

Photoemission Spectra for Liquid and Crystalline Au<sup>†</sup>

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Photoemission energy distributions have been measured for liquid and crystalline Au using photon energies from 16.8 to 40.8 eV. The nature of optical excitations is observed to change from direct interband transitions to local or nondirect transitions upon passing from the crystalline to the liquid state. For liquid Au, we measure  $d$  bands of width 6 eV, with an edge about 1.6 eV below the Fermi level  $E_F$  and two peaks in the optical density of states at 3.2 and 5.8 eV below  $E_F$ .

Photoemission measurements have been extremely valuable in yielding information about the electronic structure of disordered systems, including amorphous semiconductors, alloys, and liquid metals. We report the first photoemission energy distributions for  $d$  bands in a liquid metal. The data show two new and interesting results. First, because of our wide range of photon energies, the nature of optical excitations is observed to change from direct transitions (with conservation of energy and crystal momentum) in the crystalline state to local or nondirect transitions (with only energy conservation being important) in the liquid state. Second, well-defined  $d$  bands are observed in liquid Au, with a width of about 6 eV and two peaks in the optical density of states at 3.2 and 5.8 eV below the Fermi level  $E_F$ . This optical density of states resembles the band density of states for crystalline Au in both width and overall shape. The data indicate that short-range interactions common to both crystalline and liquid Au are most important in determining the  $d$ -band structure. The  $d$ -band width (6 eV) is much larger than the "extra" lifetime broadening ( $\leq 0.5$  eV) observed for liquid Au relative to crystalline Au. The upper  $d$ -band edge is observed to shift upwards in energy from about 2.0 eV below  $E_F$  in crystalline Au to 1.6 eV below  $E_F$  in liquid Au.

Photoemission energy distributions were measured at photon energies of 16.8, 21.2, 26.9, and 40.8 eV using He and Ne resonance lamps and a spectrometer with a deflection-type analyzer.<sup>1</sup> In addition to permitting measurements of the entire valence band width of Au (about 8 eV), the use of such high photon energies eliminates problems such as thermionic emission which accompany the high temperatures required to melt Au ( $T > 1063^\circ\text{C}$ ). Namely, the photoejected electrons of interest have much higher energies than thermally emitted electrons from the sample.

Au samples were formed as 2- to 3-mm-diam

spheres on a 0.25-mm-diam W wire about 3 cm long which served as both a support and Ohmic heater. When molten, the Au sphere remained in place because of surface tension. Clean surfaces were obtained by partial evaporation of the sample. The Au sphere was placed about 3 mm in front of the 0.5-mm entrance slit to the electron energy analyzer.<sup>1</sup> The W filament wire was shaped so as to minimize light emission and stray magnetic fields due to the heater current. One leg of the W wire was grounded to the analyzer very near the Au bead in order to eliminate any dc heater voltage drop between the sample and analyzer ground. The effects of magnetic fields due to the heater current ( $\leq 6$  A) and possible dc voltage drop were checked by reversing the polarity of the heater current.

A collimated beam of radiation about 1 mm in diameter was incident on the Au sphere at right angles to the input direction to the energy analyzer. The position of this beam was adjusted so as to irradiate about half of the hemispherical surface facing the entrance slit to the analyzer. The sample-chamber pressure rose from a base of  $\sim 2 \times 10^{-8}$  Torr to the  $10^{-6}$  Torr range with Au in the molten state. The temperature was measured by viewing the Au sphere with an optical pyrometer.

Energy distribution curves (EDC's) for liquid Au ( $\sim 1125^\circ\text{C}$ ) and crystalline Au ( $25^\circ\text{C}$ ) are shown in Fig. 1. The data for crystalline Au in Fig. 1 for  $h\nu = 16.8, 21.2,$  and  $26.9$  eV show the same structure as previously reported,<sup>1</sup> with a slight decrease in resolution due to the spherical sample geometry. For crystalline Au, the  $d$  bands are identified by their strong emission intensity and are seen to extend from about 2.0 to 7.8 eV below  $E_F$ . These EDC's show structure indicative of direct transitions. Between  $-2$  and  $-5$  eV, two  $d$ -band peaks are observed which are separated by about 1 eV at  $h\nu = 16.8$  eV, by about 2 eV at  $h\nu = 21.2$  eV, by  $\leq 1$  eV at  $h\nu = 26.9$  eV,

