Magnetoreflection Measurements on the Noble Metals*

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A technique is described which allows the change in optical dielectric function of a solid due to an applied magnetic field to be measured. Results are presented for Cu, Ag, and Au in the photon energy range 2–5.5 eV.

IN the last few years, considerable information about the optical spectra of solids has been obtained by applying small perturbations to the solid, such as electric fields and strains, and by measuring the resulting changes in reflectivity.[1,2] Since the reflectivity changes are usually small, the perturbation is applied at a fixed frequency, and synchronous detection of the small intensity modulation of the reflected beam is carried out.

It would be desirable to use the same procedure for an applied magnetic field. Turning a large magnetic field on and off can only be accomplished at very low frequencies (~1 Hz) for obvious reasons. At such low frequencies the $1/f$ noise present in any electrical system is large, reducing the signal-to-noise ratio. A few years ago Stern carried out measurements using this approach.[3] He overcame the large noise level by reflecting the beam many times (~20) between two mirrors made of the material to be studied, both mirrors being in the magnetic field. This technique is valuable only when the reflectivity of the sample is high; otherwise, the shot noise in the detected beam is too great.

This paper reports a technique which enables such measurements to be carried out at higher modulation frequencies, so that only one reflection from the sample is needed.[4] This allows the experiment to be carried out on samples with low reflectivities as well, thus greatly extending the utility of the method. Measurements similar to those reported here have been carried out on ferromagnetic solids where the signal amplitudes are larger by two orders of magnitude.[5]

For a cubic solid, the dielectric response function is diagonal. In a magnetic field, to first order in the applied field, off-diagonal elements ϵ^m are present. Upon diagonalization, the result is

$$\epsilon=\begin{bmatrix}\epsilon+\epsilon^m & 0 & 0\\ 0 & \epsilon-\epsilon^m & 0\\ 0 & 0 & \epsilon\end{bmatrix}.$$

The eigenstates are left and right circular polarizations. Since ϵ^m is linear in H, it is clear that reversing the sense of the circular polarization is completely equivalent to reversing the direction of the magnetic field. Thus, the state of polarization can be modulated instead of the magnetic field, and the resulting change in reflectivity is exactly the same.

In this experiment, the polarization is modulated by passing a linearly polarized beam through a fused quartz rod which has an alternating uniaxial strain applied to it at a frequency of 50 kHz. The angle between the plane of polarization of the beam and the strain axis is 45°. The strain causes the fused quartz rod to become slightly birefringent. For a strain amplitude such that the phase difference for light polarized parallel to and perpendicular to the strain axis is 90°, the transmitted beam will be circularly polarized. The strain in the quartz rod is produced by a −18° X-cut crystal quartz rod glued to the fused quartz rod. When the voltage applied to the piezoelectric crystal quartz rod is adjusted so the peak strain in the fused quartz rod produces circular polarization, then, as the strain alternates between compression and extension, the polarization alternates between left and right circular.

The modulated beam is then reflected at near-normal incidence from a sample in a magnetic field with the field oriented parallel to the beam. Any difference in reflectivity between left and right circular polarization will produce an intensity modulation of the reflected beam at 50 kHz. The photomultiplier tube is operated by a power supply regulated to keep the average current drawn by the phototube equal to a constant value. By dividing the ac signal by the dc average numerically after the experiment is performed, the ratio

$$\Delta R/R\equiv 2(R_+-R_-)/(R_++R_-)$$

is obtained as a function of wavelength; the intensity of the lamp and sensitivity of the phototube cancel out.

To evaluate the off-diagonal elements of the dielectric response function due to the magnetic field, it is necessary to know the phase change as well as the amplitude change caused by the field. The phase change produces a rotation of the plane of polarization (Faraday

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[3] E. A. Stern, J. C. McGroddy, and W. E. Harte, Phys. Rev. **135**, A1306 (1964).

[4] The apparatus is described in detail by S. N. Jasperson and S. E. Schnatterly, Rev. Sci. Instr. **40**, 761 (1969).

