Band-Structure-Associated Aspects of Electroreflectance Spectra of Metals

B. J. Parsons
Michelson Laboratory, China Lake, California 93555
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We comment on "Electromodulation of the Optical Properties of Gold" by W. N. Hansen and A. Prostak, Phys. Rev. **174**, 500 (1968).

In a recent communication Hansen and Prostak[1] (HP) reported electromodulated attenuated total reflection (ATR) data for gold which they interpreted in terms of electric-field-induced changes in the carrier concentration, the Fermi level, and, hence, in all interband transitions involving Fermi-level states. Their experimental data are in accord with earlier electroreflectance measurements by Feinleib[2] and by Buckman and Bashara.[3] The satisfactory agreement between experiment and the proposed theory leads one to view the proposed mechanism for the effect with some confidence.

The purpose of this comment is twofold: First, we believe that the analysis of metal electroreflectance spectra in terms of the HP theory might be of greater value at higher photon energies; second, we believe that attention should be focused on the apparent failure of the theory when applied to the measured electroreflectance spectra for silver and copper.

1. ELECTROREFLECTANCE OF GOLD IN THE 3–5-eV REGION

The reflectance spectrum for gold above the interband transition threshold at 2.1 eV is characterized by two distinct features: a low-energy edge at 2.5 eV and a high-energy minimum at 4 eV. The low-energy structure is associated with interband transitions from the d bands to the conduction band near L in the Brillouin zone (e.g., transitions L_3-$L_{2'}$). It is the field-induced spectral shift of this structure which Hansen and Prostak suggest is responsible for the low-energy electroreflectance response.

The higher-energy structure in the reflectance, near 4 eV, can be interpreted as arising in two ways. It could result from a large joint density of states between the d bands and the conduction band near X (e.g., transitions X_5-$X_{4'}$) or it could result from interband transitions from the Fermi level near $L_{2'}$ to higher conduction-band states near L_1. We note that changes in the Fermi level in response to an applied electric field would affect these transitions in different ways. If the 4-eV transitions involve d-band states and if we make $dR/dE<0$ for $E<4$ eV, which on the basis of available experimental data[4] seems reasonable, then the HP theory leads us to expect electroreflectance on the low-energy side of the 4-eV structure of the same sign as that expected at lower energies. The signal will change sign only on the high-energy side, and then only if dR/dE goes positive (i.e., if the reflectance minimum is well resolved) and the effect of even higher energy transitions is small in comparison.

If, on the other hand, the 4-eV structure is attributed to transitions of the type $L_{2'}$-L_1, the reflectance minimum would move to higher energies as the Fermi level moves down the conduction band. The electroreflectance response might then be expected to change sign near 3.5 eV on the low-energy side of the reflectance minimum, and remain positive at higher energies. This is precisely what is observed in the electroreflectance spectrum for gold as reported by Feinleib. We believe that this constitutes strong support for the proposal that the high-energy reflectance minimum for gold is dominantly the result of transitions which do not involve the d bands and which are probably of the type $L_{2'}$-L_1.

2. ELECTROREFLECTANCE OF SILVER AND COPPER

The success of the HP scheme in explaining the electroreflectance spectrum for gold is not paralleled when it is applied to electroreflectance spectra of the other noble metals, silver and copper. The data for silver,[2] for example, shows structure near 3 eV, where one would expect no contribution from plasma or interband effects and only a monotonic contribution from intraband effects. This anomalous structure may result from the close proximity near 3.9 eV of plasma and interband edges. The electroreflectance spectrum for copper, which we have investigated, is even more peculiar since there appears to be no similarity between it and the spectrum for gold. Specifically, we observe no effect in the 2–2.5-eV region near the interband transition threshold. We have no suggestions at present as to the origins of these anomalous effects; they do indicate, however, that some caution should be exercised in assuming the general applicability of the HP scheme.

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[1] W. N. Hansen and A. Prostak, Phys. Rev. **174**, 500 (1968).
[2] J. Feinleib, Phys. Rev. Letters **16**, 1200 (1966).
[3] A. G. Buckman and N. M. Bashara, J. Opt. Soc. Am. **58**, 700 (1968); Phys. Rev. **174**, 719 (1968).
[4] *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland Publishing Co., Amsterdam, 1966).