Thermoreflectance of Ag single crystals*

E. Colavita, S. Modesti, and R. Rosei
Istituto di Fisica dell'Universitá di Roma, Roma, Italy
(Received 15 March 1976)

Thermoreflectance measurements of single-crystal Ag have been performed at room temperature in order to solve some discrepancies in the position and attribution of optical gaps, which have arisen in the recent literature. An extension of a previous theoretical model allows a very detailed fit of the experimental data and elucidates completely the origin of optical structures.

I. INTRODUCTION

The optical properties of Ag (as well as of the other noble metals) have received much attention in the last decade[1] and seemed to have reached a satisfactory understanding.[2] Important theoretical work,[3] however, as well as recent work on some silver alloys,[4] suggests that the onset of the $L_2'(E_F)$ $-L_1$ optical transitions in pure Ag should occur at about 3.35 eV instead of at 3.87 eV as suggested by very-low-temperature thermomodulation measurements[2] and by precise photoemission data.[5] Some limits to the precision and sensitivity of the thermomodulation experiment were set in Ref. 2 by the authors themselves on recognizing that very-low-temperature data taken on thin films may be influenced by strains and imperfections in the films. It was confirmed later[6] that for fine optical work, very carefully prepared strain-free bulk samples of metals are always superior to the best evaporated films.[7]

In view of these uncertainties, we decided to reanalyze the situation by using thermoreflectance measurements on *single-crystal* silver.

In Sec. II we give a brief outline of the experimental arrangement and present the data we have obtained. The theoretical model used to analyze our data is outlined in Sec. III with a discussion of the results.

II. EXPERIMENTAL SETUP AND RESULTS

The experimental setup we have used is rather conventional,[8] so that only a brief sketch is given here. A single section of a D330 Hilgher and Watts monochromator gave monochromatized light from a deuterium discharge lamp and an RCA 1P28 photomultipler detected the light reflected from the sample. The sample holder, clamped on the cold finger of a cryostat, was a thin slab of silicon on which a film of chromium had been evaporated. The sample was fastened on top of the chromium film with vacuum grease and was heated indirectly by a 2-Hz current square wave dissipated in the chromium film. A careful study of the thermal behavior showed that two different time constants of about 100 and 1000 sec govern the temporal phenomena.[9] With 6.6 W of peak power in the heater, the average temperature increase of the sample was measured to be 43 °C at room temperature while the peak to peak amplitude of the temperature wave on the sample surface has been found to be 0.25 ± 0.05 °C.

The optical modulated data were taken point by point with the light level in the photomultiplier held constant, and digital integration of the lock-in amplifier output was used to reduce the statistical uncertainties.

The samples used in this study were the same which were used in a recent and very accurate electroreflectance experiment[10] and the sample preparation followed closely the same pattern.[11]

The room-temperature[12] spectrum of the differential reflectivity $\Delta R/R$ for a peak power input of 6.6 W in the indirect heater, is shown in Fig. 1. It should be noticed that while the main structure with a negative peak at 3.78 eV and a positive peak

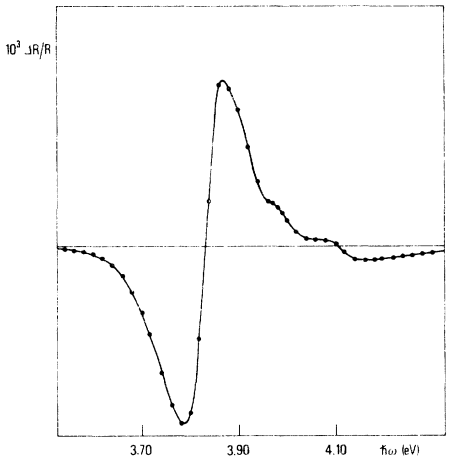

FIG. 1. Thermoreflection spectrum of Ag single crystal. Peak power 6.6 W ($T = 340$ K).

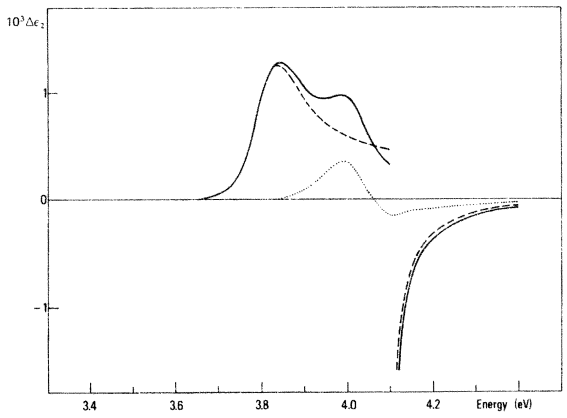

FIG. 2. Theoretical $\Delta\epsilon_2$ of Ag: dashed line, contribution of the $L_2'(E_F)$-L_1 transition (via deformation potential mechanism); dotted line, contribution of the L_3-$L_2'(E_F)$ transition (via Fermi distribution function smearing mechanism); solid line, total.

at 3.87 eV is very well known,[13] the shoulder at 3.98 eV and the downward step at about 4.11 eV are new. These new features confirm at the outset that thin-film samples are dangerous to use because interesting structures may be washed out. No thermomodulation signal has been detected below 3.60 eV down to about 3.00 eV.