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rotation). This rotation can be measured with the apparatus described above, but spurious effects due to the rotation of the quartz lenses in the stray field of the magnet prevented an accurate measurement, so the phase change was calculated with a Kramers-Kronig integral in the manner described by Garfinkel, Tiemann, and Englerer,[2] except that the relation between phase and amplitude is modified by the magnetic field. In deriving the integral relating the phase change upon reflection to the amplitude-reflection coefficient $r(\omega)$, the reality condition which is ordinarily used, $r^*(-\omega)=r(\omega)$, is modified when the eigenstates are left and right circularly polarized electric fields to $r_\pm^*(-\omega)=r_\mp(\omega)$. This was first described by Boswarva, Howard, and Lidiard in discussing Faraday rotation of semiconductors.[6]

It can readily be shown that the new relation for the difference in phase between left and right circular polarizations is

$$\theta_+(\omega)-\theta_-(\omega)=\frac{2P}{\pi}\int_0^{\infty}\frac{\omega'(\ln|r_+(\omega')|-\ln|r_-(\omega)|)d\omega'}{\omega'^2-\omega^2}.$$

If $r_+-r_-\ll r$, which is always the case in this experiment, then

$$\theta_+(\omega)-\theta_-(\omega)=\Delta\theta(\omega)=\frac{2P}{\pi}\int_0^{\infty}\frac{\omega'(\Delta r/r)(\omega')d\omega'}{\omega'^2-\omega^2}$$

$$=\frac{P}{\pi}\int_0^{\infty}\frac{\omega'(\Delta R/R)(\omega')d\omega'}{\omega'^2-\omega^2},$$

where $R=|r|^2$ is the intensity reflectivity. This integral is in error by an additive constant, since it is known[7] that the phase difference due to high-frequency absorption must approach zero at zero frequency, and this integral approaches a constant. Subtracting the value of the integral at zero frequency results in

$$\Delta\theta(\omega)=\frac{\omega^2}{\pi}P\int_0^{\infty}\frac{(\Delta R/R)(\omega')d\omega'}{\omega'(\omega'^2-\omega^2)}.$$

This integral can either be evaluated numerically by approximating the principal part, or the singularity can be removed by subtracting a suitable integral, such as

$$\frac{\omega}{\pi}P\int_0^{\infty}\frac{\omega'(\Delta R/R)(\omega')d\omega'}{\omega'(\omega'^2-\omega^2)}=0.$$

Then

$$\Delta\theta(\omega)=\frac{\omega}{\pi}\int_0^{\infty}\frac{(\omega(\Delta R/R)(\omega')-\omega'(\Delta R/R)(\omega))}{\omega'(\omega'^2-\omega^2)}d\omega'.$$

Both integrals were used in the evaluation of $\Delta\theta(\omega)$ for the measurements presented in this paper, and they gave results differing by a few percent.

The difference between the modified phase integral and the usual one appropriate for linear polarization eigenstates is a factor of ω/ω'. This causes large changes far from resonance and small changes near resonance. In the present experiment, both forms were used, and the results were practically identical in the wavelength range reported.

The rotation in the infrared range due to intraband transitions approaches a constant value which has been measured by Stern,[8] for Ag and Au, thus providing a direct measure of the low-frequency part of the Kramers-Kronig integral. Cu was assumed to have the same rotation as Au in the intraband range. In each case the measured signal approached zero near the high-frequency end of the d-band absorption. It was assumed that $\Delta R/R$ remained zero for all higher frequencies.

The off-diagonal elements of the dielectric response function ϵ^m can then be evaluated using the relation derived by Stern *et al.*[3]:

$$\Delta\theta+\tfrac{1}{2}i(\Delta R/R)=\epsilon^m/(\epsilon-1)\sqrt{\epsilon},$$

where ϵ is the dielectric constant in the absence of an applied field.

