chamber pressure was about 5×10^{-9} Torr; photoemission data were taken in this same chamber at 10^{-10} Torr. The electron spectrometer used is a commercial cocylindrical-mirror analyzer (CMA), which electrostatically focuses energy-selected (resolution 0.2 eV) electrons on a channeltron outputted to an apparatus for automatic recording of data, in digital form, on punched paper tape.

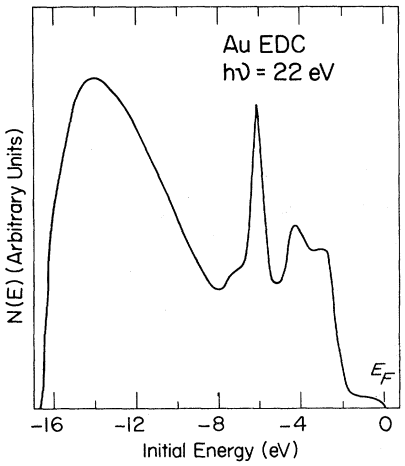

FIG. 1. EDC for metallic Au in the $d \rightarrow f$ transition region; $h\nu = 22$ eV.

Light from the exit slit of the UWPSL 1-m normal-incidence monochromator was directed through a hole machined in the CMA; the angle of incidence on the sample is the CMA angle, 42.3°, and the CMA axis is along the sample normal. Light intensity, as measured from the fluorescence of a sodium salicylate monitor, is a smooth function of photon energy and the spectral shape is used to normalize the data to counts-per-incident photon.

The traditional variable measured in photoemission studies is the energy distribution curve $N(E_f; h\nu)$, essentially the photocurrent-per-unit light intensity at a given bandwidth and per unit final-state energy E_f of the electron; $h\nu$ is the photon energy. Often the data are referred to initial-state energies $E_i = E_f - h\nu$ to emphasize the quantum structure of the occupied electrons. An EDC for Au at 22 eV is presented in Fig. 1. Final-state properties have usually been studied by analyzing EDC peak amplitudes and positions as a function of $h\nu$. The latter program is difficult to carry out with conventional light sources, e.g., discharge lamps, owing to the extremely nonuniform spectra which they emit. Synchrotron radiation on the other hand, possesses a broad smooth continuum which enables the design of experiments that *directly* measure final-state properties of optical excitations in solids. The method, applied to KCl in an earlier publication,[10] is to synchronously scan the electron kinetic energy and the photon energy; $\Delta E_i = \Delta E_f - \Delta h\nu = 0$; then by energy conservation the emission obtained in this way is referred to as a "constant-initial-state energy spectrum" (CIS). Except for inelastic scattering of the photoelectron as it makes its way to the detector (this would invalidate the formula $E_i = E_f - h\nu$), the CIS displays the density of final states, available to electrons of fixed *initial* en-

