perature relative χ value of the P-doped Si at 1.1, 4.2, and 77 °K, which is essentially in agreement with the present result. However, because of the lack of (a) a detailed analysis of the temperature dependence of χ and (b) the absolute determination and comparison with the static values, their discussions on localized-moment problem remain rather speculative.

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Light Scattering from Polaritons and Plasmaritons in CdS near Resonance

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We have investigated light scattering from polaritons and plasmaritons in CdS near resonance. These results are compared with computer-calculated dispersion curves for these excitations. We find a good agreement between theory and experiments. Particular attention is given to interesting effects arising from birefringence and resonance.

I. INTRODUCTION

It is well known[1] that there is a strong coupling between the transverse optical (TO) phonons in polar crystals and electromagnetic waves when their energies and wave vectors are nearly equal. The coupled photon-TO mode, known as the "polariton," has been investigated in a number of crystals by light scattering at small angles.[2] However, light scattering from polaritons in CdS has not been reported so far.

The polariton dispersion relation in a crystal is determined by the transverse-dielectric-response function of the crystal. It is well known[3] that the presence of free carriers in a crystal modifies its transverse dielectric function. There is, thus, a coupling between the electron plasma and the polariton in the crystals. This coupled mode has been called the "plasmariton." The only experimental observation of the plasmariton reported so far is by Patel and Slusher,[4] who also investigated the effect of magnetic field on the plasmariton in GaAs. Alfano[5] has calculated dispersion relations for the plasmariton in GaAs. However, the use of damping in these calculations has been questioned.[6] Wolff[7] has calculated the scattering cross sections for these excitations.

We have experimentally studied light scattering from polaritons and plasmaritons in CdS. The case of CdS is very complex and interesting for two reasons. First of all, CdS changes from a positive birefringent crystal to a negative birefringent crystal as one approaches the band-gap energy from below.[8] Second, resonance effects (or dispersion of the refractive index) must be taken into account because the Ar^+ laser lines used in the present experimental work are close to the band gap of CdS.

In this paper, we present our experimental results and compare them with the computer-calculated dispersion relations for polaritons and plasmaritons. We present the experimental techniques and results in Sec. III. Experimental and theoretical results are compared in Sec. IV.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

Most of the experiments were performed using 5145- and 4965-Å lines from a 200-mW Ar^+ laser. A He-Ne laser operating at 6328 Å was also used. Since the coupling between electromagnetic waves and transverse excitations in the crystals is strong only at small wave vectors, the Stokes scattered radiation was measured at very small angles (θ) with respect to the incident beam. Apertures were used to select the desired scattering angle θ. The scattered radiation was analyzed using a double spectrometer.

Data were obtained for three different samples: (a) a "pure" sample ($n \sim 10^{15}$ cm^{-3}); (b) an indium-doped sample with $n \sim 4\times10^{18}$ cm^{-3}; and (c) an indium-doped sample with $n \sim 2\times10^{19}$ cm^{-3}. All measurements were performed at ~5 °K. At this temperature, the 5145-Å laser beam was not significantly absorbed by any of the samples. The 4965-Å laser beam was strongly absorbed by the two doped samples even at this low temperature. The plasmariton data is thus available only at one laser frequency.

All the measurements were carried out in either the $x(yz)\bar{x}$ or $x(zy)\bar{x}$ geometry. [$x(yz)\bar{x}$ implies that the incident laser was along x direction, the scattered radiation was approximately along x, and the incident and scattered polarizations are along y and z directions, respectively. The z direction is along the crystal c axis.] The direction of the phonon propagation was always chosen to be the z direction.

