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Wavelength Modulation Spectra of Single Crystals of Silver and Gold

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ABSTRACT

The logarithmic derivative of the reflectivity is measured for Ag and Au for $2.0 \leqslant \hbar\omega \leqslant 6.0$ eV at T = 5, 80, and 300K. The results are compared with a calculated spectrum.

In this letter we present experimental and theoretical wavelength modulation spectra for Ag and Au from 2.0 to 6.0 eV. Measurements were done on electropolished samples. The results are shown in Figs. 1a and 2a respectively for Ag and Au at 5 and 300K. The spectra at 80K are not very different from those at 5K.

As in the case of Cu,[1] the structure in the measured derivative spectra for Ag and Au can be identified by comparison with a theoretical spectra based on a band structure calculation using the empirical pseudopotential method.[2] The four local pseudopotential form factors and the four parameters relating to the $\ell = 2$ nonlocal pseudopotential (see TAble I) are determined by fitting the density of states for these materials which was measured

by Smith.[3] To calculate the logarithmic derivative reflectivity, $R'(\omega)/R(\omega)$, we first calculate the imaginary part of the dielectric function $\varepsilon_2(\omega)$ for interband transitions by using wavefunctions including core effects.[1] The important core states (4s and 4p for Ag; 5s and 5p for Au) are approximated by hydrogenic wavefunctions with an effective atomic number, Z_{eff}. For Ag, we use $Z_{eff} = 17.5$ and for Au, $Z_{eff} = 16$. To the interband dielectric function, we add the free-electron contribution, $\varepsilon^f(\omega)$; since the electron lifetime is of the order of 10^{-14} sec[4] for Ag and Au, the imaginary part of $\varepsilon^f(\omega)$ can be neglected. We use $m^* = 1.09\ m_o$ for Ag and $m^* = 1.38\ m_o$ for Au.

The results of the calculated and measured $R'(\omega)/R(\omega)$ for Ag and Au are plotted in Figs. 1 and 2 respectively. For Ag, the calculated interband transitions start at 3.99 eV. Most of the transitions come from states near the Δ point in the Brillouin zone between the 4th and 5th bands and the Fermi surface. Core contributions to the dipole matrix elements enhance the interband $\varepsilon_2(\omega)$ which when combined with ε^f yield the strong dip in this region of $R'(\omega)/R(\omega)$. The difference in the position of this dip between theory and experiment is 0.22 eV. This could have been improved if we had fit the pseudopotential parameters to $R'(\omega)/R(\omega)$ instead of photoemission measurements. The calculated $R'(\omega)/R(\omega)$ shows some structure in the region $\hbar\omega \approx 4.3$ eV. From the critical point, (c.p.) analysis, there is an M_o type c.p. from $L_{2'} \rightarrow L_1^u$ transitions at 4.27 eV. These transitions are strengthened by the transitions inside the Brillouin zone. The corresponding experimental curve does have a hint of structure and there is a flattening of the $R'(\omega)/R(\omega)$ in this region of photon energy. The zero of $R'(\omega)/R(\omega)$ at

photon energy higher than 4.5 eV is at 4.55 eV in the experimental result while the theoretical result gives the corresponding zero at 4.7 eV. Both the measured and the calculated $R'(\omega)/R(\omega)$ do not exhibit any pronounced structure for photon energy between 5.0 and 6.0 eV. The c.p. analysis show that there is an M_1 c.p. at X from $X_5 \rightarrow X_{4'}$ transitions at $\hbar\omega = 5.54$ eV. However, there is not much contribution from the transitions within the Brillouin zone to strengthen this critical point.

For Au, the general structure of the experimental and calculated $R'(\omega)/R(\omega)$ agrees quite well. For the theoretical curve, the interband transitions starting at 2.3 eV, come from Δ with final states on the Fermi surface. As in the case of Ag, the strong dip in $R'(\omega)/R(\omega)$ at 2.55 eV arises from the onset of interband transitions and from $\varepsilon^f(\omega)$. Experimentally, the dip occurs at 2.5 eV. The "shallow" zero of the calculated $R'(\omega)/R(\omega)$ at 3.3 eV comes from a large volume effect while an M_1 c.p. from bands $5 \rightarrow 6$ at X gives rise to the zero in $R'(\omega)/R(\omega)$ at 4.05 eV; the corresponding zero in the experimental curve is at 3.8 eV. The structure beyond 5.0 eV in the theoretical curve arises from a volume effect of $2 \rightarrow 6$ transitions. Since we have taken a rather coarse mesh for the $\varepsilon_2(\omega)$ calculation, volume effects are emphasized. We believe this is why the structure near 3.3 and 5.3 eV in the theoretical curve is not apparent in the measured $R'(\omega)/R(\omega)$.

