Thermomodulation spectra of high-energy interband transitions in Cu, Pd, Ag, Pt, and Au

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Abstract
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Keywords
Ames Laboratory, thermotransmission, thermoreflectance, Brillouin-zone

Disciplines
Atomic, Molecular and Optical Physics | Condensed Matter Physics | Physics

Comments

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Thermomodulation and thermoreflectance spectra were obtained for Cu, Pd, Ag, Pt, and Au in the 10-30 eV spectral region. Structures due to transitions from the Fermi level to high-density bands 15 eV above the Fermi level were identified in Pt. All metals showed structures arising from interband transitions between the d bands and the same flat bands, 15-20 eV above the Fermi energy. Attempts to fit to interband critical points in Au revealed over 40 possible critical points in the region of these structures, most of them near the Brillouin-zone centers. Systematic trends in the series of metals make the qualitative identification of the structures more secure, and no energy shifts of calculated energy bands are required. The observed widths of structures are sometimes much narrower than the widths of free-electron-like bands at comparable energies.

Several years ago the thermoreflectance spectrum of Au was reported in the 10-30 eV region. Among the many structures in the spectrum were five relatively sharp peaks attributed to transitions from the 5d bands to one or more flat bands, partly based on 5f states, some 16 eV above the Fermi level. The original, tentative interpretation assigned these structures to transitions at the Brillouin-zone center. (The detailed assignment was disputed, but this arose primarily because the symmetry labelling of these states was in error in one calculated band structure.) In the following we report thermomodulation measurements on Au, Ag, Pd, and Cu and thermoreflectance measurements on Pt. The results demonstrate that modulation spectroscopy is a useful technique at high energy for metals other than Au, and the data for the series of metals allow a more reliable, albeit still tentative, assignment of interband transitions. Recent calculated partial joint densities of states of Au (Ref. 5) make it clear, however, that there are many possible interband critical-point transitions in a narrow energy range because of the flatness of the bands involved, and definitive assignment of transitions appears to await the calculation of interband electric dipole matrix elements.

Thermomodulation spectra of unsupported thin films, 275-450 Å thick, were measured using synchrotron radiation from the electron-storge ring Tantalus I. The samples were mounted over a 1×3 mm² slot in a block of machinable ceramic. A unipolar square-wave current through the sample produced a temperature modulation of about 1 K at 7 Hz while the ambient temperature of the sample could be varied from 20 to 300 K. The photodetector was an electron multiplier, the first Be-Cu dynode serving as photocathode. It was used in the current mode with an equivalent single-photon count rate of over 10⁹ Hz to ensure a good signal-to-noise ratio. When the storage ring was operated in the stable mode, the noise in the spectra was photon-shot noise. The ac component of the signal was synchronously detected, then digitized to allow long integration times, but times longer than 10 s were rarely needed to produce essentially noise-free spectra. The dc component was processed by an electrometer and the two signals were ratioed numerically. The bandpass of the normal-incidence monochromator was adjusted so that no structures were resolution limited. The shapes of the spectra for different films of any one material were very reproducible. Only the magnitudes changed, and these also changed for one film upon changing the ambient temperature, because the temperature-oscillation amplitude for a given modulation power input depended on thermal time constants and the degree of thermal isolation.

The data are ΔT/T, the fractional change in transmission of films thin enough that interference effects could be important. Multiple reflections can be neglected, however, because of the strong absorption in the spectral region of interest. Moreover, thermomodulation of the reflectance of the sample can be neglected as well. This can be demonstrated two ways. We know the real and imaginary parts of the differential dielectric function for Au, obtained from a Kramers-Kronig analysis of the thermoreflectance data. We calculated the exact ΔT/T using multiple reflections and the modulation of both the absorption coefficient and the reflectance. However, the spectrum...
was almost identical to what was calculated for modulation of the absorption coefficient alone upon a single pass of the beam through the film. In this case the $\Delta T/T$ spectrum is just $-d\Delta \mu$, the thickness multiplied by the change in the absorption coefficient. Experimentally, the modulated spectra of several films of different thicknesses were the same, except for the amplitude, implying that the contribution of $AR/R$ to $\Delta T/T$ is not important. These simplifications may not be universally valid for this spectral range, for they depend on the optical constants and the differential optical constants; but for the metals reported below, the optical constants and the causative electronic excitations are all similar to those of Au. To obtain the differential dielectric function from our data one can use the above simplification and Kramers-Kronig analysis $\Delta T/T = -d\Delta \mu$ to get $\Delta n$, the differential refractive index. $\Delta \mu$ and $\Delta n$ give $\Delta \varepsilon$. Without the simplifications the Kramers-Kronig analysis gives a differential phase shift, but because of the multiple reflections and the modulated reflectance the equations to get $\Delta \varepsilon$ from $\Delta T/T$ and the differential phase shift are transcendental and numerical iterative methods are necessary.