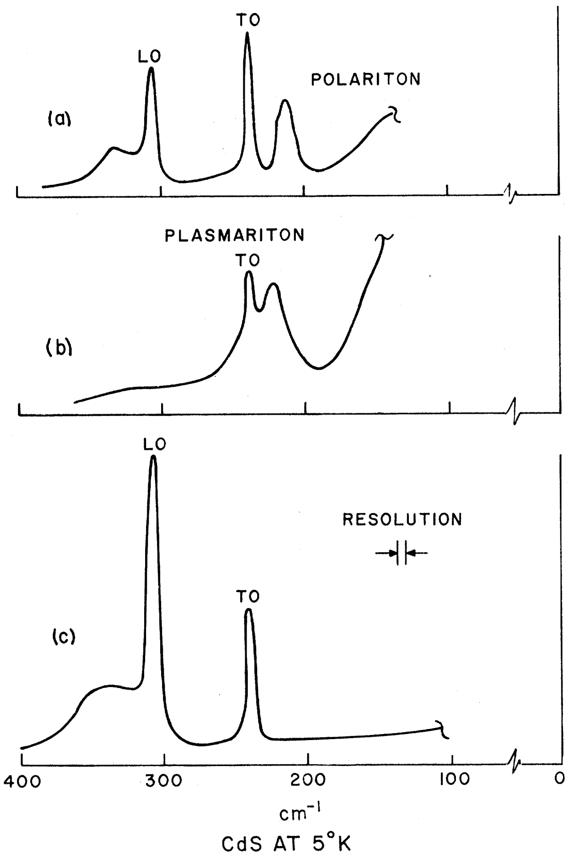

FIG. 1. Experimental Stokes scattered radiation at $\theta \approx 0.6°$ for two samples: (a) "pure" and (b) doped $n \sim 4\times10^{18}$ cm^{-3}. Curve (c) is the spectrum obtained from the pure sample at $\theta = 90°$ and is shown here for comparison. The 5145-Å laser line was used. Samples were taken at 5 °K. The TO in (a) and (b) is due to back scattering.

Figures 1(a) and 1(b) show the Raman spectra obtained for two samples at $\theta \simeq 0.6°$ for $x(yz)\bar{x}$ geometry. For comparison we have also shown [Fig. 1(c)] the spectrum obtained for $\theta = 90°$ for the pure sample. In Figs. 1(a) and 1(b), we see an additional peak which is at lower energy than the TO mode. We note that the difference between the energies of this peak and the TO mode decreases as the carrier concentration increases. We identify this peak as due to light scattering from the plasmariton, or the coupled plasma-polariton mode.

For all three samples, data were obtained at various scattering angles and for the two scattering geometries described above. In Sec. IV, we will present these data in a reduced form and compare them with computer calculations of the dispersion relations to be obtained in Sec. III. We conclude this section with one comment. The He-Ne laser operating at 6328 Å would be ideal for investigating polaritons and plasmaritons in CdS for two reasons: (i) The complicated effects of resonance can be neglected, and (ii) since the laser is not strongly absorbed even at 300 °K, plasmariton data could also be obtained at two frequencies. We did attempt to observe these effects with a 200-mW He-Ne laser. However, no TO mode was observed at 6328 Å.[9] Therefore no data for the He-Ne laser could be obtained.

III. DISPERSION RELATIONS FOR PLASMARITONS IN CdS NEAR RESONANCE

The transverse-dielectric function of a system consisting of optical phonons and conduction electrons in CdS in the long-wavelength and self-consistent-field (SCF) approximation is[10]

$$\epsilon_T(\omega)=\epsilon_\infty-\frac{4\pi}{i\omega}\,\sigma_T-\frac{(\epsilon_0-\epsilon_\infty)\omega_{\mathrm{TO}}^2}{\omega^2-\omega_{\mathrm{TO}}^2}\,, \tag{1}$$

where we have neglected phonon damping. ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively, and ω_{TO} is the TO phonon frequency. σ_T, which is the transverse conductivity, can be shown[11] to be given by

$$4\pi\sigma_T/i\omega=(\omega_p^2/\omega^2)\epsilon_\infty\,,$$

where

$$\omega_p=(4\pi n e^2/\epsilon_\infty m_e^*)^{1/2}$$

is the $q=0$ plasmon frequency. Here n is the density of free carriers, e is the charge of the carrier, and m_e^* is their effective mass.