The optical properties of the noble metals are dominated in the visible and near-uv ranges by transitions between the filled d-band and empty states above the Fermi energy. A magnetic field adds to the total Hamiltonian the small perturbation term $H_Z=\beta\mathbf{H}\cdot\mathbf{L}+2\beta\mathbf{H}\cdot\mathbf{S}$. The first term will mix nondegenerate states, producing small changes in the wave functions, and hence, the optical absorption. As an example, consider transitions from two d-like states having rotational symmetry XZ and YZ to a p-like state having symmetry Z. Suppose the d-like states are split by the crystal field by an energy Δ. Then, according to second-order perturbation theory, assuming a magnetic field applied in the Z direction,

$$|XZ\rangle_1=|XZ\rangle_0+|YZ\rangle_0\frac{\langle YZ_0|\beta HL_z|XZ_0\rangle}{\Delta}$$

$$=|XZ\rangle_0+i\epsilon|YZ\rangle_0,$$

$$|YZ\rangle_1=|YZ\rangle_0+i\epsilon|XZ\rangle_0.$$

The magnitude of ϵ_2, the absorptive part of the dielectric function, contains contributions proportional to

$$\epsilon_2^{\pm}\sim|\langle XZ_1|P_\pm|Z_1\rangle|^2=|\langle XZ_0|P_\pm|Z_0\rangle|^2\{1\mp2\epsilon\},$$

so $\epsilon_2^+-\epsilon_2^-\sim\epsilon_2(1\mp4\epsilon)$. Hence, the difference in ϵ_2 measured with right and left circular polarizations is proportional to the amount of mixing of the states by the

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[7] M. J. Stephen and A. B. Lidiard, J. Phys. Chem. Solids **9**, 43 (1958).

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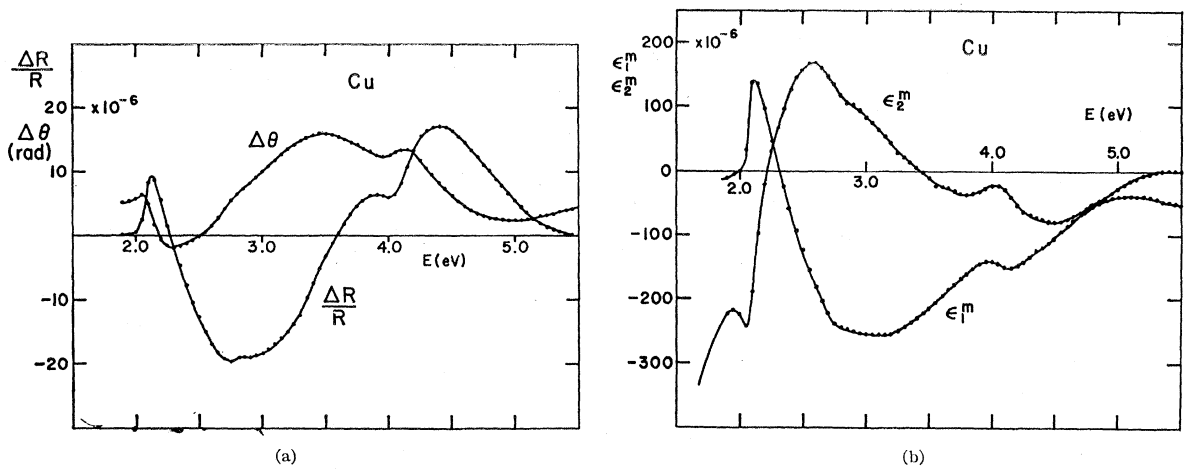

FIG. 1. Copper. (a) Measured values of $\Delta R/R$ and calculated values of $\Delta\theta$. (b) Calculated values of $\epsilon_1{}^m$ and $\epsilon_2{}^m$.

