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Magneto-optical properties of metallic colloids in insulators

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Magnetic-circular-dichroism spectra are reported for Na colloids in NaCl and Ca colloids in CaF_2. The spectra are interpreted by applying Mie theory and by taking account of the perturbation of the magnetic field. The theory gives a good explanation of the spectra and implies values for cyclotron masses that agree with values predicted for the metallic colloids. Interband contributions to the magnetic circular dichroism are significant for the Ca colloids and unimportant for the Na colloids.

I. INTRODUCTION

Colloidal particles of metal are readily formed in many insulating crystals.[1] The colloids are produced when a metallic impurity or constituent precipitates as the result of a thermal treatment, photothermal treatment, or redox reaction.[1-4] Metallic colloids are one of the more stable end products of radiation damage,[5] and they also have been produced by ion implantation.[6] Colloids have attracted interest in connection with nuclear waste storage[7] and with solar energy absorbers.[8] Colloidal particles have been studied by a variety of techniques that includes electron microscopy and small-angle neutron scattering,[9] light scattering, and optical-absorption spectroscopy.[1-3] The absorption and scattering of light by colloids often gives a characteristic color to an otherwise transparent host. The absorption bands of noble-metal colloids in photosensitive glasses have been extensively studied.[10]

This paper presents a study of the magnetic circular dichroism (MCD) of the optical bands of two kinds of metallic colloids: sodium and calcium precipitates in NaCl and CaF_2, respectively. Magneto-optical methods have been employed extensively in studies of the optical bands of point defects in insulators,[11] but they have not been applied to study colloid bands in detail. Although colloids of Na and Ca exhibit very small magneto-optical effects, they are otherwise suited for magneto-optical studies. The optical properties of Na and Ca are known and their approximately free-electron conductivity permits a simple interpretation of their magnetic properties.

II. EXPERIMENTAL PROCEDURES

High-purity crystals of NaCl and CaF_2 were purchased from the Harshaw Chemical Company. Cleaved specimens of NaCl were heated to 1000 K for several hours in Na vapor in a Van Doorn apparatus.[1,2] The specimens were then heated in air to a temperature of 600 K for 10 min. This procedure produces a narrow absorption band that is almost entirely due to colloids.[2] It is interesting that a change in the thermal treatment produces a different distribution of particle sizes which modifies the position and width of the optical band. The specimens of CaF_2 were irradiated at room temperature with 2-MeV electrons. The irradiation produces a colloid band and a smaller band near 380 nm which may be associated with some kind of F center.[3]

The dichroic spectra were induced by the 10-kG field of an electromagnet. Dichroism measurements were taken by using a photoelastic polarization modulator and a lock-in amplifier.[12] Absorption spectra were measured with a Cary 17 spectrophotometer. All spectra were measured at room temperature. A Hewlett Packard 9825 calculator was used for data reduction and theoretical computations.

III. THEORY

The optical attenuation produced by spherical colloids imbedded in a transparent, homogeneous medium is described by an effective absorption coefficient (α) that can be computed in the form of a series by use of Mie theory[13]:

$$\alpha = N_p n_0^2 \frac{\lambda^2}{2\pi} \mathrm{Re}\left[\sum_{l=1}^{\infty}(-i)^{l+1} l(l+1)({}^{e}B_l + {}^{m}B_l)\right] , \tag{1}$$

where N_p is the particle density, n_0 is the refractive index of the host medium, and Re indicates that the real part of the sum is to be taken. The ${}^{e}B_l$ and ${}^{m}B_l$ are functions of the particle size, the wavelength (λ), and the particle and host dielectric functions. The functions are proportional to increasingly higher powers of the ratio of the particle radius (r) to the wavelength (i.e., ${}^{e}B_l \sim q^{2l+1}$ and ${}^{m}B_l \sim q^{2l+3}$, where $q = 2\pi n_0 r/\lambda$). For the relatively small particles that are considered here (i.e., $q < 1$), the series converges rapidly. In fact, the electric dipole term predominates, and retaining only ${}^{e}B_1$ gives a good first approximation:

$$\alpha \sim \frac{24\pi^2 N_p n_0^3 r^3}{\lambda} \frac{\epsilon_2}{(\epsilon_1 + 2n_0^2)^2 + \epsilon_2^2} , \tag{2}$$

where ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric function of the particles. If there is a wavelength where $\epsilon_1 = -2n_0^2$, Eq. (2) predicts a resonance in the absorption spectrum that produces a band with a peak intensity proportional to ϵ_2^{-1}. For metallic colloids in dielectric hosts, such resonance bands are frequently observed. When the dielectric functions are known, Eq. (2) or a higher-order approximation to Eq. (1) can be used to predict or interpret these bands.

Present interest is primarily in the interpretation of the magnetic circular dichroism of colloid bands. The MCD is simply the magnetically induced difference between the absorption of left- and right-circularly-polarized light. An interpretation of the MCD follows if the effect of the magnetic field on the absorption coefficient can be established. Since Eqs. (1) and (2) relate the absorption to the dielectric function, the problem can be reduced to determining the effect of the field on the dielectric function of the metal. For nearly-free-electron metals, it is convenient to distinguish between the intraband contribution to the dielectric function, which can be expressed in the simple Drude form, and the interband contribution, which generally is more complicated. The magnetic field enters the intraband terms as the cyclotron frequency (ω_c) and it enters the interband terms as a frequency shift ($\Delta\omega$) that corresponds to a change in the interband transition energies.[14] When these magnetic effects are included, the dielectric function is polarization dependent and of the form

$$\epsilon_1^{\pm} = 1 - \frac{\omega_p^2(\omega \mp \omega_c)}{\omega[(\omega \mp \omega_c)^2 + \omega_0^2]} + \beta_1^{\pm}(\omega \mp \Delta\omega) , \tag{3a}$$

$$\epsilon_2^{\pm} = \frac{\omega_p^2 \omega_0}{\omega[(\omega \mp \omega_c)^2 + \omega_0^2]} + \beta_2^{\pm}(\omega \mp \Delta\omega) , \tag{3b}$$

where $\omega_p = 4\pi N e^2/m^*$ and $\omega_c = |e|H/m^*c$, respectively, denote the plasma and cyclotron frequencies, and $\omega_0 = 1/\tau$ is a relaxation frequency. The upper and lower signs, respectively, refer to left- and right-circular polarization, and the β_1 and β_2 denote the interband contributions.

The derivation of Eq. (3) follows from classical and quantum mechanical considerations that are described in detail elsewhere.[14–16] Because a detailed knowledge of the band structure is required, the interband terms are difficult to evaluate. Moreover, they are usually described in terms of Landau quantization and optical selection rules that reflect the opposing changes in the angular momentum that are induced by left- and right-circularly polarized light. The Landau description is not valid in the present context, because the particle sizes are smaller than Landau orbits. Nevertheless, magnetically induced changes in the interband transition energies are to be expected, and the customary linear magnetic field dependence of the energy shift is a valid parametric description:

$$\Delta E = \hbar\Delta\omega = g_{\mathrm{eff}}\mu_B H , \tag{4}$$

where g_{eff} is an effective g factor.

A very simple description of the MCD is obtained if the interband contributions are completely ignored and Eqs. (2) and (3) are used. To this order of approximation and for the usual case where the MCD is small and $\omega \sim \omega_r >> \omega_0 > \omega_c$, it is straightforward to compute the MCD in the form:

$$\Delta\alpha = \alpha^+ - \alpha^- = -\frac{2\omega_c\omega^2}{\omega_r^2 + \omega^2}\frac{\partial\alpha(\omega)}{\partial\omega} \sim -\omega_c\frac{\partial\alpha(\omega)}{\partial\omega} , \tag{5}$$

where ω_r is defined by $\epsilon_1(\omega_r) = -2n_0^2$. The absorption-derivative-like form of the MCD implies that the predominant effect of the magnetic field is to shift the position of the band by $+\omega_c/2$ or $-\omega_c/2$ in energy when it is observed with left- or right-circularly polarized light, respectively.

