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TEMPERATURE-MODULATED REFLECTANCE OF GOLD FROM 2 TO 10 eV

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The temperature-modulated reflectance, $\Delta R/R$, of gold films has been measured from 2 to 10 eV. The range of modulated reflectance experiments is thus extended into the vacuum ultraviolet. The observed structure, which is much more complex than the conventional reflectance spectra, is of considerable significance to band-structure studies.

The results to be presented in this paper indicate that a recently reported method of modulating the reflectance of semiconductors[1] is a very sensitive way of studying the optical properties of metals. In this technique a pulsed electric current is passed through a sample while synchronously detecting the modulated reflectance $\Delta R/R$. The method has some obvious experimental advantages over the electroreflectance method[2,3] in that (1) the photon energy limit is not restricted by absorption in the electrolyte or electrode; (2) the sample may be cooled to lower temperatures; and (3) there is no possible chemical reaction with an electrolyte. Its advantages over the piezoreflectance method[4] are not as pronounced except that it may be experimentally simpler, particularly for low-temperature work. It appears to be as sensitive, on the basis of published results.[4] As the discussion to be presented will show, each technique offers different information and all methods should be used in order to be able to understand best the band structure of solids.

This paper presents results for gold, one of the noble metals which are of particular interest since there is considerable discussion about the interpretation of optical measurements and photoemission results and their relation to the band structure.[5] Experimentally, the films are easy to prepare and are stable against oxidation.

The gold films, about 2000 Å thick, were evaporated onto 0.150-mm glass substrates. Other substrates such as Mylar and silicon were used and gave substantially identical results. The samples were then cemented to a liquid-nitrogen–cooled heat sink using silicone vacuum grease mixed with silver powder to improve its thermal conductivity. Electrical leads were silver cemented to the sample. The optimum pulse rate was about 15 Hz at unit duty cycle with 6 A passing through the sample. It was observed that at higher pulse frequencies the signal deteriorated, indicating that the modulation effect is thermal. This is reasonable since the slow pulsing frequency gives the sample and substrate, with their fi-

nite heat capacity, a chance to heat and cool. The gold film with an area of about 0.6 cm^2 had a resistance of about 0.2 Ω so that at 6 A the peak power dissipated is about 12 W/cm^2. This caused a measured dc temperature rise of about 40°K above the base temperature near 77°K. The modulation of the temperature at 15 Hz is of the order of 1° or 2°. The sample Dewar was mounted in a vacuum monochromator with an optical range of 2-12 eV. The dc output of the photomultiplier detector was kept constant by a servo system which controlled the tube gain. The modulated component was measured by a lock-in amplifier and the output, which is directly proportional to $\Delta R/R$, was displayed on a recorder.

The results obtained for $\Delta R/R$ of a gold film are shown in Fig. 1, along with the conventional reflectance of the same film. The $\Delta R/R$ curve shows well-defined structure out to 10 eV, the first time modulation measurements have extended into the vacuum ultraviolet. The most prominent features of the curve are the sharp dispersion-like shape at 2.5 eV which is only 0.1 eV wide from minimum to maximum and the detailed structure above 5 eV which is in contrast to the rather featureless reflectance spectrum. Below 5 eV, the $\Delta R/R$ curve is similar to that of Garfinkel, Tiemann, and Engeler[4] (GTE) who used the piezoreflectance method in the range 1.5-5.0 eV, but quite different from that of Feinleib[6] who used the electroreflectance method. The peaks at 3.3 and 4.4 eV are well resolved here due to the low temperature used.

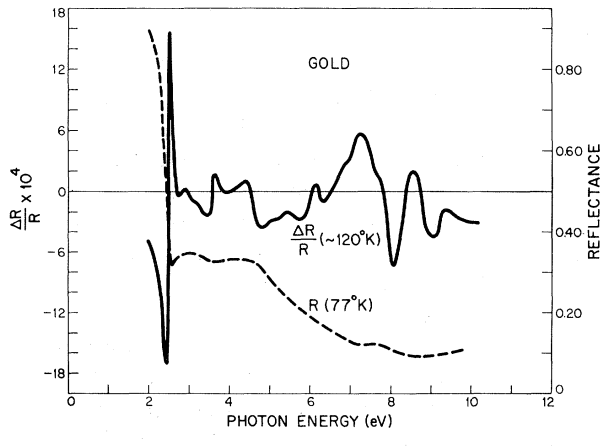

FIG. 1. The temperature-modulated reflectance, $\Delta R/R$, and the reflectance, R, for a gold film from 2 to 10 eV.

A detailed analysis and interpretation of the results are beyond the scope of this paper. Similar measurements are being made on the other noble metals, silver and copper, and a more comprehensive discussion will be forthcoming when comparisons of those results with the results presented here are made.