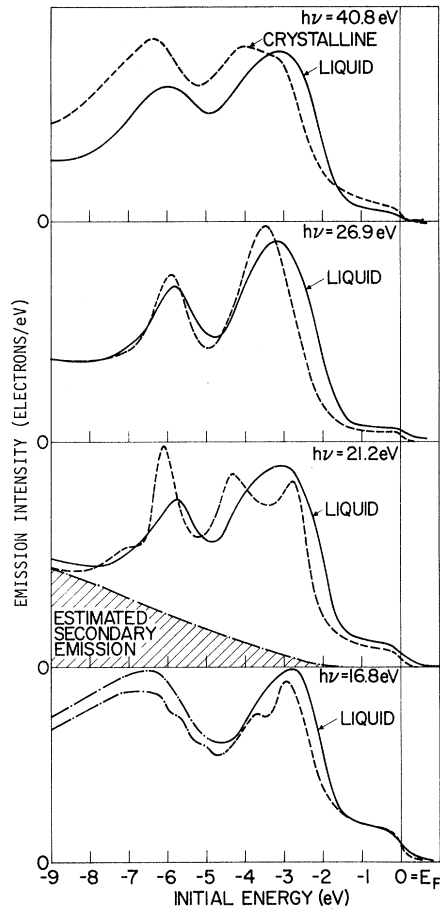


FIG. 1. Photoemission-energy distribution curves for liquid and crystalline Au. All curves are plotted versus the initial energy measured below the Fermi level  $E_F = 0$ .

and by about 1.2 eV at  $h\nu = 40.8$  eV.<sup>2</sup> As previously discussed,<sup>1</sup> this behavior in the EDC's is consistent with optical excitations via direct interband transitions. In this case, structure in the EDC's corresponds to structure in the energy distribution of the joint density of states and not the band density of states.<sup>3</sup>

The EDC's for liquid Au in Fig. 1 for  $h\nu = 21.2$ , 26.9, and 40.8 eV show emission from well-defined  $d$  bands which extend from about 1.6 eV to 7.5 eV below  $E_F$ . These EDC's all have the same shape,<sup>2</sup> with  $d$ -band peaks at 3.2 and 5.7 eV below  $E_F$ , and do not show the peak splittings and shape changes seen for crystalline Au. The occurrence of this behavior for liquid Au over such a wide range of photon energies is indicative of local, or nondirect transitions. That is, we see no dependence of the EDC's on the final-state crystal momenta, which undergo large changes over our wide range of energies. In this case,

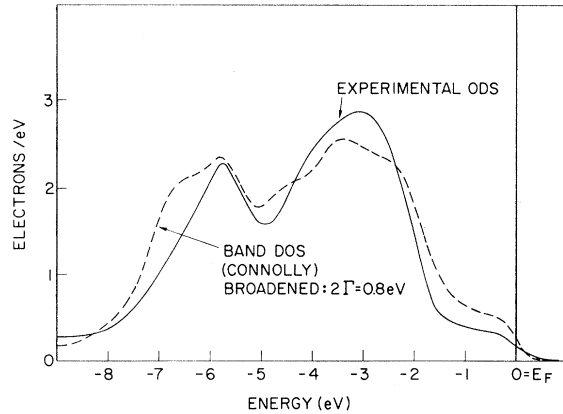


FIG. 2. Optical density of states (ODS) for liquid Au and band density of states for crystalline Au (dashed line). See text.

the observed emission spectra can be described by an optical density of states (ODS) which is expected to be similar to the electronic density of states.<sup>1,3</sup> This ODS includes transition probabilities and thus is not directly equal to the electronic density of states.

In Fig. 2, we show our experimental ODS for liquid Au. A smooth distribution of secondary electrons due to inelastic electron-electron scattering has been subtracted out (see EDC for  $h\nu = 21.2$  eV in Fig. 1). In lieu of any known calculation of the density of states for liquid Au, we have compared the ODS in Fig. 2 (solid line) with the density of states for crystalline Au calculated by J. Connolly<sup>4</sup> using the relativistic Korringa-Kohn-Rostoker method and a full Slater exchange approximation. In order to obtain a qualitative "best fit" to our measured ODS, we have folded Connolly's "sharp" density of states with a Lorentzian lifetime broadening function of width  $2\Gamma = 0.8$  eV. In Fig. 2, qualitative agreement between the ODS and band density of states is observed. Both curves show  $d$ -band widths of about 6 eV, with two  $d$ -band peaks and a minimum at about 5 eV below  $E_F$ .<sup>5</sup> This similarity would appear to indicate that short-range interactions are the most important interactions in determining the  $d$ -band structure. The existence of such short-range interactions common to liquid and crystalline Au is consistent with reported structural data,<sup>6</sup> i.e., both phases have close-packed, 12-coordination structures. Destruction of long-range order upon passing into the liquid state is seen to have a relatively small effect on the overall  $d$ -band structure of Au, that is, only fine structure much smaller than the 6-eV  $d$ -band width is seen to change.