An analysis of the optical spectra requires that particle size effects be recognized and that some adjustments be made to the data for the dielectric functions of the bulk metals. First, the electron has a shorter relaxation time (τ) in a small particle than it has in the bulk metal. To account for this difference, the simple correction of Kreibig[10] is used:

$$\omega_0 = 1/\tau \sim \omega_{0b} + v_F/r , \tag{6}$$

where ω_{0b} is the relaxation frequency for the bulk metal and v_F is the Fermi velocity. Second, the metal colloids have a distribution of sizes.[1,7] The particle size enters the B_1 of Eq. (1) directly and through the dielectric function via Eq. (6), and it affects both the position and width of the optical band. The effect of a known distribution on the band can be readily computed:

$$\alpha(\omega) = \int_0^{\infty} F(r)\alpha(\omega,r)\,dr , \tag{7}$$

where $F(r)$ is the size distribution function and $\alpha(\omega,r)$ is given by Eqs. (1) or (2). Since a size distribution has an equivalent effect on the MCD, the validity of Eq. (5) is independent of the distribution function. Consequently, Eq. (5) gives an approximate relation between the MCD and absorption that can be used even if the distribution of sizes is unknown. As is discussed below, a suitable size distribution function was not found for sodium colloids in NaCl. For Ca colloids in CaF_2, the distribution function that was used by Orera and Alcalá to study particle ripening gives a good description of the band.[17] This distribution function is

$$F(\rho)=\begin{cases}3\rho^5\exp[3/(2\rho-3)]/[(3/2-\rho)^{11/3}(\rho+3)^{7/3}], & \rho<\frac{3}{2}\\ 0, \quad \rho\geq\frac{3}{2}, & \end{cases} \tag{8}$$

where $\rho=r/r_c$ and r_c is the critical particle radius for ripening.[17] Finally, the optical properties of a metal can be changed by pressure. Calcium colloids are believed to be under significant hydrostatic pressure, but Na colloids are not. Orera and Alcalá have deduced that Ca colloids are under a pressure of 7.8 kbar and that there is a 10% reduction in the plasma frequency as a consequence.[17] This result is assumed here.

IV. RESULTS

Figure 1 shows measured optical density and MCD spectra for Na colloids in NaCl. A particle size distribution that would give a satisfactory fit to the width of the band was not found, even though attempts were made to fit the three different theoretical distributions that have been proposed by Jain and Hughes.[1] Nevertheless, recourse to Eq. (5) gives a very good fit to the MCD without any adjustment of parameters. The shape of the MCD is nearly that of the absorption derivative, and the intensity of the MCD is predicted if the value of the cyclotron mass is assumed to be equal to Smith's value for the optical mass.[18] The range of validity of Eq. (5) was investigated by comparing its predictions for sodium colloids with calculations made by using Eqs. (1), (3), (6), (7), and (8), and retaining terms through quadrupole in Eq. (1). For small particles, the derivative approximation agrees with the more accurately calculated MCD. However, as the maximum particle sizes become approximately equal to the optical wavelength, the derivative approximation deviates significantly from the more exact result. Thus, the approximation is valid, but only for small particles.

Figure 2 shows the measured spectra of calcium colloids together with theoretical curves computed from Eqs. (1), (3), (6), (7), and (8) and Ca dielectric functions obtained from Hunderi's data[19] by adjusting the intraband contribution to account for reduction in the plasma frequency induced by pressure.[17] The larger band near 560 nm is the colloid band; the smaller band near 380 nm is believed to be associated with a defect.[3] The Ca spectra are interesting because the close fit of the theoretical data and the measured absorption allows more exact Mie theory to be applied. Moreover, calcium has the overlapping band structure of a semimetal[20] and the interband contributions to the Ca dielectric function are larger than for sodium. It is not possible to achieve a good fit to the MCD of Ca colloids without including a magnetic contribution to the interband portion of the dielectric function. However, a reasonably good fit to