However, let us analyze at this time the kind of behavior one should expect for $\Delta R/R$ in modulation experiments so that we might compare, on a preliminary basis, our results with those obtained using other methods, particularly the piezoreflectance technique which gave similar results. Consider R as a function of ϵ_1 and ϵ_2, the real and imaginary parts of the dielectric constant. Then

$$\frac{\Delta R}{R}=\frac{1}{R}\left[\frac{\partial R}{\partial \epsilon_1}\Delta\epsilon_1+\frac{\partial R}{\partial \epsilon_2}\Delta\epsilon_2\right]. \tag{1}$$

Thus, $\Delta R/R$ not only depends on the incremental change of ϵ_1 and ϵ_2 produced by the modulation effect but also on the parital derivatives $\partial R/\partial\epsilon_1$ and $\partial R/\partial\epsilon_2$. Since these derivatives are the same for any modulation experiment on the same sample, let us first consider their effect on $\Delta R/R$. Straightforward manipulation of the relation between R and ϵ_1, ϵ_2 yields

$$\frac{1}{R}\frac{\partial R}{\partial \epsilon_1}=\left\{\frac{\sqrt{2}(\epsilon_1+\epsilon)^{1/2}}{\epsilon[(\epsilon_1-1)^2+\epsilon_2{}^2]}\right\}[2\epsilon_1-\epsilon-1] \tag{2}$$

and

$$\frac{1}{R}\frac{\partial R}{\partial \epsilon_2}=\left\{\frac{\sqrt{2}}{\epsilon(\epsilon_1+\epsilon)^{1/2}[(\epsilon_1-1)^2+\epsilon_2{}^2]}\right\}[2\epsilon_1+\epsilon-1], \tag{3}$$

where $\epsilon^2=\epsilon_1{}^2+\epsilon_2{}^2$. The terms in braces are all positive definite so that the sign of the derivatives is determined by the terms in the right brackets. Inspection shows that if $\epsilon_1\leq 1$, then $(1/R)\partial R/\partial\epsilon_1\leq 0$ for all ϵ_2, but otherwise the sign and magnitude of the derivatives depends on the relative values of ϵ_1 and ϵ_2. This implies that peaks in $\Delta R/R$ may be due to the coefficients in Eq. (1) as well as to peaks in $\Delta\epsilon_1$ and $\Delta\epsilon_2$ themselves. This agrees with the statement of GTE that interpretation of peaks in $\Delta R/R$ in terms of transitions between electronic states may be misleading. Applying these results, examination of ϵ_1 and ϵ_2 obtained by Cooper, Ehrenreich, and Philipp[7] (CEP) on gold at room temperature show that from 0 to 10 eV, $\epsilon_1\leq 1$ so that $(1/R)\partial R/\partial\epsilon_1$ is always negative, although not monotonically so. However, $(1/R)\partial R/\partial\epsilon_2$ is both positive and negative. In particular, around 2.6 eV, $(1/R)\partial R/\partial\epsilon_2$ goes

through 0 from a negative value, remaining positive to 10 eV, although again not monotonically so.

Let us now consider $\Delta\epsilon_2$, where $\Delta\epsilon_2 = \Delta\epsilon_2^{f} + \Delta\epsilon_2^{b}$, the contributions of the free and bound electrons, respectively. In our experiment $\Delta\epsilon_2$ results from thermal modulation which produces dilatation due to thermal expansion along with other changes due to temperature. Since the sample film is bonded to the glass substrate, which has a lower coefficient of thermal expansion, there is also some strain introduced which we may include as part of the dilatation effect. Thus, the thermal modulation and the piezoreflectance experiments are similar in that they both depend at least partly on dilatation effects.

GTE have in fact calculated $\Delta\epsilon_2^{f}(V)$ which is the contribution of the dilatation effect to $\Delta\epsilon_2^{f}$, and obtain[8]

$$\Delta\epsilon_2^{f}(V)/\epsilon_2^{f} = A\,\Delta V/V, \tag{4}$$

where A depends on the material and $\Delta V/V$ is the volume dilatation. In our experiment,

$$\frac{\Delta\epsilon_2^{f}}{\epsilon_2^{f}} = \frac{\Delta\epsilon_2^{f}(V)}{\epsilon_2^{f}} + \frac{\Delta\epsilon_2^{f}(T)}{\epsilon_2^{f}}, \tag{5}$$

where the first term on the right is given by Eq. (4) and the second term is the contribution of temperature effects other than dilatation. In the piezoreflectance experiment, the second term in Eq. (5) is missing.

