Experimental Observation of Specular Optical Activity

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We report the first positive experimental observation of the optical activity effect on normal reflection. The experiment was performed along the optic axis in a gyrotropic semiconductor crystal of α-HgS, cinnabar, in a spectral region of strong absorption. Reflected light polarization azimuth rotation resulting from the reflection is of the order of 10^{-4} rad and has pronounced dependence on $\hbar\omega - E_g$.

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This Letter concerns the known problem in linear optics of whether the effect of specular optical activity on normal reflection from the interface with a gyrotropic (optically active) medium exists or not. This question has been the subject of a long and controversial theoretical discussion. Different approaches to the problem of the correct material equation describing the optical properties of media with nonlocal response have led to arguments both in favor of [1–3] and rejecting this effect [3–5]. Specifically, it was thought to be firmly established that the Landau-Lifshitz equation [6] predicted the effect whereas the approach developed by Casimir [7] claimed it to be forbidden. Previous attempts to detect normal-incidence specular polarization effects due to optical response nonlocality have been unsuccessful [8,9]. More recently, however, we have shown theoretically [10] that there is no contradiction between the Landau-Lifshitz and the Casimir approaches if developed correctly from first principles. Both sets of equations predict optical activity on normal reflection from an optically active medium. We report here the first decisive experimental observation of the effect of polarization azimuth rotation for normal reflection along the optic axis of a crystal of α-HgS (cinnabar).

To estimate the expected magnitude of the specular optical activity we will be considering the interface between a vacuum and an isotropic gyrotropic medium. Because optical phenomena described by tensors up to fifth rank are treated equally in an isotropic direction or along a three- or sixfold axis, this consideration is also valid for light beams propagating in and reflecting from a crystal along the direction of these axes and therefore is applicable in the consideration of the α-HgS crystal reported here. As shown in [10], the Landau-Lifshitz approach, which operates with the electric field strength **E** and the magnetic induction **B** of the wave and the electric induction **D** of the medium, is entirely equivalent to the Casimir approach, operating with **E**, **B**, and the medium magnetization **M**, if no external magnetic field is present and first-order spatial dispersion phenomena are examined in a nonmagnetic material. Adopting here the Landau-Lifshitz material equation,

$$\mathbf{D} = \epsilon \mathbf{E} + [\mathbf{E} \times \nabla\gamma] - \gamma[\nabla \times \mathbf{E}] , \tag{1}$$

one should be aware of the dramatic change of the material parameter $\gamma(\mathbf{r})$, from one medium to the other. If steplike behavior of the material parameters is assumed (that is $\epsilon = 1$ and $\gamma = 0$ at $z < 0$ and $\epsilon > 1$ and $\gamma \neq 0$ at $z > 0$), the spatial derivative $\nabla\gamma$ results in a δ-function contribution to **D** on the border. Consequently a δ distribution of the surface current of $\mathbf{J} = \partial[(\mathbf{D} - \mathbf{E})/4\pi]/\partial t$ arises which is in fact the driving force for the polarization rotation of the reflected light. The electrodynamic boundary conditions may be obtained by integrating the Maxwell equations $[\nabla \times \mathbf{B}] = (1/c)\, \partial\mathbf{D}/\partial t$ and $[\nabla \times \mathbf{E}] = -(1/c)\, \partial\mathbf{B}/\partial t$ over the area of a loop immersed in the interface [2]:

$$[(\mathbf{B}^{(1)} - \mathbf{B}^{(2)}) \times \mathbf{n}] = -\frac{\gamma}{c}\left[\frac{\partial \mathbf{E}}{\partial t} \times \mathbf{n}\right] , \tag{2}$$

$$[(\mathbf{E}^{(1)} - \mathbf{E}^{(2)}) \times \mathbf{n}] = 0 , \tag{3}$$

where **n** is the unit vector normal to $z = 0$ and the indices (1) and (2) label the vacuum and gyrotropic medium, respectively. Now by solving the boundary problem for circularly polarized waves $E_{\pm} = E_x \pm iE_y$ one can get the reflection coefficients:

$$R_{\pm} = \frac{E_{r\pm}}{E_{i\pm}} = \frac{[1 - n_{\mp}]}{[1 + n_{\mp}]} , \tag{4}$$