III. THEORETICAL MODEL AND DISCUSSION

For analyzing our data we have resorted to an extended version of the model used in Ref. 2. The original version of the model[14] considers only Fermi surface involving optical transitions so that it is only suitable for line-shape analysis of very-low-temperature thermomodulation data. At room temperature, modulation mechanisms other than Fermi distribution smearing may become important[15]: the shift of energy levels via their deformation potential[16] may even become the dominant mechanism.[17]

Using the deformation potentials determined from a fit[18] of $\epsilon_2(\hbar\omega)$ spectra of Ag bulk samples at different temperatures,[19] a preliminary study[17] has shown that the L_3-$L_2'(E_F)$ transitions contribute to room-temperature thermomodulation spectra in Ag predominantly via the Fermi distribution smearing mechanism (FDSM). Therefore the contribution of the L_3-$L_2'(E_F)$ transitions to the variation of the imaginary part of the dielectric constant $\Delta\epsilon_2$ has been calculated using the model of Ref. 14 without modifications[20]:

$$\Delta\epsilon_2^{d\to p}{}_{\rm FDSM}(\hbar\omega,T)=\frac{8\pi^2e^2\hbar^4}{3m^2}\frac{|P(d\to p)|^2}{(\hbar\omega)^2}\left[\int \mathfrak{D}(E,\hbar\omega,\hbar\omega_{2'},\hbar\omega_3)\left(-\frac{\partial f(E,T)}{\partial T}\right)dE\right]\Delta T\ , \tag{1}$$

where $|P(d\to p)|^2$ is the square of the dipole matrix element of the L_3-$L_2'(E_F)$ transition,[21] ΔT is the amplitude of the temperature modulation, and $f(E,T)$ is the Fermi distribution function. The function $\mathfrak{D}(E,\hbar\omega)$ is the energy distribution of the joint density of states and its explicit dependence from the energy positions of the levels L_3 and L_2' (denoted by $\hbar\omega_3$ and $\hbar\omega_{2'}$) is given in Ref. 14.

The $L_2'(E_F)$-L_1 transitions have a particularly high deformation potential[18,19] and the temperature-induced shift of the bands provides the strongest effect of the thermomodulation signal[17] (by more than an order of magnitude). This contribution has been calculated using an extension of the model which in practice performs the calculation[20]

$$\Delta\epsilon_2{}^{p\to s}_{\rm DPM}(\hbar\omega,T)=\frac{8\pi^2e^2\hbar^4}{3m^2}\frac{|P(p\to s)|^2}{(\hbar\omega)^2}\Delta T\int f(E,T)\frac{\partial}{\partial T}\mathfrak{D}(E,\hbar\omega,\hbar\omega_{2'}(T),\hbar\omega_1(T))dE, \tag{2}$$

where the subscript DPM stands for deformation potential mechanism. Here again $\hbar\omega_{2'}$ and $\hbar\omega_1$ give the energy position of the L_2' and L_1 levels, respectively. Their temperature dependence is explicitly shown to emphasize the fact that also their deformation potentials are involved in the calculation.

Figure 2 gives the theoretical $\Delta\epsilon_2$ spectrum and shows also separately the individual contributions of the L_3-$L_2'(E_F)$ and $L_2'(E_F)$-L_1 transitions.

The values of the parameters introduced in the calculation are the same which give the best fit of the experimental $\Delta R/R$ spectrum (see below) and are reported in Tables I and II.

The strong negative spike at 4.11 eV originates from the M_2 critical point L_2'-L_1 and is especially prominent because no broadening parameter[20] has been introduced in the calculation.

For a direct comparison of the experimental results with the theoretical model, we have to deal with homogeneous sets of data. We have therefore Kramers-Kronig analyzed our $\Delta\epsilon_2$ spectra to get the variation of the real part of the dielectric constant $\Delta\epsilon_1$. The "theoretical" differential reflectivity spectrum is then given by[8]

$$\Delta R/R=\alpha\Delta\epsilon_1+\beta\Delta\epsilon_2\ . \tag{3}$$

TABLE I. Dipole matrix elements and deformation potentials obtained from Ref. 18. They have been kept fixed in the fit of the experimental data.