Since Maxwell's equations require that $\epsilon_T(\omega)=c^2q^2/\omega^2$, where c is the velocity of light and q the wave vector of the normal mode, we have

$$\frac{c^2q^2}{\omega^2}=\epsilon_\infty\left(1-\frac{\omega_p^2}{\omega^2}\right)-\frac{(\epsilon_0-\epsilon_\infty)\omega_{\mathrm{TO}}^2}{\omega^2-\omega_{\mathrm{TO}}^2}\,. \tag{2}$$

In order to facilitate comparison between theory and experiments, it is desirable to express ω as a function of θ, the scattering angle, rather than q. To do this, we make use of energy and momentum conservation equations

$$\omega=\omega_i-\omega_s\,, \tag{3}$$

$$q^2=k_i^2+k_s^2-2k_ik_s\cos\theta\,, \tag{4}$$

where $\omega_i(\omega_s)$ and $k_i(k_s)$ are the frequency and wave vector of the incident (scattered) photon. In eliminating q, one must remember two complications: (i) CdS is a birefringent material so that the index of refraction for the ordinary and extraordinary rays are different, i.e., $n_0\neq n_e$. (ii) In our experimental situation, $\hbar\omega_i$ is close to the band-gap energy so that dispersion must be taken into account.

If we approximate

$$n(\omega)=n(\omega_i)+(\omega-\omega_i)\,\frac{\partial n}{\partial\omega}\,,$$

we obtain the following expressions:

Case (i). For incident-ray ordinary and scattered-ray extraordinary [$x(yz)\bar{x}$ in our notation]

$$\frac{1}{\omega^2}\left\{\left[\omega_i(n_0-n_e)+\omega\left(n_e+\omega_i\frac{\partial n_e}{\partial\omega}\bigg|_i\right)\right]^2+n_0n_e\omega_i^2\theta^2\right\}\approx\epsilon_\infty\left(1-\frac{\omega_p^2}{\omega^2+\Gamma^2}\right)-\frac{(\epsilon_0-\epsilon_\infty)\omega_{\mathrm{TO}}^2}{\omega^2-\omega_{\mathrm{TO}}^2}\,. \tag{5}$$

Here $(\partial n_e/\partial\omega)|_i$ means that $\partial n_e/\partial\omega$ is to be evaluated at ω_i. In arriving at Eq. (5), we have assumed that $\omega_i\gg\omega$ and $n_e\gg\omega(\partial n_e/\partial\omega)|_i$. The actual numbers to be presented later will show that these conditions are very well satisfied in the case of CdS. We have also introduced a phenomenological damping constant Γ for the electron plasma.

Case (ii). For incident-ray extraordinary and scattered-ray ordinary [$x(zy)\bar{x}$ in our notation], n_0 and n_e are interchanged to give

$$\frac{1}{\omega^2}\left\{\left[\omega_i(n_e-n_0)+\omega\left(n_0+\omega_i\frac{\partial n_0}{\partial\omega}\bigg|_i\right)\right]^2+n_0n_e\omega_i^2\theta^2\right\}\approx\epsilon_\infty\left(1-\frac{\omega_p^2}{\omega^2+\Gamma^2}\right)-\frac{(\epsilon_0-\epsilon_\infty)\omega_{\mathrm{TO}}^2}{\omega^2-\omega_{\mathrm{TO}}^2}\,. \tag{6}$$

From Eqs. (5) and (6), we can calculate the frequencies of the plasmariton expected at a given scattering angle. Setting $\omega_p=0$ would give the curves for the polariton in CdS. In Sec. IV we present these computer-calculated results and compare them with the experimental data.

IV. COMPARISON BETWEEN THEORY AND EXPERIMENTS

Before presenting the results of any calculations, it should be pointed out that no adjustable parameters were used in these calculations. The values of all the required constants for CdS are well known. The calculations need values of n_0, n_e, $\partial n_0/\partial\omega$, and $\partial n_e/\partial\omega$ at two different frequencies at 5 °K. These quantities were measured by Gobrecht and Bartschat[8] at 300 and 80 °K. We have assumed that the values at 5 °K can be reasonably well obtained by linearly extrapolating the data of 300 and 80 °K to 20 °K. The appropriate values used are given in each figure caption. The only other unknown is the value of ω_p. The two doped samples used in these experiments are the same as those used in our experiments on the plasmon–LO-mode coupling.[12] These experimentally determined values of ω_p and Γ were used for calculations.