For Pt the measurements were of thermoreflectance, since sufficiently thin unsupported films could not be produced. The thermoreflectance technique used for gold was not applicable, since the optical properties of Pt films on glass or quartz in this energy range are a function of deposition conditions. Therefore, the samples used were thin (20 $\mu$m) foils that had been annealed and cleaned in situ. The foil was held under slight tension in such a way that thermal expansion could not produce a motion that would cause a spurious background signal. The measurement technique used was essentially the same as for thermoremission except the angle of incidence was 30° with $p$ polarization, the modulating frequency was lower (1–2 Hz), and integrating times were longer because of the small $AR/R$ signal.

Figure 1 shows a general comparison of the spectra for all materials studied. (For Pt we show $-\Delta \mu$ obtained from a Kramers-Kronig analysis of $AR/R$.) The obvious features are the shift of the main structures as the top of the filled $d$ band shifts (the final states may shift as well), the loss of the first major structures upon going from Ag to Pd, in which the top of the $d$ band is not full, and the loss of sharpness in the structures upon going from $5d$ to $4d$ to $3d$ initial states. (It is often assumed that 20-eV excitations in metals have short lifetimes and only broad structures are expected, but it is clear that certain excited states in Au have a lifetime broadening of no more than 0.1 eV. The lack of structures this sharp in the other metals may be due to the overlap of many structures rather than shorter lifetimes.) Although data were taken over a range of ambient temperatures from about 330 to 20 K the spectra depended only slightly on this temperature, with two exceptions. The most notable are the structures near 20 eV in Au. The ratio of peak heights to the background increased dramatically upon cooling. (The spectrum in Fig. 1 is for 55 K.) The other spectral feature showing considerable dependence on ambient temperature is the 15-eV peak in Pt. The strength of this structure diminished upon cooling. It also diminished with sample quality, being weaker for unannealed foils.

![Figure 1. Thermoreflectance spectra ($\Delta T/T = -d\Delta \mu$) for Au, Ag, Pd, and Cu, and $-\Delta \mu$ for Pt. The latter was obtained by a Kramers–Kronig analysis of the thermoreflectance spectrum. The ambient temperatures are 52 K for Au and about 200 K for the other metals. $\Delta T/T$ is in arbitrary units and the magnitudes of two spectra cannot be compared.](image-url)
There are no core electron excitations in this energy region. The electrons we must consider are the $d$-band electrons, there being too few $s$-$p$ electrons above the $d$ bands to account for the structures seen. The only modulation mechanisms we need consider are the shifts induced in the bands by thermal expansion-induced changes in the crystal potential, and the broadening of transitions as the phonon population is modulated. Both of these give characteristic line shapes for $\Delta \varepsilon_1$ and $\Delta \varepsilon_2$ for each type of critical point.\textsuperscript{10} For Pt and Pd, the Fermi function may also be modulated for transitions originating at the Fermi level in the $d$ band.\textsuperscript{14}