where $n_{\pm} = (\gamma^2 + \epsilon)^2 \pm \gamma$ and E_i, E_r, and E_t are, respectively, the electric field magnitudes of the incident, reflected, and transmitted waves. If the incident wave is linearly polarized, polarization azimuth rotation on reflection α_r and induced reflected light ellipticity angle η_r may be expressed in terms of the transmission effect:

$$\eta_r + i\alpha_r = -i\frac{\eta_t + i\alpha_t}{z}\frac{\lambda}{\pi(1-\epsilon)} , \tag{5}$$

where λ is the wavelength, $(\eta_t + i\alpha_t)/z = i(\omega^2/2c^2)\gamma$ is the specific complex optical activity parameter for transmitted light, and $\rho = \alpha_t/z$ is the specific optical rotation power of the medium.

In previous, unsuccessful experiments with optically active crystals of TeO_2 [8] and $LiIO_3$ [9], the authors only attempted to detect the differential reflection of left and right circularly polarized light leading, in accordance with formula (5), to the ellipticity of the reflected light. Here, for the first time, we have studied experimentally specular polarization azimuth rotation which may be derived from (5):

$$\alpha_r = \frac{2\pi \operatorname{Im}\{\gamma\}}{\lambda(n^2 - 1)} + \frac{\xi\lambda^2 n\rho}{\pi^2(n^2 - 1)^2} , \tag{6}$$

where ξ is the absorption coefficient. One can see that specular polarization azimuth rotation is only possible if either pronounced absorption coefficient $\xi=(\pi/\lambda n)\mathrm{Im}\{\epsilon\}$ or the imaginary part of the optical nonlocality tensor $\mathrm{Im}\{\gamma\}$ exists. Since the imaginary parts of both of these material parameters rise up in the absorption spectral range, a pronounced specular polarization azimuth rotation may be expected only in a strongly absorbing material.

For our experiment a crystal of α-HgS (cinnabar) was chosen. This is a gyrotropic crystal belonging to the 32 point group. It is a direct-band-gap semiconductor and consequently has a very sharp spectral absorption dependence for wavelengths close to the band gap. The exact band-gap energy for α-HgS is not known, but in accordance with [11,12] it is likely to be in the region of 2.09–2.1 eV at 27 °C.

Unlike in previous, unsuccessful experiments undertaken by replacing the optically active sample by a mirror and measuring the difference in reflected signals, the dependence of the material parameters on temperature (T) was exploited in our experiment. This gave us a nonviolating, mechanically stable and very reproducible technique for "switching off" and "switching on" the temperature-dependent part of the specular optical activity simply by variation of the sample temperature. Evidently this type of technique is more effective near the band gap where strong temperature dependencies of the material parameters may be expected. Near-band-gap measurements in α-HgS are very conveniently studied with a 543 nm green HeNe laser because the band-gap energy E_g is close to its quantum energy, $\hbar\omega=2.28$ eV. The energies may be even more closely matched by cooling the crystal and exploiting its pronounced band-gap temperature dependence of $\mu=-7\times10^{-4}$ eV/°C [11,12]. This gives an opportunity to scan near the band gap using a fixed wavelength laser. The polarization experiments were undertaken with a synthetic cinnabar monocrystal of perfect natural hexagonal prism shape and physical dimensions of approximately $1\times1\times1.5$ mm. The reflecting surface, cleaved normally to the z axis of the crystal, had mirror-like quality.

To evaluate the expected polarization azimuth rotation on reflection from the α-HgS crystal one needs exact data on ϵ and γ at the wavelength 543 nm inside the band gap. These data are not available, but may be partially estimated. The rotatory power may be found from the Drude formula $\rho[\mathrm{deg/mm}]=A(\lambda^2-\lambda_1^2)$, which is one of the most accurate for this crystal [11]. Here at $T=27\,°\mathrm{C}$ one should use the following values: $A=33.70$ μm^{2}deg/mm, $\lambda_1=0.5389$ μm, and correspondingly $A=33.92$ μm^{2}deg/mm, $\lambda_1=0.5326$ μm at $T=-25\,°\mathrm{C}$. This gives $\rho=7597$ deg/mm at $T=27\,°\mathrm{C}$ and $\rho=3032$ deg/mm at $T=-25\,°\mathrm{C}$ (unfortunately the Drude parameters are not available for higher temperatures).

