Splitting of the interband absorption edge in Au: Temperature dependence

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(Received 31 March 1975)

The optical absorption spectra of bulk gold were measured polarimetrically at 90, 295, and 725 K in the 1.0–3.5-eV region. The experimental data have been fitted using a model calculation which accounts for the temperature-induced smearing of the Fermi surface. The optical gaps and the interband matrix elements for the d-bands to Fermi-surface transitions near X and L have been determined as a function of temperature. The present data show that the parabolic shape of the absorption edge, which has been reported to extend to 3.5 eV, is largely coincidental for photon energies above 2.65 eV. Rather a tentative analysis suggests that the transitions in the vicinity of L lose their dominant importance in shaping the absorption edge above 2.65 eV.

In a recent paper[1] we have shown that the absorption edge of gold has a composite nature, being the superposition of contributions due to transitions near the X and L points in the Brillouin zone (BZ). The interband onset, located at 1.94 eV at 295 K, results from d-band to Fermi-surface transitions in the vicinity of X. The shape of this absorption was completely accounted for on topological grounds. A fitting of the over-all absorption edge was also presented, using a model calculation recently developed by one of the present authors.[2–4] The precision with which the optical gaps can be determined with this procedure compares favorably with the best results of modulation spectroscopy. The fitting also yields good estimates of the dipole matrix elements for X and L transitions. Therefore the same approach is presently extended to the optical spectra of gold taken at lower and higher temperatures, so as to obtain the complete temperature dependence of these optical parameters.

Figure 1 shows the imaginary part of the dielectric constant ϵ_2 for temperatures of 90, 295, and 725 K in the 1.0–3.5-eV photon energy region. The measurements were taken using the method of Beattie.[5] The experimental setup and sample preparation were described before[1]; a more detailed exposition will be published elsewhere.[6]

The fitting procedure has been reported a number of times[1,4] and will not be repeated here. The parameters which can be varied are the effective temperature T^*,[7] the transition strengths[7] for X and L transitions, and the gaps $\hbar\omega_L$ and $\hbar\omega_X$, which mark the onset of the L and X transitions.

Figure 2 shows the results obtained by fitting the interband contribution to ϵ_2. The intraband contribution has been subtracted from the experimental spectra assuming a Drude-like behavior.[8] The 295-K results have already been published[1] and are included for completeness. Table I gives the parameters used at each temperature. The accuracy of the optical gaps is estimated to be 0.01 eV for $\hbar\omega_L$ and 0.02 eV for $\hbar\omega_X$. The larger error in $\hbar\omega_X$ is due to a more marked sensitivity of this gap to the detail of the Drude subtraction.

The effective temperature is consistently higher than the actual one. It seems plausible to infer that some smearing mechanism other than temperature is effective at the Fermi surface.[9] Whether

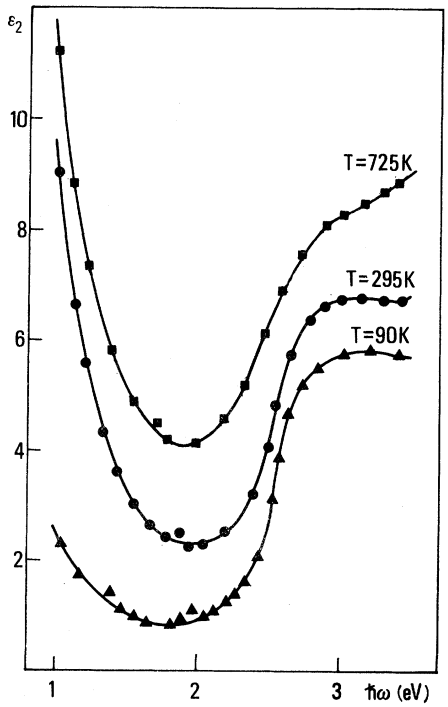

FIG. 1. Imaginary part of the dielectric constant for Au in the 90–725-K temperature range. The values on the ϵ_2 axis refer only to Au at 90 K, the curves for other temperatures are successively displaced upwards by $\epsilon_2 = 1$.