Several band calculations extending to energies high enough for our purposes now exist. There are two for Au,\textsuperscript{3,12} two for Ag,\textsuperscript{13,14} one for Pd,\textsuperscript{15} and one for Cu.\textsuperscript{16} In addition, partial-joint densities of states have been calculated for Au, Ag, and Pd, the former two having been calculated as a function of volume as well.\textsuperscript{5} Figure 2 shows the energy bands for Au.\textsuperscript{7} The partial-joint densities of states show many sharp peaks in the range 18–25 eV. In addition to these peaks there are many interband critical points which cause structures which are nearly imperceptible in the partial-joint density of states, but which can give large structures in modulation spectra, while the peaks in the partial-joint densities of states may contribute only a background. This makes direct comparison with photoemission measurements difficult, for our spectra show primarily strongly modulated critical-point transitions which may contribute only weakly to photoemission. The line shapes expected from all types of three-dimensional critical points are asymmetric positive or negative peaks for modulation arising either from a shift of the critical-point energy or from broadening. If both mechanisms contribute, the shapes are altered. Unfortunately there are so many overlapping structures that the shape of an individual structure is difficult to determine.

A first attempt was made to identify the structures by assuming that the interband-transition energies given by the band calculations of Christensen\textsuperscript{3,5,12,14} were exact and to see where they predict structure. He has calculated bands for Au, Ag, and Pd, all by the same relativistic augmented plane-wave technique, so that even if there are errors in the gap energies themselves, the trends upon going from one metal to another may be correct. The letters in Fig. 1 give the interband critical points for allowed transitions at $\Gamma$ and $L$, identified in Table I. See also Fig. 2.

![Energy bands of Au](image)

**FIG. 2.** Energy bands of Au obtained by a Fourier-series fit to the eigenvalues of Ref. 3.

### TABLE I. Identification of critical-point transitions in Fig. 1.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a $L(6) \rightarrow L(8)$</td>
<td>$L(1) \rightarrow L(9)$</td>
</tr>
<tr>
<td>b $L(5) \rightarrow L(6)$</td>
<td>$L(2) \rightarrow L(10)$</td>
</tr>
<tr>
<td>c $L(4) \rightarrow L(8)$</td>
<td>$L(6) \rightarrow L(11)$</td>
</tr>
<tr>
<td>d $L(3) \rightarrow L(8)$</td>
<td>$L(1) \rightarrow L(12)$</td>
</tr>
<tr>
<td>e $L(5) \rightarrow L(9)$</td>
<td>$L(6) \rightarrow L(12)$</td>
</tr>
<tr>
<td>f $L(4) \rightarrow L(9)$</td>
<td>$L(5) \rightarrow L(10)$</td>
</tr>
<tr>
<td>g $L(2) \rightarrow L(8)$</td>
<td>$L(4) \rightarrow L(7)$</td>
</tr>
<tr>
<td>h $L(5) \rightarrow L(10)$</td>
<td>$L(2,3) \rightarrow L(7)$</td>
</tr>
<tr>
<td>i $L(3) \rightarrow L(9)$</td>
<td>$L(5,6) \rightarrow L(8)$</td>
</tr>
<tr>
<td>j $L(4) \rightarrow L(10)$</td>
<td>$L(5,6) \rightarrow L(9,10)$</td>
</tr>
<tr>
<td>k $L(1) \rightarrow L(8)$</td>
<td>$L(4) \rightarrow L(9,10)$</td>
</tr>
<tr>
<td>l $L(2) \rightarrow L(9)$</td>
<td>$L(2,3) \rightarrow L(8)$</td>
</tr>
<tr>
<td>m $L(3) \rightarrow L(10)$</td>
<td>$L(2,3) \rightarrow L(9,10)$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}These transitions are not expected in Pd because the initial state is empty.

\textsuperscript{b}Bands 11 and 12 have been calculated only for Au so these transitions are not labeled for Ag, Pd, and Cu in Fig. 1.
In fact, this first attempt is seen to be promising, for the \( \Gamma \) critical points occur consistently in regions of the largest structure. Such critical points however, rarely dominate modulation spectra because only small regions of \( \mathbf{k} \) space are associated with them. Moreover, the interband critical point \( \mu \), although allowed, should be weak, for it is allowed only via the spin-orbit interaction. Figure 2 shows that there can be interband critical points along \( \Sigma \) and \( \Lambda \) very close to \( \Gamma \). These should enhance the structures near \( \Gamma \) and may dominate them (see below). Critical-point transitions at \( \Lambda \) contribute to some of the weaker low-energy structure in Fig. 1.