The absorption coefficient is likely to be in the range between a typical direct-gap semiconductor value of 10^4 cm^{-1} and the maximum limiting value of 3.6×10^5 cm^{-1} obtained from the reflection measurements described below. Correspondingly, the contribution of the second term from formula (6) should be on the scale of 2.1×10^{-4}–7.6×10^{-3} rad at 27 °C. Now, the temperature variation of the effect may be estimated. In order to do this we may adopt the simplest model for the band-gap variation of the absorption coefficient $\xi\propto[\hbar\omega-E_g(T=27\,°\mathrm{C})-\mu\Delta T]^{1/2}$, where μ is the rate of the band-gap collapse with temperature and ΔT is the temperature variation from 27 °C. In accordance with this model the absorption coefficient should decrease by 11% as temperature drops from 27 °C to -25 °C. Correspondingly, taking into account variations of ρ, the expected change of the specular polarization azimuth rotation should be about 65% of its value at 27 °C, if the temperature drops from 27 °C to -25 °C and the resulting observed polarization plane rotation may be estimated as 1.3×10^{-5}–5×10^{-3} rad. A direct specular polarization rotation estimate of the circular dichroism contribution to (6) is not possible since no data on $\mathrm{Im}\{\gamma\}$ are available. Nevertheless, for microscopic reasons the absolute values of the two contributions in formula (6) should be of the same order of magnitude and the estimate produced above should be correct.

The polarimeter (see Fig. 1) was based on a birefringent calcite polarization prism (CP) which splits the light into two orthogonally polarized beams. Initially, the laser beam passes through the prism acting as the polarizer and then through the Faraday polarization modulator (FM) consisting of a 5 mm long high-quality terbium gallium garnet crystal and driven by a low-frequency generator. After reflection from the sample it returns again through the FM and the same prism, now acting as an analyzer. This gives perfect mutual mechanical stability: Any unwanted deviation of the polarizer orientation does not affect the polarimeter setting because the analyzer, being the same prism as the polarizer, is exposed to exactly the same perturbations. The component of the reflected beam with unchanged polarization state follows the incident path and is dissipated by the optical isolator consisting of a Glan prism (GP) and a second permanent

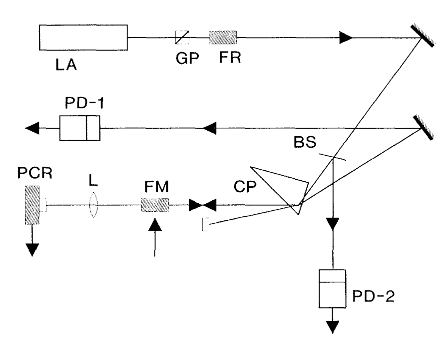

FIG. 1. Block diagram of the apparatus for specular polarization-plane rotation measurements.

Faraday rotator (FR), thus preventing interference effects between the incoming and outgoing beams and crucially allowing us to perform perfectly normal incidence experiments. A polarization component orthogonal to the initial one, resulting from a polarization-changing interaction of the light with the crystal, follows a different path in the prism and is detected by a Si photodiode (PD-1) with a low noise, temperature stabilized FET-DIFET amplifier. The sample is enclosed in a Peltier-type cryostat (PCR) and may be held at any temperature between -20 and $+80\,^\circ$C. The cryostat was designed to minimize the deviation of the sample when the cryostat was in operation and it was found that during the cooling-heating cycle the angular deviation of the reflection surface was less than 2×10^{-4} rad. The entire polarimeter is situated on a thermally stabilized granite table, enclosed in a box, minimizing temperature fluctuation.