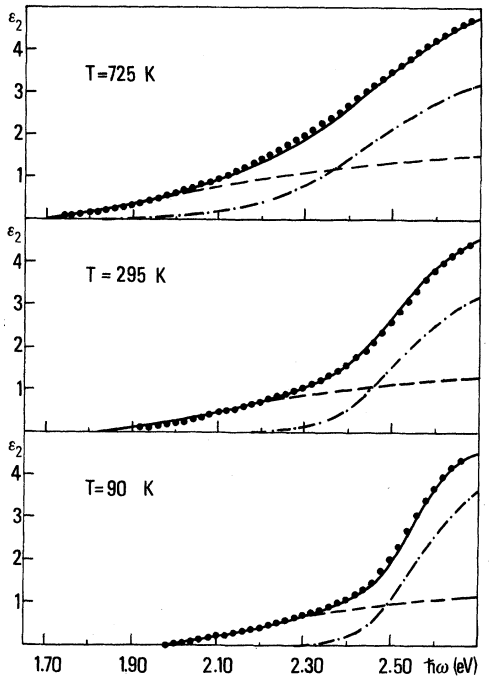

FIG. 2. Interband contribution of the dielectric constant ϵ_2 for Au at different temperatures: ●●● experimental; – – – X-transitions contribution; -·-·- L-transitions contribution; —— total theoretical.

the interband onset of transitions near L is temperature dependent is widely disputed.[10–15] Our results indicate a slight but definite decrease of the onset energy on going from 90 to 725 K.

Theory predicts that as the temperature is raised, the top of the d band is lowered. From their relativistic band calculations for normal and expanded lattices Christensen and Seraphin[16] found that the energy gap between the upper d band at $L_{5^+6^+}$ and the "muffin-tin zero" decreases by 0.40 eV on increasing the lattice constant by 0.1 a.u. (equivalent to a temperature increase of 920 K). Christensen[17] also calculated that under these circumstances the Fermi energy (with respect to the same zero) shifts from 7.21 to 6.76 eV, i.e., a decrease of 0.45 eV. The shift of E_F is, therefore, almost compensated for by the simultaneous displacement of the top of the d band such that the calculated shift of the absorption theshold is -0.05 eV or about -0.5×10^{-4} eV/K. This figure should be compared with our value of -1.7×10^{-4} eV/K.

Szczepanek and Glosser[18] determined a hydrostatic deformation potential of -0.8 eV for this energy gap, which would be equivalent to about -0.3×10^{-4} eV/K. This experimental evaluation, however, does not include the contribution of electron-phonon interaction.

This shift of the d band to Fermi surface transitions near X is much more pronounced. This greater temperature dependence is somewhat surprising. Christensen and Seraphin[16] found that on dilation the calculated energy of the fifth band at X falls by 0.43 eV. Given the fall of 0.45 eV in the Fermi energy, a considerably smaller change in $\hbar\omega_X$ with respect to $\hbar\omega_L$ would be expected. Unfortunately, no other experimental data exist in the literature concerning the temperature dependence of the X transitions so that no other comparison is possible at present.

It should be noted that our procedure allows a quantitative determination of the interband matrix elements and of their temperature dependence. Table I shows that the matrix element for the L transitions drops steadily on increasing the temperature, while the matrix element for the X transitions is virtually temperature independent. For[19] Al and[20] Cu the Debye-Waller factor has been shown

TABLE I. Parameters used for fitting the interband contribution to ϵ_2 at different temperatures. T is the real temperature and T^* the effective temperature.

T (K)	T^* (K)	$\hbar\omega_L$ (eV)	$\hbar\omega_X$ (eV)	$\lvert P_L\rvert^2$ (arb. units)	$\lvert P_X\rvert^2$ (arb. units)
90	450	2.50	2.04	2.70	0.80
295	600	2.45	1.94	2.04	0.80
725	1050	2.39	1.84	1.98	0.80