In Fig. 1, the  $d$ -band edge of liquid Au is seen to be shifted towards  $E_F$  by  $0.35 \pm 0.1$  eV relative to crystalline Au. This shift has been observed to accompany the phase transition into the liquid state, and does not occur gradually between  $25^\circ\text{C}$  and  $1125^\circ\text{C}$ . Data for crystalline Au at about  $950^\circ\text{C}$  exhibited structure qualitatively similar to that observed at  $25^\circ\text{C}$  and did not show this shift. This shift of the  $d$ -band edge is consistent with the optical measurements for liquid Au by Miller<sup>7</sup> for  $2 < h\nu < 4.2$  eV, who did not measure far enough into the infrared to see the  $d$ -band edge. From Fig. 1, the center of the  $d$  bands,  $E_d$ , is estimated to shift upwards by  $\sim 0.3 + 0.1$  eV relative to  $E_F$  between  $25^\circ\text{C}$  and  $1125^\circ\text{C}$ . Moriarty<sup>8</sup> has calculated a shift of  $E_F - E_d = 0.26$  eV for Au over this temperature range; this is in good agreement with our measurement.

A rough estimate of the electron damping, or lifetime broadening, of  $d$  states in liquid Au can be made using Fig. 1. Comparison of the EDC's for crystalline and liquid Au at  $h\nu = 21.2$  eV (for which we have the best signal-to-noise ratio) indicates that the "extra" broadening  $\Delta E$  in liquid Au at the  $d$ -band edge near  $-2$  eV and in the structure near  $-6$  eV is about  $0.2 \text{ eV} \lesssim \Delta E \lesssim 0.5$  eV. Schwartz and Ehrenreich<sup>9</sup> have calculated a value of about 0.5 eV for the electron damping of

$d$  bands in liquid Cu. This value is qualitatively similar to our estimates for liquid Au.

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<sup>1</sup>D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. **24**, 310 (1970).

<sup>2</sup>The EDC's for  $h\nu = 16.8$  eV are distorted by the energy-dependent transmission factor of the energy analyzer, especially at low kinetic energies, i.e., initial energies  $\lesssim 5$  eV (broken lines in Fig. 1). See Ref. 1 for slightly better resolution of the  $d$ -band peaks for crystalline Au.

<sup>3</sup>N. V. Smith and W. E. Spicer, Opt. Commun. **1**, 157 (1969).

<sup>4</sup>J. W. D. Connolly, unpublished.

<sup>5</sup>The agreement in  $d$ -band edges in Fig. 2 is fortuitous and is an artifact of the calculation. The use of a full Slater exchange approximation (Ref. 4) results in a  $d$ -band edge at about 1.6 eV below  $E_F$ , i.e., about 0.4 eV less than the actual edge for crystalline Au.

<sup>6</sup>H. Richter and G. Breitling, Advan. Phys. **16**, 293 (1967).

<sup>7</sup>J. C. Miller, Phil. Mag. **20**, 1115 (1969).

<sup>8</sup>J. A. Moriarty, Phys. Rev. B **1**, 1363 (1970).

<sup>9</sup>L. Schwartz and H. Ehrenreich (to be published).

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## Quantum Aspects of the Azbel'-Kaner Resonance in Bismuth

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We report the observation of Azbel'-Kaner cyclotron resonance in the limit where distinct transitions between quantized levels have to be considered. A multiplet structure is found in the subharmonic resonances arising from the unequal spacing of the Landau levels in the nonparabolic conduction band of Bi. The data are satisfactorily interpreted in terms of the ellipsoidal-nonparabolic band-structure model due to Lax. The sharpness of the resonances ( $\Delta H/H \lesssim 2\%$ ) makes it possible to re-examine previously reported band-structure parameters of this model.

Studies of the high-frequency surface resistance of Bi in a magnetic field have a long and venerable history stretching over more than a decade. At the lower end of the frequency spectrum are the Azbel'-Kaner (AK) cyclotron-resonance studies in the microwave regime, typically 10-70 GHz. Khaikin and co-workers<sup>1</sup> have observed a rich spectrum of subharmonic resonances for each of various possible orbits about

the electron ellipsoids of the Bi Fermi surface. The line shape and subharmonic structure are characteristic of classical AK resonance, and the experiment measures  $m_c^*$ , the cyclotron mass at the Fermi energy. At much higher frequencies, typically  $\sim 25\,000$  GHz ( $\hbar\omega \sim 0.1$  eV), there exist the infrared inter- and intraband magnetoreflexion experiments that provide a measure of the parameters describing the non-