The technique of specular polarization azimuth rotation measurements is based on phase-sensitive detection of the polarimeter output due to a forced polarization-plane modulation inside the polarimeter. The incident light polarization is modulated, typically with 0.001 rad amplitude, by the FM at a frequency (Ω) of approximately 290 Hz. If we presume that the incident light is polarized along the x direction, and that the polarizer and analyzer are ideal, then the Stokes vector immediately after the polarizer is $S_i = I\{1;1;0;0\}$, where I is the initial light beam intensity. If no forced modulation is introduced by the FM, then the reflected wave Stokes vector S_r should be $I_r\{1;\cos2\eta_r\cos2\alpha_r;\cos2\eta_r\sin2\alpha_r;\sin2\eta_r\}$. The polarization modulation in the FM may be taken into account in the analyzer function by assuming that the main axis of the analyzer oscillates with frequency Ω. Since the Faraday modulator is a nonreciprocal device, the amplitude A of the beam polarization modulation doubles on the way back. The condition of perfectly crossed polarizer and analyzer pair is met automatically in our experiment and the effective orientation of the analyzer is given by $\phi = \pi/2 + 2A\cos\Omega t$. Consequently the intensity of light, detected after the analyzer, is

$$I_{\text{PD-1}} = I_r[1+\cos2\phi\cos2\eta_r\cos2\alpha_r+\sin2\phi\cos2\eta_r\sin2\alpha_r]/2\,. \tag{7}$$

Assuming that the polarization azimuth rotation α_r and ellipticity η_r, appearing as the result of reflection from the sample, and the forced polarization azimuth modulation amplitude A in the FM are small, i.e., $\alpha_r,\eta_r,A \ll \pi$, one can find that the light intensity and correspondingly the output current of the signal photodetector (PD-1) has, besides a dc basis, spectral components on the second harmonic of modulation $I_{\text{PD-1}}(2\Omega) = 2A^2 I_r\cos2\Omega t$ and on the frequency of modulation itself $I_{\text{PD-1}}(\Omega) = -4A\alpha_r \times I_r\cos\Omega t$. The signal at the frequency of modulation is proportional to the desired angle α_r and is measured by a phase-sensitive detector locked at frequency Ω. In order to prevent influence of the reflection change on the accuracy of the polarization measurements, the magnitude $I(\Omega)$ was normalized against the reference channel PD-2. The polarimeter had zero drift not worse than 3×10^{-7} rad/min, which allowed us to do polarization-sensitive experiments with an accuracy better than 3×10^{-6} rad within our cooling-heating circle of approximately 10 min.

Measurement of the crystal reflectivity confirmed that we were working in a spectral region where there was a strong dependence of the optical parameters of α-HgS on temperature. These data are presented in Fig. 2. If the measured variation of the reflectivity is attributed to change of the refractive index n only, neglecting the absorption, n should vary from 2.93 ($T=-20\,^\circ$C) to 3.68 ($T=+80\,^\circ$C). If, however, it is due to an absorption change only, the corresponding absorption coefficient has to vary from $\xi = 7\times10^4$ cm^{-1} to $\xi = 3.3\times10^5$ cm^{-1}, which should be considered as the maximum possible value of the absorption coefficient. A conclusive decision about the exact reason for the reflection variation cannot be made on the basis of these data and it is most likely that both refractive index and absorption change contribute to it. However, the data prove that in the temperature range of -20 to $+80\,^\circ$C the optical parameters of the α-HgS crystal change dramatically. Correspondingly, strong variation of optical activity on reflection may be

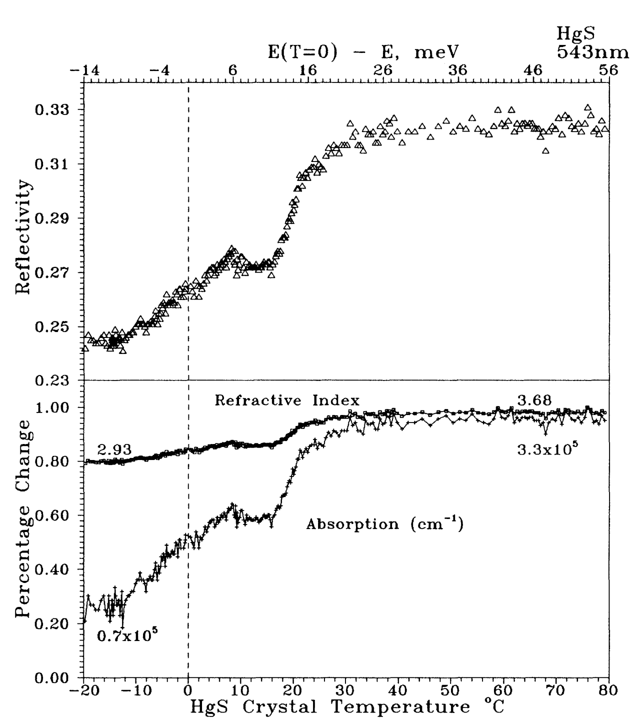

FIG. 2. Upper: Measured reflectivity of the α-HgS crystal as a function of crystal temperature, normal incidence along the optical axis. Lower: Corresponding variation of refractive index (assuming zero absorption) and absorption variation (assuming constant refractive index $n = 2.9$).