Zeeman perturbation term and thus provides a measure of Δ, the energy separation between the two states. To find the total change in ϵ_2 at a given frequency, it is necessary to sum the changes due to all states contributing to the absorption at that frequency. Since there may be many contributions, each with different values of Δ, the net change will not simply be proportional to the total absorption. This discussion is very similar to the Kittel-Argyres interpretation of the ferromagnetic Kerr effect, except that it is the orbital Zeeman interaction rather than the spin-orbit interaction which mixes the two states.[9]

The spin term in the above perturbation Hamiltonian also contributes via the spin-orbit interaction, as first explained by Bennett and Stern.[10] The contribution to the change in ϵ_2 is given by the difference in absorption for spin-up and spin-down states multiplied by a factor measuring the amount of spin-orbit mixing of the two d-like states. The size of the contribution is of the order $\Delta\epsilon_2 \sim (\Delta\epsilon_2/\partial\omega)(g\beta H)(\delta/\Delta)$, where δ is the matrix element of the spin-orbit interaction connecting the two states and g is the spin g factor. This estimate applies to transitions from spin-split d states to states at the Fermi energy where spin-up and spin-down states have the same energy and slightly different wave vector.

These two contributions to $\Delta\epsilon_2$ are of the same order of magnitude, although the spin terms should be smaller for Cu, since the spin-orbit interaction is smaller.

The s-p–band contribution to ϵ^m can be estimated using a free-electron model. The result is[7]

$$\epsilon_1{}^m(\omega) = \omega_p{}^2\omega_c/\omega^4\tau\,,$$
$$\epsilon_2{}^m(\omega) = \omega_p{}^2\omega_c/\omega^3\,,$$

where $\epsilon_1{}^m$ is the absorptive part of the off-diagonal element of the dielectric constant, and $\epsilon_2{}^m$ is the dispersive element.

One useful result of measurements of $\Delta R = R_+ - R_-$ in the case of a simple metal is that the optical mass can be evaluated. In the magnetic field, all orbital eigenstates are shifted up or down in energy by an

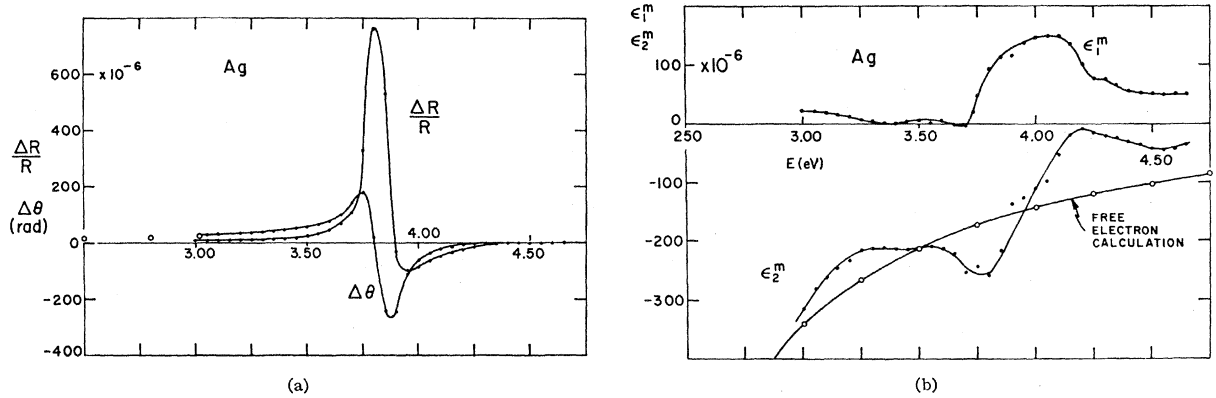

FIG. 2. Silver. (a) Measured values of $\Delta R/R$ and calculated values of $\Delta\theta$. (b) Calculated values of $\epsilon_1{}^m$ and $\epsilon_2{}^m$.

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[10] H. S. Bennett and E. A. Stern, Phys. Rev. **137**, A448 (1965).