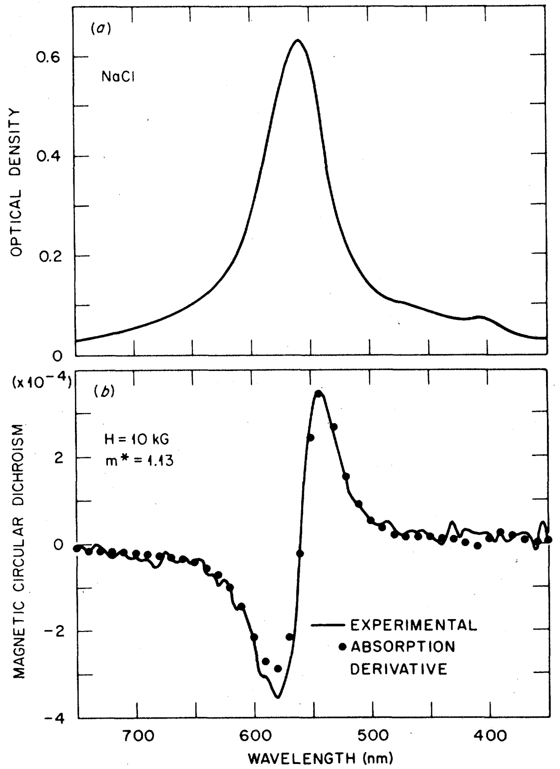

FIG. 1. The optical-absorption and magnetic-circular-dichroism spectra of Na colloids in NaCl. The dichroism is the difference between the absorption of left- and right-circularly polarized light. The solid points represent the dichroism that is predicted from the derivative of the absorption spectrum. Units are base 10 absorbance.

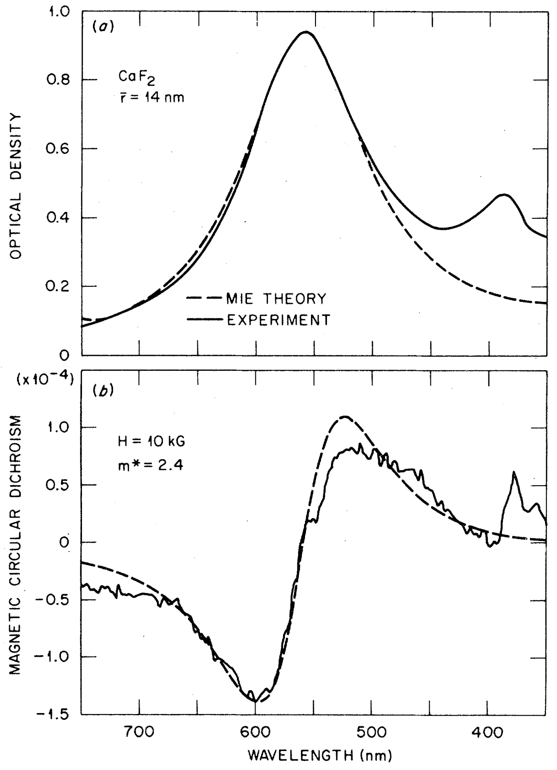

FIG. 2. The optical-absorption and magnetic-circular-dichroism spectra of Ca colloids in CaF$_2$. The dashed curves are the predictions of Mie theory.