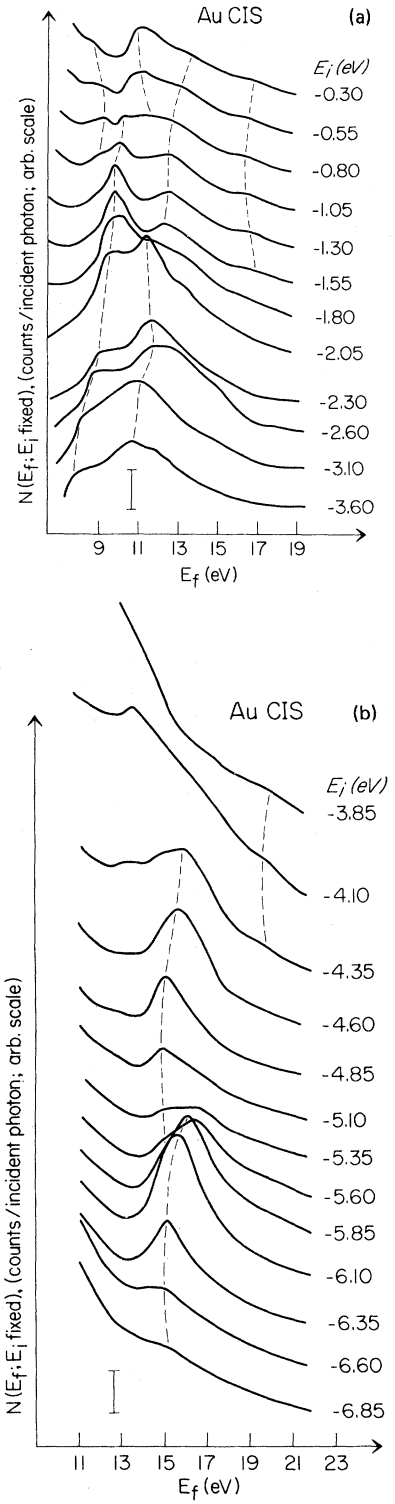

FIG. 2. CIS data for Au; the initial energy $E_i = E_f - h\nu$ is the family parameter. The base lines are shifted upwards by equal increments for clarity; the vertical shift is given by the bar appearing under the first CIS. (a) Has $-3.6 < E_i < -0.3$ eV; the range for (b) is $-6.85 < E_i < -3.85$ eV.

ergy, modulated by the dipole-transition probability for the optical excitation. The CIS, $N(h\nu; E_i$ fixed), is clearly complementary to the EDC, $N(E_f; h\nu$ fixed), and far better suited to the investigation of the quantum structure of empty electron states in solids, since it is unnecessary, in the CIS, to unfold initial- and final-state properties in order to study the latter.

III. RESULTS AND INTERPRETATION

CIS's for final-state energies in the range $7 < E_f < 21$ eV have been separated into two sets of curves; the initial state energy is the family parameter for each set. Figure 2 (a) contains results that tend to emphasize transitions near the edge of the Brillouin zone, including the Fermi surface region. This is because the selected initial-state energies are in the range $-3.6 < E_i < -0.3$ eV relative to the Fermi energy E_F, while the uppermost d band at the zone center has $E_i = -3.30$ eV according to Ref. 7. The observed spectra contain pronounced final-state structures whose strength and location depend sensitively on initial-state energy. A glance at the band diagram[7] of Fig. 3 is sufficient to suggest that a large region of the Brillouin zone contains transitions terminating in final states 9–13 eV above E_F, and in which the intial-state energies lie above the d-band edge at Γ. Note especially the bands near the zone corners X, W, and K; most of the complex structure in Fig. 2 (a) is probably attributable to this region, although detailed computations like those in Ref. 8 are required to make difinitive assignments. The weak structure near $E_f = 16.5$ eV, $E_i = -1.0$ eV is probably due to transitions near L ($L_4^+ - L_5^-$).[7] This transition may account for the TR structure at 17.3 eV.[5] The photon energy for this transition is 17.6 eV according to the data in Fig. 2(a). In general, the complex evolution of final-state structures in this figure is consistent with the direct, but not the indirect transition model.

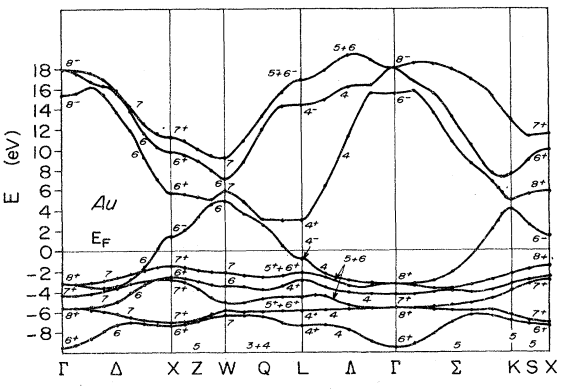

FIG. 3. Energy bands for Au, according to the relativistic calculation of Ref. 7. All energies are defined relative to the Fermi level.

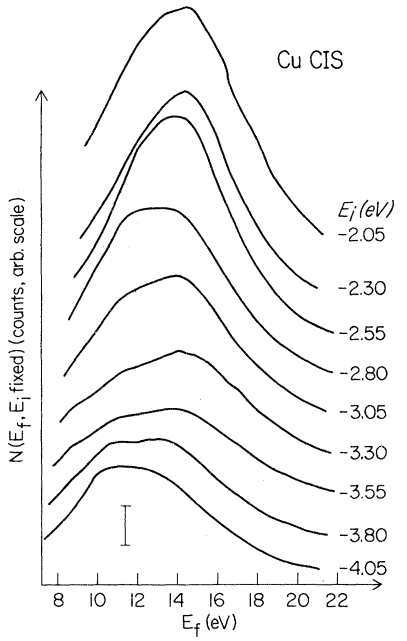

FIG. 4. CIS data for Cu, with initial energies in the d-band range. No light curve adjustment has been made for these data. The vertical bar appearing under the first CIS shows the relative base-line shift of each successive curve.