$\lvert P(d\rightarrow p)\rvert^2$ (a.u.)	$\frac{\partial}{\partial T}\hbar\omega_1(T)\left(\frac{\text{eV}}{\text{K}}\right)$	$\lvert P(p\rightarrow s)\rvert^2$ (a.u.)	$\frac{\partial}{\partial T}\hbar\omega_2'(T)\left(\frac{\text{eV}}{\text{K}}\right)$
1.51	-0.68×10^{-3}	2.02	$+0.11\times10^{-3}$

The functions α and β (Seraphin's coefficients) were calculated using the room-temperature optical constants given by Winsemius.[22]

The parameters which can be varied to fit the experimental data with our theoretical model are those reported in Tables I and II. We have, however, some constraints which should be taken into account: A previous work[18] has already determined the optical gaps, dipole matrix elements, and deformation potentials of the transitions involved, at three different high temperatures (578, 688, and 773 K). We have therefore kept fixed several parameters (which we report in Table I). The deformation potentials we used were the same already determined[18] while the squares of the dipole matrix elements where obtained extrapolating down to 340 K the values of Ref. 18. For T and ΔT we have used the values determined experimentally.

The optical gaps were used as adjustable parameters and we report the values for which we obtained the best match between the experimental and theoretical differential reflectivity spectra in Table II. Also reported for comparison are the values obtained by other authors. The results we have obtained are shown in Fig. 3. Our good results seem to establish firmly our attribution of optical transitions in Ag and the nature of their contribution to thermomodulation spectra. An analysis of the individual contributions shows that the prominent structure comes almost entirely from the $p\rightarrow s$ transitions while the shoulder at 3.98 eV has to be ascribed to the $d\rightarrow p$ transitions. The critical point structure at 4.11 eV is still evident in the theoretical $\Delta R/R$ spectrum but its prominence has been dramatically reduced by the modulation introduced by the Seraphin's coefficients.

In Fig. 4 we report the energy position of the optical gaps as a function of temperature. The straight lines through the previously determined values[18] have been extrapolated to lower temperature (dashed lines) and the empty symbols show the values determined in this work. The results are very good and the internal consistency of our model can be appreciated considering that the highest deviation from the "predicted" value [for the $L_2'(E_F)$ $-L_1$ optical gap] is only 0.04 eV. The values of the gaps at 15 K determined in Ref. 2 would fall outside the extrapolated lines. This is to be expected, however, because the deformation potentials below room temperature become progressively smaller and go to zero at very low temperature.

Chen and Segall[23,24] have used recently an effective mass expansion model to fit very accurately both piezomodulation[25] and photoemission data[5] using the same set of optical parameters. The values of the optical gaps determined in our work are in substantial agreement with their values as well as with the values determined by various authors with different techniques if it is taken into account that our measurements were taken at slightly higher temperature (see Table II). It should also be noted that the value we have used for the deformation potential of the gap L_2'-L_1 is

TABLE II. Literature review of the optical gaps near L in Ag. The values determined in the present work are reported in the last line.

Reference	Source	Temperature	L_3-$L_2'(E_F)$ (eV)	$L_2'(E_F)$-L_1 (eV)	L_2'-L_1 (eV)
Rosei[2]	Low temp. thermomod.	15 K	4.03	3.87	4.16
Christensen[3]	RAPW calculation		3.98	3.3	3.48
Flaten[4]	Optical prop. Ag alloys	Room temp. (RT)	•••	3.3	•••
Walldén[5]	Photoemission	RT	•••	3.80	4.17
Liljenvall[19]	T- dependence opt. prop.	RT	•••	•••	4.14
Winsemius[22]	Ellipsometry	RT	3.98	3.86	4.11
Chen[24]	Fit piezomod. data	RT	•••	3.87	4.20
Segall[23]	Fit photoem. data	RT	•••	3.87	4.20
Becker[26]	Angular- resolved photoem.	RT	3.98	3.89	4.18
Morris[27]	Piezorefl. Ag alloys	RT	•••	4.07	4.15
This work	Thermomod. single crystal	340 K	4.02	3.81	4.11

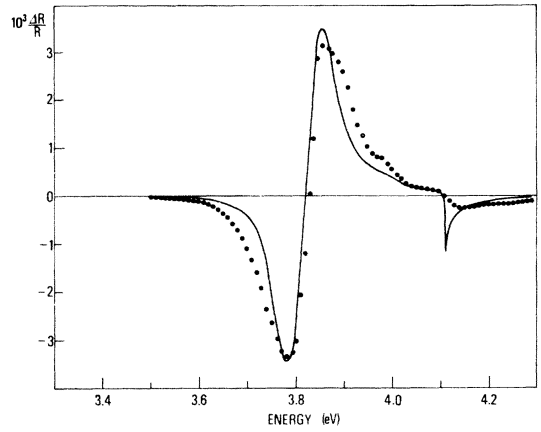

FIG. 3. Thermoreflection spectra of Ag. Circles, experimental (~340 K); solid line, theoretical.

in very good agreement with the value determined by Liljenvall *et al.*,[19] and Wallden *et al.*[5] with photoemission techniques.