Although we do not have information regarding the total temperature dependence of $\Delta\epsilon_2^{f}$ for gold,[9] Roberts's[10] results for copper show $\Delta\epsilon_2^{f}/\epsilon_2^{f} \approx 1.5\times10^{-3}/°\mathrm{C}$ whereas Eq. (4) gives for copper $\Delta\epsilon_2^{f}(V)/\epsilon_2^{f} \approx 4\times10^{-5}/°\mathrm{C}$, using GTE's value of A and handbook thermal expansion values. Equation (4) gives for gold $\Delta\epsilon_2^{f}(V)/\epsilon_2^{f} \approx 1\times10^{-4}$ in both the piezoreflectance and thermal-modulation experiments, since $\Delta V/V$ is approximately the same either for thermal dilatation due to a 1° temperature rise or for the values of strain obtained in GTE. These results indicate that if the behavior of gold is similar to that of copper, then the dilatation effect due to a 1° rise contributes only a small amount to the total $\Delta\epsilon_2^{f}/\epsilon_2^{f}$.

The bound-electron contribution, $\Delta\epsilon_2^{b}$, is less amenable to calculation since it has no simple analytic form such as ϵ_2^{f}. However, ϵ_2^{b} is a measure of the strength of interband transitions; also, we know that the threshold and curve shape for this quantity is strongly temperature dependent in all materials. Therefore, in a thermal modulation experiment, we should expect a substantial contribution, $\Delta\epsilon_2^{b}$, in the spectral region corresponding to the onset of such transitions. The value of $\Delta\epsilon_2^{b}$ is also strain- and electric-field–dependent so that we would not expect a priori to get the same contribution to $\Delta\epsilon_2^{b}$ in each of the experimental methods.

From the above considerations, it is fairly evident that one should not expect to obtain the same $\Delta R/R$ curve for each of the three experimental methods, although there may be similarity in the thermal modulation and piezoreflectance results because they both depend at least partly on dilatation effects. In fact, as we have noted, the curves are similar, particularly above 2.7 eV, but there is a striking difference too. The line shape around 2.5 eV in Fig. 1 is considerably sharper (0.1 eV compared with about 0.2 eV) and stronger, is shifted to higher energy, and is inverted compared to the other structure in GTE. In particular, in this region ϵ_2^{b} rises abruptly, a feature which is attributed by CEP to d-band–to–Fermi-surface transitions near L. Such transitions will be temperature dependent and no doubt some of the differences between our results and those of GTE are due to the fact that our measurements are carried out near 77°K whereas theirs were performed at room temperature. In the electroreflectance experiment,[6] the line shape around 2.5 eV is considerably different from that obtained using either the piezoreflectance or thermal-modulation technique. It seems obvious that results obtained using all the methods would be of great help to the theorist since he would have some knowledge of the variation of ϵ_1 and ϵ_2 with temperature, strain, and electric field.

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EXCITONS IN METALS

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It is shown that exciton states exist in metals, occurring near the interband threshold in optical absorption and substantially altering the shape and strength of the absorption edge. Their relation to the corresponding donor states is discussed.

Theoretical calculations of interband optical absorption in metals have met with mixed success.[1] Band-structure calculations predict sucessfully many of the energy thresholds,[2] but miss by factors of 3 to 5 on predicting the strength of the absorption. This Letter points out that exciton states exist in metals, and that the inclusion of these exciton states in optical absorption calculations should resolve many of the above discrepancies. As in the semiconductor case,[3] these exciton states arise from the final-state Coulomb scattering between the electrons and holes. However, quite unlike the semiconductor excitons, an exciton state in the absorption spectra does not require that the corresponding donor state exist. Discrete exciton bound states only occur in special cases. Yet, in many types of transitions, metallic excitons will cause large resonances which enchance the interband absorption.

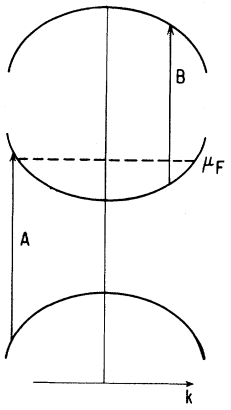

FIG. 1. Two types of interband transitions discussed in the text.

It has already been shown[4] that large exciton resonances occur in the interband transition A of Fig. 1. The optical spectra can be evaluated by treating the absorption as the photon creation of an electron-hole pair.[3] The absorption spectra is found by evaluating the electron-hole correlation function[5]

$$\pi(i\omega_n)=\frac{\alpha_0}{V}\sum_{\vec{p}\vec{p}'}\int_0^\beta d\tau\exp[i\omega_n(\tau-\tau')]\times\langle T_\tau c_{\vec{p}}(\tau)d_{\vec{p}}(\tau)d_{\vec{p}}(\tau)d_{\vec{p}}^{\dagger}(\tau')c_{\vec{p}'}^{\dagger}(\tau')\rangle, \quad (1)$$

where c_p refers to electrons in the conduction band and d_p to holes in the valence band. This form assumes that the band-to-band dipole transition is allowed. After evaluating $\pi(i\omega_n)$, the retarded function $\pi_{\mathrm{ret}}(\omega)$ is obtained by letting $i\omega_n \to \omega - E_G - \mu_e - \mu_h + i\delta$, where E_G is the en-