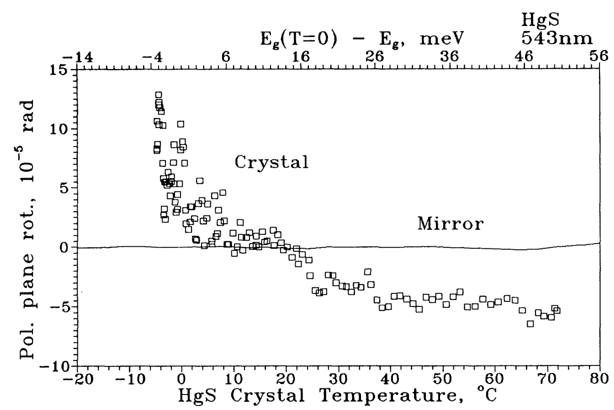

FIG. 3. Measured variation of polarization azimuth of a light wave normally reflected from the crystal of α-HgS along the optical axis as a function of crystal temperature. The zero here corresponds to the position of the polarization azimuth at $T=20\,°C$. The solid line represents a typical curve obtained when the crystal is replaced by a metal mirror.

expected here.

Rotation of the polarization azimuth with variation of the sample temperature was clearly observed in the α-HgS crystals. No polarization alteration above the noise level of 3×10^{-6} rad was detected in the same temperature range with an aluminum mirror in place of the sample of α-HgS. The variation of the polarization azimuth with temperature in α-HgS is presented in Fig. 3 with respect to the measured orientation of the reflected light polarization plane at $T=20\,°C$. Note, the zero of the graph in Fig. 3 does not refer to the total zero of specular optical activity and indicates only relative instrument zero which may be affected by both the temperature-independent contribution to specular rotation and errors in tuning the polarimeter. Therefore the dependence indicating strong temperature variation of the effect does not necessarily show greater magnitude of optical rotation when there is least resonance or change of its sign at $T=20\,°C$. The experiment with α-HgS was undertaken under perfectly normal incidence. The deviation of the beam from the direction of the normal was measured to be less than $\beta_{max}=4\times10^{-4}$ rad during the heating-cooling cycle. Despite this, to ensure that there is no contribution to the polarization change from the linear dichroism appearing as the result of not having perfectly normal incidence, the experiments were repeated with the sample turned by 90° about the optic axis. In this case, if for any reason there is some divergence of the light direction from the optic axis and correspondingly there is some birefringence along the light propagation direction, the polarization plane rotation due to the linear dichroism will change sign as a result of the interchanging of the ordinary and extraordinary axes. No dependence of the polarization rotation curve on the crystal orientation was observed. This leads to the conclusion that the observed specular polarization azimuth rotation was solely due to the optical activity effect. The observed value also meets that predicted by formula (6).

The main difference between this study and previous reflection optical activity experiments [8,9,13] is that here we have taken measurements from a strongly absorbing material which enabled us to measure polarization azimuth rotation in reflected light rather than left-right differential reflection, which is the only permitted phenomenon in low-absorption media. Purely normal incidence is also very important because the different sets of material equations discussed by various authors predict specular polarization effects at inclined incidence to the interface but produce controversial results for normal incidence. Because of this, the positive experimental results recently obtained by Silverman, Badoz, and Briat [13], where differential reflection of left and right circularly polarized light was reported, while being an important achievement, cannot provide an argument in this discussion.

Finally we claim here that optical activity on normal reflection from a gyrotropic medium exists. In a strongly absorbing medium it manifests itself as a polarization azimuth rotation. This also confirms that the theoretical treatment [10] establishing the equivalency of the Casimir and the Landau-Lifshitz approaches to the material equation is correct.

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