Our results definitely show that the onset of the $L_2'(E_F)$-L_1 transitions has to be placed at 3.81 eV at about room temperature (340 K).

It seems ascertained therefore that both Christensen's relativistic-augmented-plane-wave (RAPW) calculation and Stern's results on AgCd alloys place the L_1 s-like level about 0.5 eV below its real position.

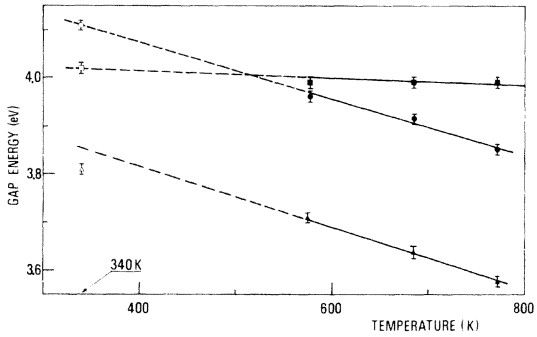

FIG. 4. Temperature dependence of optical gaps. L_3-$L_2'(E_F)$: ■, Ref. 18; □, this work. L_2'-L_1: ●, Ref. 18; ○, this work. $L_2'(E_F)$-L_1: ▲, Ref. 18; △, this work.

It is hoped that some further theoretical effort would be undertaken to see whether the RAPW determination of this important optical gap can be reconciled with the experimental results.

At present thermomodulation measurements on very dilute Ag alloys are under way in our laboratory, to discover the origin of the discrepancy with Stern's results.

ACKNOWLEDGMENTS

We thank Dr. J. E. Furtak for providing us with one of his samples. We thank also S. Rinaldi for continuous technical help.

*Work supported by the Gruppo Nazionale di Struttura della Materia of the Consiglio Nazionale delle Ricerche, Sezione di Roma.

[1]P. O. Nilsson, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1974), Vol. 29.

[2]R. Rosei, C. H. Culp, and J. H. Weaver, Phys. Rev. B 10, 484 (1974), and references therein.

[3]N. E. Christensen, Phys. Status Solidi B 54, 551 (1972).

[4]C. J. Flaten and E. A. Stern, Phys. Rev. B 11, 638 (1975).

[5]L. Wallden and T. Gustafsson, Phys. Scr. 6, 73 (1972).

[6]M. Guerrisi, P. Winsemius and R. Rosei, Phys. Rev. B 12, 557 (1975).

[7]M. L. Thèye, Phys. Rev. B 2, 3060 (1970).

[8]M. Cardona, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Suppl. 11.

[9]The details of this study and the optimization of the thermal system will appear elsewhere.

[10]T. E. Furtak and D. W. Lynch, Phys. Rev. Lett. 35, 960 (1975).

[11]T. E. Furtak, Ph.D. thesis (Iowa State University, 1975) (unpublished).

[12]The actual temperature of the sample surface was ~340 K.

[13]G. Baldini and N. Nobile, Solid State Commun. 8, 7 (1970), and Ref. 2.

[14]R. Rosei, Phys. Rev. B 10. 474 (1974).

[15]R. Rosei and D. W. Lynch, Phys. Rev. B 5, 3883 (1972).

[16]In this paper "deformation potential" is defined as the change in a band energy per unit change of the modulation parameter (temperature).

[17]E. Colavita, thesis (University of Rome, 1975) (unpublished).

[18]F. Antonangeli, E. Colavita, R. Rosei, and S. Salusti, Nuovo Cimento B 24, 121 (1974).

[19]H. G. Liljenvall and A. G. Mathewson, J. Phys. C 3, 341 (1970).

[20]The reader is referred to Ref. 2, 14, and 18 for the details of calculation and for a discussion of the parameters involved and approximations used.

[21]The temperature dependence of $|P(d \rightarrow p)|^2$ has been neglected.

[22]P. Winsemius, Ph.D. thesis (University of Leiden, 1973) (unpublished), and private communication.

[23]B. Segall and A. B. Chen, Solid State Commun. 17, 1557 (1975).

[24]A. B. Chen and B. Segall, Solid State Commun. 18, 149 (1976).

[25]P. O. Nilsson and B. Sandell, Solid State Commun. 8, 721 (1970).

[26]H. Becker, E. Dietz, U. Gerhardt, and H. Angermüller, Phys. Rev. B 12, 2084 (1975).

[27]C. E. Morris, D. W. Lynch, Phys. Rev. 182, 719 (1969).