Let us first consider the results obtained for the 5145-Å laser.

In Fig. 2, we show four computed polariton curves. Let us consider the solid curves (a) and (c) which represent cases (i) and (ii), respectively,

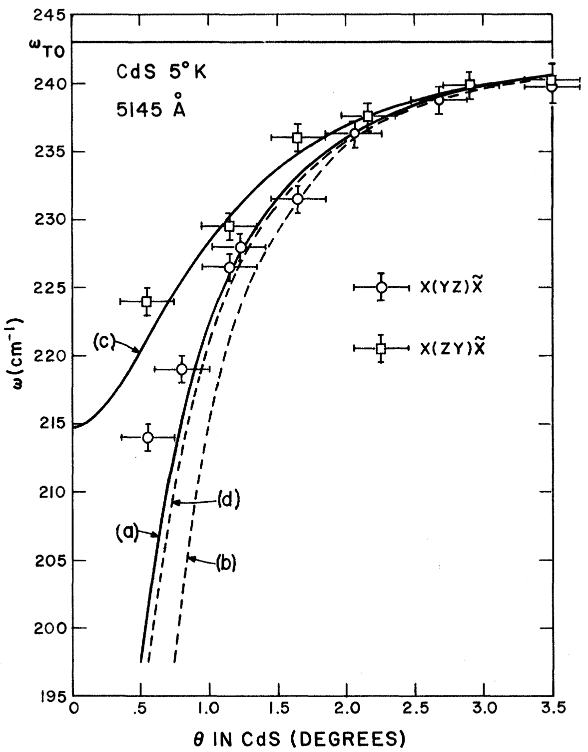

FIG. 2. Polariton frequency ω vs scattering angle. θ. Circles and squares are experimental points obtained with 5145 Å. The solid and dashed curves are calculated. The following values of parameters were used: $\epsilon_\infty = 5.10$, $\epsilon_0 = 8.60$, $\omega_{TO} = 243\ \mathrm{cm}^{-1}$, $\omega_l = 19\,431.0\ \mathrm{cm}^{-1}$, $n_0 = 2.600$, and $n_e = 2.605$. Curve (a): case (i) [Eq. (5)], $(\partial n_e/\partial\omega)\,|_l = 7.5\times10^{-5}$ cm; curve (b): case (i) but $(\partial n_e/\partial\omega)\,|_l = 0$; curve (c): case (ii) [Eq. (6)] $(\partial n_0/\partial\omega)\,|_l = 1\times10^{-4}$ cm; curve (d): case (ii) but $(\partial n_0/\partial\omega)\,|_l = 0$. The sample temperature is 5 °K; $\omega_p = 0$.

for the true values of CdS parameters. The circles are the experimental points obtained for $x(yz)\tilde{x}$ geometry. One can see that the agreement between these points and curve (a) is good except for $\theta < 1°$. The calculated value of ω at $\theta \approx 0$ for case (i) is rather sensitive to $n_0 - n_e$. Since this number $(n_0 - n_e)$ was obtained from an extrapolation, the poor agreement might be due to an error in extrapolation. The squares are experimental points for $x(zy)\tilde{x}$ geometry. They agree well with curve (c) calculated for case (ii). Notice that at 5145 Å, $n_e > n_0$ in CdS, i.e., CdS is a positive birefringent crystal (like ZnO and quartz). Therefore, in agreement with the data on ZnO [13] and quartz, [14] the frequencies for $x(yz)\tilde{x}$ (here measured in wave-number units) geometry [case (i)] are smaller than those for $x(zy)\tilde{x}$ geometry [case (ii)].