In conclusion, the main structure in the measured and the calculated curves agree to around 0.2 eV. This effective mass for Ag is determined to be 1.09 m_o; this value is in good agreement with the estimate of Ehrenreich et al.[5] of $(1.03 \pm 0.06)m_o$. For Au, we used an effective mass of 1.38 m_o, similar to that for Cu. This value is in disagreement

with the value 1.04 m_o obtained by Cooper, Ehrenreich, and Philipp.[6]

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TABLE CAPTION

Table I. Pseudopotential parameters for Ag and Au.

FIGURE CAPTIONS

Fig. 1. The measured and the calculated $R'(\omega)/R(\omega)$ for Ag.

Fig. 2. The measured and the calculated $R'(\omega)/R(\omega)$ for Au.

Table I

Pseudopotential Parameters	Ag	Au
$V(G^2=3)$	0.022 ryd.	0.0031 ryd
$V(4)$	0.023	0.0089
$V(8)$	0.0362	0.0362
$V(11)$	0.0162	0.0339
A_2	-8.4610	-5.2164
R_S	0.9447Å	1.059Å
α	0.43	0.292
κ	$2.08(2\pi/a)$	$2.53(2\pi/a)$
k_F	$2.4Å^{-1}$	$2.4Å^{-1}$
a(lattice constant)	4.08Å	4.08Å

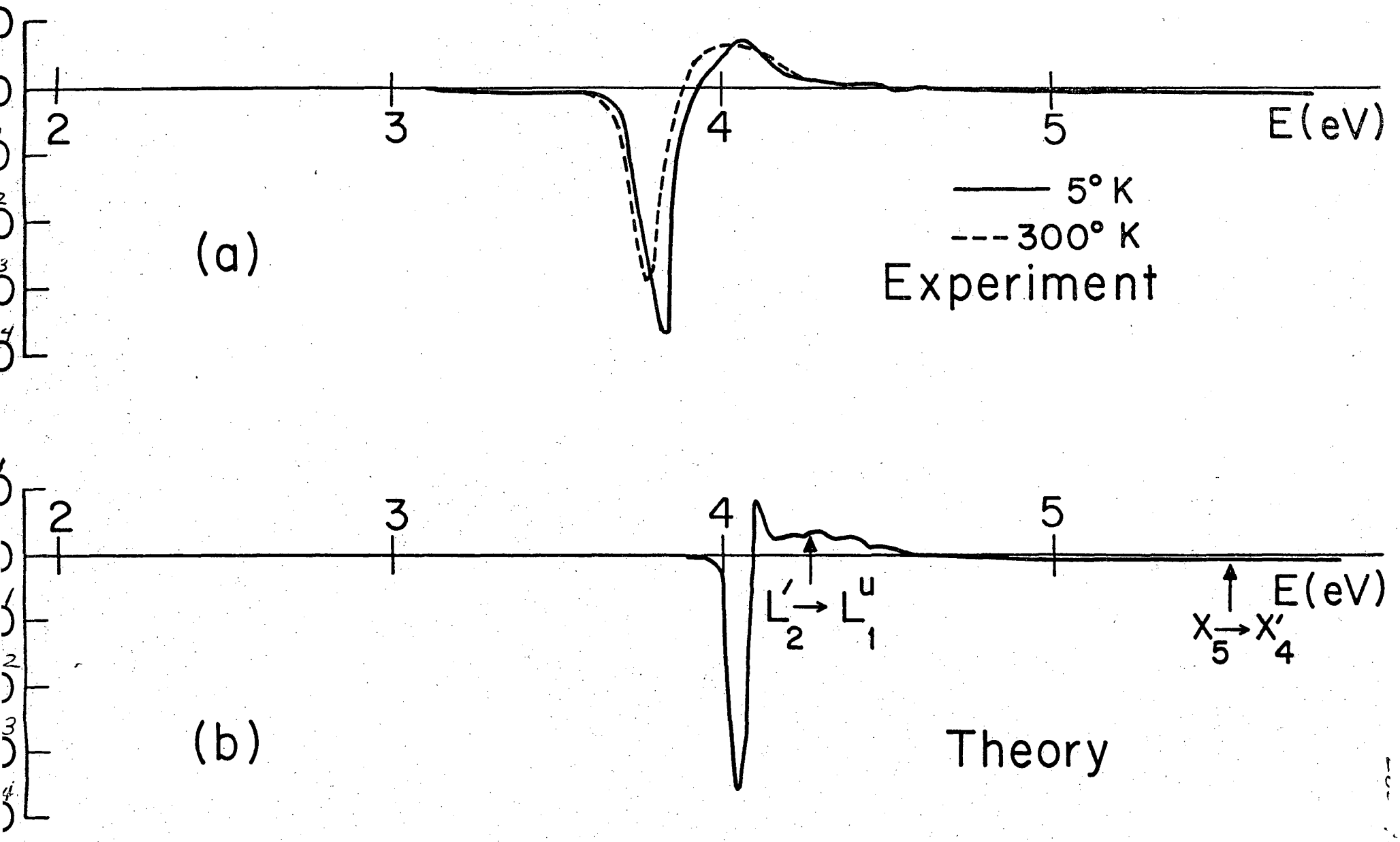
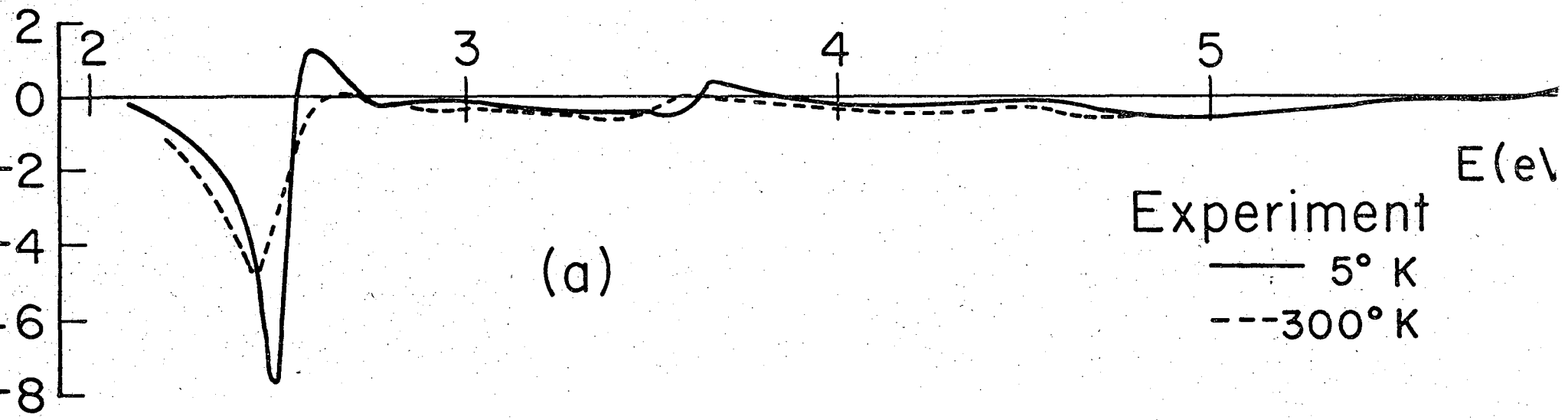