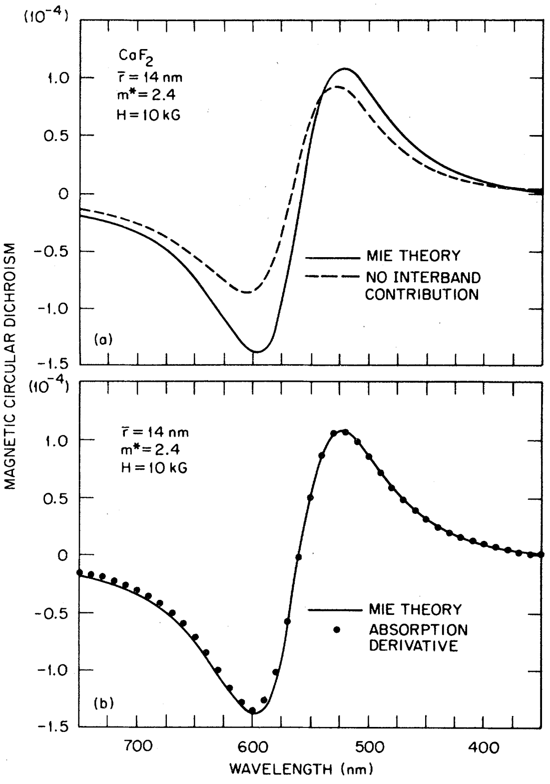

FIG. 3. A comparison of three calculations of the MCD of Ca colloids in CaF$_2$. In (a), computations which include and neglect interband contributions are compared. In (b), a Mie theory computation that includes interband effects is compared with the derivative of the absorption spectrum.

the MCD is obtained if it is assumed that $m^* = 2.4$ (in units of free electron mass) and $g_{\text{eff}} = 2m/m^*$. The value for the effective mass is large compared to the value $m^* = 2.0$ that was deduced by Hunderi from the optical properties of the bulk metal. However, the 20% increase over Hunderi's value is consistent with the assumption that the plasma frequency is 10% less in the particle than in the bulk metal. An effective g factor that corresponds to a magnetically induced shift in the interband transition energies of $\Delta E = \pm\hbar\omega_c$ has been assumed. This is a rough approximation but it is consistent with the expectation that a g value should scale inversely with the effective mass from the free electron g factor. In Fig. 3, a comparison is made of three calculations of the MCD of Ca colloids. In Fig. 3(a), a Mie theory computation that includes an interband contribution to the MCD is compared to a similar computation that neglects the interband contribution. Not only is the magnitude of the MCD different, but the shape of the MCD is significantly different. On the other hand, Fig. 3(b) shows that the shape of the absorption derivative is in close agreement with a Mie theory computation that includes an interband contribution.

V. DISCUSSION

A good explanation of the MCD of Na and Ca colloids is obtained from Mie theory when the perturbation of the magnetic field is taken into account. Moreover, the good agreement between theory and experiment is obtained without freely adjusting any parameters. Parameter values have been fixed by other measurements, *a priori* expectations, or reasonable assumptions. The magneto-optical spectra of both Na and Ca colloids are due mostly to intraband effects. The nearly free-electron approximation appears to be valid even for Ca, which has the relatively more complicated band structure of a semimetal. Neither the measurement temperature nor the small particle sizes would allow a direct observation of cyclotron resonance, and the optical frequencies are far removed from the resonance. It is remarkable that even rough values for cyclotron resonance frequencies can be inferred from such measurements. The results tend to support Orera and Alcalá's conclusion that Ca colloids in CaF$_2$ are under hydrostatic pressure, which causes the effective mass to increase over the value found in the bulk metal.

The MCD of Ca colloids reveals significant interband contributions. No detailed explanation of the interband effect has been attempted, but the size of the effect conforms to reasonable expectations. The magnitude of the wavelength derivative of the interband portion of the dielectric function determines whether a significant interband contribution to the MCD will result from an interband energy shift. The interband contributions to the MCD of Na colloids are less than for Ca because the interband contributions to the Na dielectric function are relatively small and nearly constant in the vicinity of the optical band.

It is interesting to note that the rigid-shift approximation gives a better description of the MCD of colloid bands than of the MCD of point defects. The reason appears to be related to the different mechanisms that broaden the bands as well as to the different origins of the magneto-optical effect. The bands of point defects do not shift rigidly in a magnetic field because they are broadened in large part by low-symmetry lattice modes. Colloid bands are broadened by particle size distributions and lifetime effects.

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