In order to learn more about the interband critical points, we used Christensen’s energy eigenvalues for gold\(^a\) in a band-fitting scheme which used 60 symmetrized Fourier coefficients to fit \( E(\mathbf{k}) \) throughout the Brillouin zone, with a root mean-square error of about 1 m\( \text{eV} \) at the input energies. We plotted interband energies along principal axes for each apparent interband critical point at \( \Gamma \), \( L \), and along \( \Lambda \) and \( \Sigma \). We found a large number of interband critical points at the symmetry lines \( \Sigma \) and \( \Lambda \), critical points at energies near those of the \( \Gamma \) critical points. These are listed in Table II. The actual energies, and perhaps the occurrence of some of the critical points, are influenced by the band-fitting procedure. A few of the critical points appear to be two-dimensional or nearly so. Moreover, many of these critical points lie at small wave vectors, usually less than one-fourth of the distance from \( \Gamma \) to the zone boundary and often less than one-eighth of this distance. This means that if a critical point at \( \Gamma \) shifts with increasing temperature, the nearby critical points along \( \Sigma \) and \( \Lambda \) will shift at about the same rate, provided they involve the same pair of bands. This is often the case, and in Table II we have labeled with primed letters those interband critical points “going with” the critical points labeled with unprimed letters. These are usually critical points of different types and they are displaced somewhat in energy. While the behavior of the \( \Sigma \) and \( \Lambda \) critical points is assumed to be that of the \( \Gamma \) points, the line shapes will be different because the \( \Gamma \) critical points are all \( M_6 \) or \( M_3 \), while all four types occur along \( \Lambda \) and \( \Sigma \). Positive peaks in \( -\Delta\varepsilon_\gamma \) and \( -\Delta\mu \) can arise from \( M_2 \) or \( M_3 \) critical points shifting to lower energy upon a temperature increase, from \( M_6 \) or \( M_3 \) points which shift to higher energy, and from \( M_6 \) or \( M_3 \) points which broaden, assuming a single dominant mechanism. Thus \( M_3 \) critical points which shift “red” and broaden upon a temperature increase may dominate the spectrum.

We can model the expected structure under the assumptions that there is a single modulation mechanism for these critical points and that the dipole matrix elements and broadening parameters are the same for those critical points along \( \Sigma \) and \( \Lambda \) which are near \( \Gamma \) and which involve the same bands. Then the expected line shape will be a sum of components, weighted by the degeneracies of the points, 1 (or 2), 8 or 12 for \( \Gamma \), \( \Lambda \) and \( \Sigma \), respectively. Two examples of such superpositions are illustrated in Fig. 3. It is clear that the only role the \( \Gamma \) critical points play is to provide a slight sharpening in one side of the peak, and the dom-
nant structure arises from the nearby critical points along $\Sigma$, $\Lambda$, or both. If both thermal expansion and broadening play a role, the expected spectrum is a linear combination of the two types of spectra shown in Fig. 3. We thus conclude that, although Fig. 1 shows a good match between the energies of several major structures and the energies of interband critical points at $\Gamma$, the structures probably arise from nearby critical points along $\Sigma$ and $\Lambda$, critical points involving the same band pairs, but with higher degeneracies.

As can be seen in Fig. 1 the interband critical points at $L$ contribute to the spectra in about the same energy region as the $\Gamma$, $\Sigma$, and $\Lambda$ critical points, and one does not know a priori that theirs is a minor contribution. However, by looking at calculated positions for the interband transitions at $L$ for Au, Ag, and Pt (Fig. 1, Table I) we can see that transitions at $L$ do not provide as consistent an interpretation for the major peaks as we give above. A reliable estimate of dipole matrix elements is required to decide definitively between the $L$ critical points and the points at and around $\Gamma$.

Not labeled in Fig. 1 is the contribution from critical points at $X$. These all fall at lower energies (transitions to flat bands 10 and 11, expected near 20 eV, are forbidden) and contribute to the structures below those labeled in the figure. For example, the allowed $X$ interband critical points lie between 12.6 and 19 eV in Au and cluster at the three regions of positive slope in Fig. 1 at 12.6, 14.6, and 17.0 eV. In Ag they occur in the (14.6–19)-eV range, and lie on the rising part of the 15.6-eV peak and on the shoulder at 18 eV. In Cu the $X$ contributions are at 15 and 18 eV, in the broad positive peak of Fig. 1. The corresponding structure in Pd is much weaker because bands 4 and 5 are unoccupied at $X$.