A second set of CIS's are presented in Fig. 2(b), with initial-state energies in the d-band range $-5.85 < E_i < -3.85$. The dominant feature of these spectra is a large final-state peak whose energy location varies slowly with initial-state energy. CIS data for Cu in the d-band region are shown in Fig. 4 for comparison. Final-state effects are not prominent here, presumably due to the absence of f-like states in the spectral region considered. It is apparent that the conduction bands in Au contain a pronounced density-of-states peak in the spectral region 15–16 eV above E_F, which is strongly coupled to d-band states. Noting further the energy location,[7] -4.34 and -5.65 eV, of d-band edges at Γ, it is natural to interpret the observed structure as (nominal) $5d \rightarrow 5f$ transitions at the zone center.[11] These transitions were inaccessible in experiments below 13 eV, although they play a major role in high-energy optical and photoemission studies, and provide additional information with which to test the accuracy of existing band calculations. Indeed the energy bands of Fig. 3 have Γ_6^- states at 15.6 eV, consistent with our interpretation of the dominant peak in Fig. 2(b). On the other hand, the empirically adjusted bands of Ref. 5 place the f-band edge at 17.2 eV; this placement is not supported by our data.

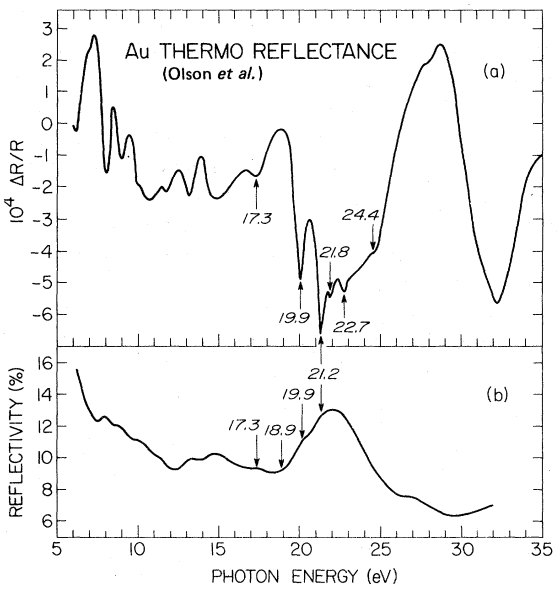

FIG. 5. Thermoreflectance data for Au, taken from Ref. 5. The arrows denote the principal features in the region of $d \rightarrow f$ transitions.

IV. THERMOREFLECTANCE INTERPRETATION

Having presented data that tend to support the energy band calculation of Christensen and Seraphin[7] in the $d \rightarrow f$ transition region, we now show that a slight adjustment of the second f-band edge Γ_8^-, which we have not resolved in our experiment, makes possible a consistent interpretation of all five TR structures in the 18–26 eV region.[5,11]

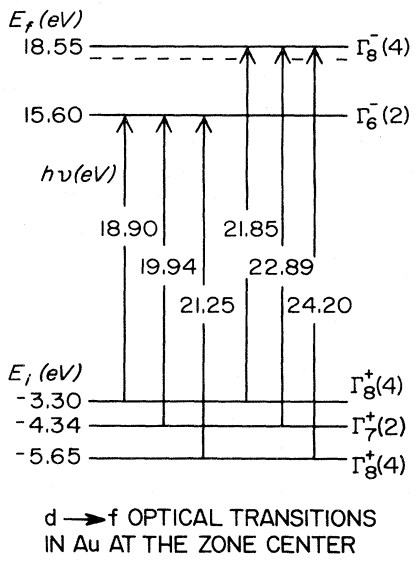

FIG. 6. Energy level diagram near Γ, exhibiting our interpretation of TR features in Fig. 5.

TABLE I. Thermoreflectance (TR) interpretation.