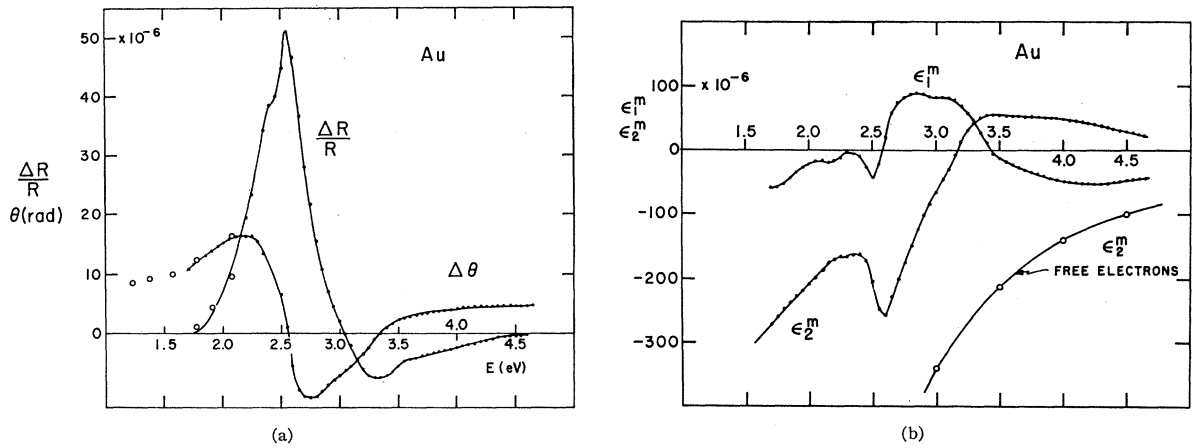

FIG. 3. Gold. (a) ●: Measured values of $\Delta R/R$ (this work) and calculated values of $\Delta\theta$. ○: Measured values of $\Delta R/R$ and $\Delta\theta$ (Stern, Ref. 8). (b) Calculated values of $\epsilon_1{}^m$ and $\epsilon_2{}^m$.

amount $\frac{1}{2}\hbar\omega_c$. Right and left circularly polarized light couples to the upper and lower states, respectively. To first order in H,

$$R_+(\omega)-R_-(\omega)=[\partial R(\omega)/\partial\omega]\omega_c$$

and

$$\int_0^\infty [R_+(\omega)-R_-(\omega)]d\omega=-\omega_c.$$

The cyclotron mass as measured by either of these formulas is, for a simple metal, the bare-band mass, not renormalized by phonon coupling, since the probe frequency used is large compared with the phonon frequencies. Since the present values of optical masses of simple metals are rather puzzlingly large, an alternative method of measurement will provide an interesting comparison.

The results of measurements of Cu, Ag, and Au are shown in Figs. 1–3 normalized to an applied field of 10 kG. The plasma frequency in Ag at 3.8 eV clearly appears in $\Delta R/R$ as expected, and ϵ^m for Ag is quite free-electron-like in the low-energy range. The structure in the curves for Cu near 2.1 and 4.0 eV is probably due to nearly degenerate parts of the d band near L and X which contribute at these energies.[2] The structure in ϵ^m for Au is smaller than for Cu. This is probably due to near cancellation of the orbital and spin contributions to ϵ^m.

The samples were prepared by evaporation onto a microscope slide in a bell jar at room temperature and at a pressure of approximately 10^{-5} Torr. The observed structure in Cu near 2 eV where Cu_2O has an absorption threshold was checked by using the Cu-glass interface as the reflecting surface, and by overcoating the Cu film with a thin evaporated layer of MgF_2 before removal from the vacuum system. No differences were found between freshly prepared unprotected samples and samples so protected from oxidation. Thus, the reported results appear to be characteristic of pure Cu.

The zero line for the $\Delta R/R$ curves is accurate to approximately $\pm1\times10^{-6}$. A larger zero uncertainty exists for the calculated values of ϵ^m, since uncertainties in the values of ϵ_1 and ϵ_2 used in obtaining ϵ^m from $\Delta R/R$ and $\Delta\theta$ generally have the effect of shifting the ϵ^m curves up or down by as much as $\pm0.5\times10^{-4}$ without, however, appreciably changing the structure.

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