2
3
4
5
E(eV)
5° K
300° K
(a)
Experiment
2
3
4
5
E(eV)
$L_2' \rightarrow L_1^u$
$X_5 \rightarrow X_4'$
(b)
Theory

fig 1


2
0
-2
-4
-6
-8
2
3
4
5
E(eV
Experiment
5° K
300° K
(a)

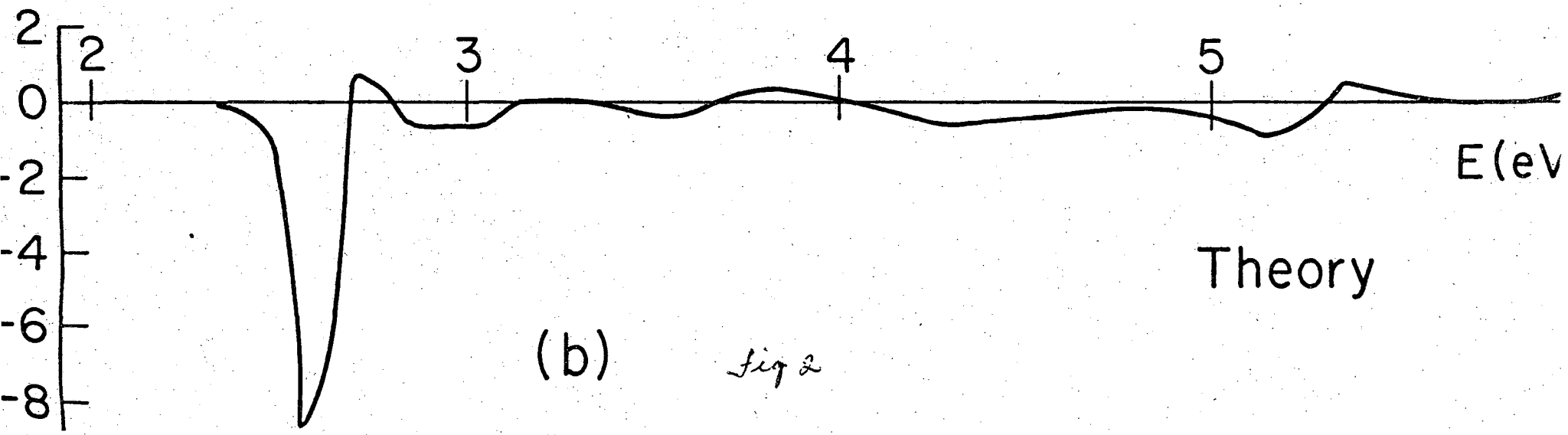

2
0
-2
-4
-6
-8
2
3
4
5
E(eV
Theory
(b)

fig 2

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