TR $h\nu$ structures (eV)	Interpretation present study	Theory (Ref. 3) (eV)	Ref. 5 assignments (Ref. 11)
...	$\Gamma_8^+ \rightarrow \Gamma_6^-$	18.90	...
19.9	$\Gamma_7^+ \rightarrow \Gamma_6^-$	19.94	$\Gamma_8^+ \rightarrow \Gamma_7^-$
21.2	$\Gamma_8^+ \rightarrow \Gamma_6^-$	21.25	$\Gamma_7^+ \rightarrow \Gamma_7^-$
21.8	$\Gamma_8^+ \rightarrow \Gamma_8^-$	21.85	...
22.7	$\Gamma_7^+ \rightarrow \Gamma_8^-$	22.89	$\Gamma_8^+ \rightarrow \Gamma_7^-$
24.4	$\Gamma_8^+ \rightarrow \Gamma_8^-$	24.20	...

The computed initial energies at Γ are the following: -3.30 (Γ_8^+), -4.34 (Γ_7^+), and -5.65 eV (Γ_8^+); final-state energies are 15.6 (Γ_6^-) and 18.05 eV (Γ_8^-). Upon revising the last figure upwards by 0.5 eV and using the energy conservation formula, $h\nu = E_f - E_i$, the six transition energies were computed and compared with the TR data,[5] reproduced in Fig. 5. A schematic energy-level diagram for $d \rightarrow f$ transitions near Γ is given in Fig. 6; our interpretation of TR structures is shown. The assignments, and the comparison between computed and measured energies is given in Table I. Note that the discrepancy in no case exceeds 0.2 eV. The threshold transition $\Gamma_8^+ \rightarrow \Gamma_6^-$ (18.90 eV) is apparently too weak to observe in TR, although the *reflecivity* peak has a threshold at about this energy. Also note that all assignments made in Ref. 5 differ from ours, for both initial *and* final states.[12] We do not attempt an interpretation of lower-energy structures, which unlike the above, probably cannot be attributed solely to critical points.[8] Both the d bands and the f bands are flat near Γ, and the absence of competing mechanisms for the pertinent range of initial and final energies has made the task of interpretation less uncertain in this region. A stronger test of our conclusions would require a complete band-structure calculation, within the direct model, of the shape and evolution of structure in Fig. 2(b). Such a calculation would also shed light on the nature of the transitions in Fig. 2(a).

V. CONCLUSIONS

Application of the CIS technique has enabled us to study, in a direct and decisive fashion, the energy location of final-state structures associated with f-like conduction bands in Au. Our measurements emphasized the region of k space near the zone center, which is inaccessible to photoemission experiments in which $h\nu < 19$ eV (the $d \rightarrow f$ threshold). The dominant feature of the CIS attributable to d-band excitations near Γ is a pronounced peak

with $E_f \simeq 15$–16 eV. Thus our results support the relativistic energy-band calculation of Christensen and Seraphin,[7] in which the f-band edge Γ_6^- is located 15.6 eV above the Fermi energy. Lower-energy EDC's obtained by earlier workers[2] have provided ample validation[8] of these calculations in the d-band region.

By coupling the final-state information obtained in our CIS data and initial-state information derived from the EDC's at lower energy,[2,8] it is possible to construct an energy-level diagram at Γ that provides a consistent interpretation of the five TR structures in the 18–26-eV region. The reflectivity[4] in this region has a large broad peak attributed to $5d \rightarrow 5f$ transitions split by crystal field and relativistic effects. The level diagram we put forth differs from that of Ref. 7 only in that the second f-band edge Γ_8^- is placed 0.5 eV higher in our model. We have not observed final-state structures corresponding to this edge. However, it should be noted that the corresponding dips (three) are rather weak in the TR spectrum[5]; see Fig. 5. If our model is correct the $d \rightarrow f$ threshold at 18.9 eV is not observed in either the CIS or in TR, although the reflectivity peak appears to have a threshold at about 19 eV.

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[11]Although we have based our analysis on the energy bands bands of Ref. 7 along symmetry lines, the same reference contains band diagrams for general points in k space which indicate additional transitions which might also contribute significantly to the observed CIS structures. A calculation like that of Ref. 8 is required to settle the issue.

[12]The f-band threshold at Γ has the symmetry label Γ_6^- in Ref. 3, and Γ_7^- in Ref. 6.