The 15-eV structure in Pt does not fit the pattern of the other elements. The line shape of the spectrum indicates there is a dominant contribution from the modulation of the Fermi function for transitions originating at the Fermi level. This is normally a very strong effect in thermomodulation spectra whenever it can occur. The peak-to-peak width of the 15-eV structure in Pt implies that a band of final states some 1-eV wide is involved, an estimate based on a convolution of the shape given in Ref. 11 with densities of states of various shapes, but with 1-eV characteristic widths.

Relativistic energy bands have not been calculated at high energies for Pt. It is probable, however, that the structures at 18.6 and 19.7 eV correspond to the sharp structures $v$ and $w$ in Au. The line shape is a sum of contributions not dominated by $\Gamma$, but by analogy with Au, the net peak separation is slightly less than the difference in initial state separation, i.e., of $\Gamma(2,3)$ and $\Gamma(4)$. The final states are estimated to be 14.9 eV above the Fermi level.

Knapp et al.\textsuperscript{17} have measured the lifetime widths of one band of excited states in Cu by photoemission. They find that the $\Delta$, band, a free-electron like band, increases in width from 1 to 2 eV in the region from 10 to 20 eV above the Fermi energy, a width larger than some of the spectral features we have measured for Au. Since the lowest excited state we consider, $\Gamma^\prime_2$, can decay only into states of lower energy, i.e., into the free-electron-like states below it, our narrow width implies that there can be measurable effects of selection rules in electron-electron scattering, i.e., states with large $f$ components are scattered less

![Fig. 3](image_url)
than predominately s-p-like states, a complication not often considered. This merits theoretical investigation. The widths of some 3d-band hole states in Cu have been measured as well.\textsuperscript{17,18} Our data support the narrower widths.\textsuperscript{19} Recent photoemission measurements\textsuperscript{20} on Ag also show that excited electrons tend to become "trapped" at a minimum in a flat band about 17.5 eV above $E_F$, an excited band with a lifetime longer than states below or above it.

We have not attempted a detailed assignment of all structures in the spectra. As we have shown, for a limited energy range and a limited volume of $k$ space, there is an overwhelming number of critical points not confined to symmetry points. Additionally (fortuitously, not for Au) the energy separation between critical points is sufficiently small that high-resolution spectra are not possible. However, the systematics of the spectra are informative. The dominant structures in the (20-25)-eV range appear to be due to critical points near $\Gamma$. [Recent reflectance measurements on Au resolve structures in the (18-30)-eV range when differentiated, but they are assigned principally to transitions away from $\Gamma$, perhaps at the Brillouin-zone boundary.\textsuperscript{21}] In general, the agreement with calculated band structures is excellent. Taking the $\Gamma'(2,3) - \Gamma(7)$ and $\Gamma(4) - \Gamma(7)$ doublet as an example, we see that in Au, Ag, and Cu the calculations and experiment agree to within our ability to assign the location of the $\Gamma$ contribution to the line shape. In Pd our best fit places $\Gamma(7)$ at $18.0 \pm 0.2$ eV while the calculated position is 17.7 eV. This fit is within the uncertainty of the value of $18.4 \pm 0.5$ eV from angle-resolved photoemission.\textsuperscript{22} The agreement for the energy of $\Gamma(7)$ in Ag is also consistent with angle-resolved photoemission data.\textsuperscript{19} $\Gamma(7)$ has not been calculated for Pt, but we place it at 14.9 eV, consistent with photoemission data.\textsuperscript{22} For Au, recent photoemission measurements along $\Delta$ place the calculated band $A(7)$ too low by about 3.5 eV near the center of the $\Lambda$ line.\textsuperscript{23} Our interpretation, involving $\Lambda$ critical points much closer to $\Gamma$ would not allow such a rigid upward shift.

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