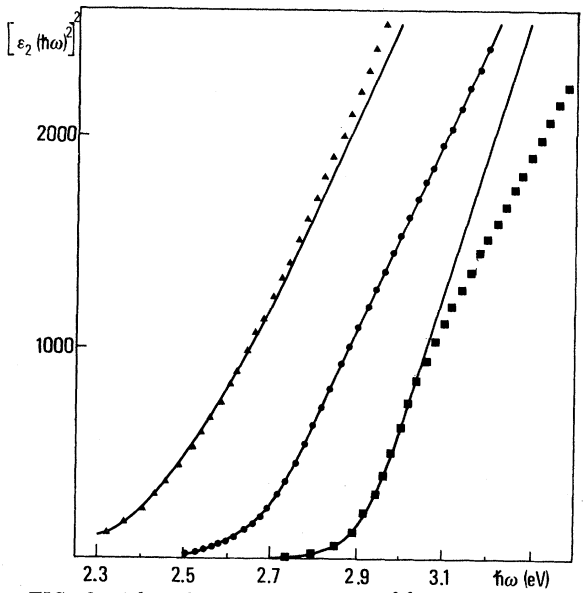

FIG. 3. Plot of the function $[\epsilon_2(\hbar\omega)^2]^2$ vs $\hbar\omega$ for T = 725 K (▲), 295 K (●), and 90 K (■). The full line gives the results of the theoretical fit. The values on the energy axis refer only to the 725 K data, the curves for other temperatures are successively displaced to the right by $\hbar\omega = 0.2$ eV.

to be responsible for the temperature dependence of the strength of interband absorption and a possible alternative mechanism has been proposed for Ag.[4] However, we feel that a very extensive calculation of the influence of electron-phonon interaction on the dipole matrix elements would be needed to clarify this effect.

An interesting feature of the absorption edge can be shown by plotting $[\epsilon_2(\hbar\omega)^2]^2$ as a function of photon energy. Nilsson *et al.*[21] and Thèye[22] found that in such a plot their room-temperature data could be fitted by a straight line up to 3.5 eV, thus indicating a parabolic absorption edge. As may be seen from Fig. 3, this is confirmed by our room-temperature data. However, the high- and low-temperature data suggest that such a straight-line fit extending beyond 2.65 eV is largely coincidental. Whereas up to about 2.65 eV all data are well described by a linear relationship, above this photon energy the 725-K data deviate upwards while the 90-K data deviate downwards.

Although at photon energies higher than 2.65 eV our model may collapse for several reasons,[23] we may speculatively attempt an interpretation of this behavior. Szczepanek and Glosser,[18] in strain optic spectra on Au single crystals, identify a narrow L contribution in the 2.40–2.65-eV energy region. Thus it may reasonably be assumed that the L contribution to the total absorption levels off at 2.65 eV or—maybe more appropriately—the transitions occur in regions so far removed from L that they lose their typical L-like character. The spectra in Fig. 3 can now be understood if one accepts the existence of a second X (X-like) contribution, the magnitude of which increases fairly rapidly at these photon energies.[24] At room temperature these various contributions add up to shape the virtually parabolic absorption edge (i.e., straight line in Fig. 3) extending to above 3.2 eV. However, on lowering the temperature the L contribution strength increases relative to that of the X transitions causing the knee to appear in the 90 K data in Fig. 3. At high temperature, on the other hand, the lowering of the L contribution reveals the additional X contribution to the absorption in the form of an upward deviation in Fig. 3.

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*Part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.) supported by the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Ondersoek (Z.W.O.) and by the Centrale Organisatie voor Toegepast-Natuurwetenschappelijk Onderzoek (T.N.O.) (Metaal institut).

†Gruppo Nazionale di Struttura della Materia of the Consiglio Nazionale delle Ricerche.

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[7]For a discussion and definition of the parameters involved see Refs. 1, 3, and 4.

[8]For the 90-K data it was necessary to introduce an energy-dependent relaxation time, while at the higher temperatures this correction is unessential. A thorough discussion of the intraband part of the spectra and details on the intraband parameters can be found in P. Winsemius, Ph.D. thesis (University of Leiden, 1973) (unpublished), available upon request.

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[24]This assumption is confirmed by piezomodulation data. See Ref. 18 and P. S. Szczepanek, thesis (University of Maryland, 1973), Tech. Rept. 73-123, p. 112, Fig. 6-5).