The dashed curves (b) and (d) are computed for cases (i) and (ii), respectively, by assuming that there is no resonance [i.e., $(\partial n/\partial\omega)\,|_l = 0$]. We can see that the absolute frequencies are smaller than those for the corresponding cases (a) and (c). This is in agreement with the result previously obtained for ZnSe. [15]

We have just seen that in CdS for both cases (i) and (ii), the effect of resonance is to increase the polariton frequency for a given scattering angle θ. It is, however, clear from the equations that this need not be the case for all materials. For example, if $n_0 = 2.40$ and $n_e = 2.60$ and other parameters are the same as in Fig. 2, then our calculations show that introduction of resonance $(\partial n/\partial\omega = 3.5\times10^{-4}$ cm) will decrease the polariton frequency for case (i), and increase the polariton frequency for case (ii) for a given scattering angle. Thus the value of parameters like n_0, n_e, $\partial n/\partial\omega$, etc., will determine the effect of resonance in a given material.

Let us now consider the effect of doping. We have seen in Fig. 1 that doping increases plasmariton frequency. The reduced data at different scattering angles for the case $x(yz)\tilde{x}$ are presented in Fig. 3 together with three computed curves (one for each sample) for case (i). Curve (a) for the pure sample

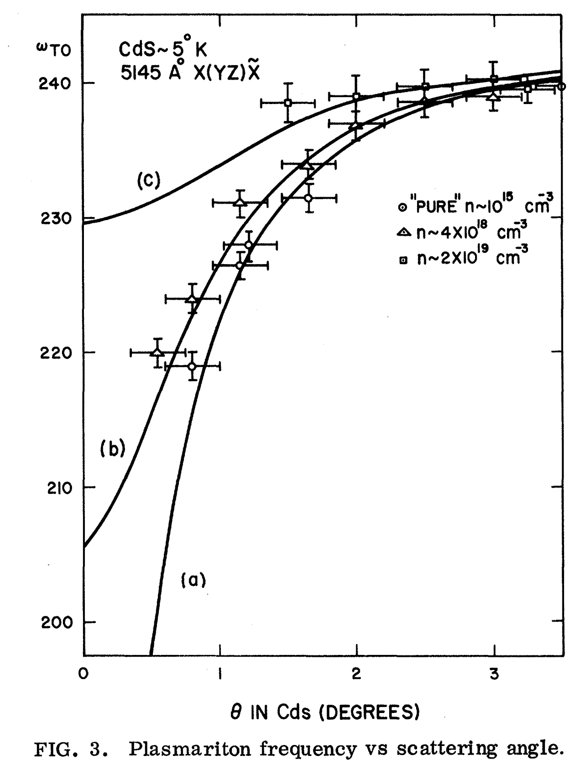

FIG. 3. Plasmariton frequency vs scattering angle. The values of the parameters are the same as in Fig. 2. Solid curves are calculated for case (i) [Eq. (5)]. Curve (a): "pure" sample; curve (b): $n \sim 4\times10^{18}\ \mathrm{cm}^{-3}$; curve (c): $n \sim 2\times10^{19}\ \mathrm{cm}^{-3}$. Curve (a) is identical to (a) in Fig. 2. Circles, triangles, and squares correspond to samples a, b, and c, respectively. Samples taken at 5 °K. $\omega_p = 0$, 300, and 700 cm^{-1} for a, b, c, respectively. $\Gamma = 160$ (200) cm^{-1} for b and c.

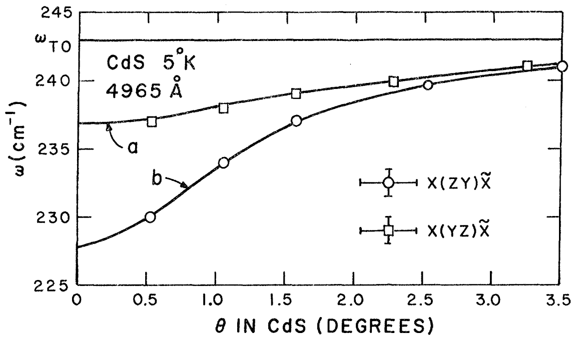

FIG. 4. Polariton frequency vs scattering angle. Circles and squares are experimental points. Solid curves are computed using the following parameters: $\epsilon_\infty = 5.10$, $\epsilon_0 = 8.60$, $\omega_{TO} = 243\ \text{cm}^{-1}$, $\omega_l = 20\,135.4\ \text{cm}^{-1}$, $n_0 = 2.765$, $n_e = 2.75$, and $\omega_p = 0$. A 4965-Å laser line was used. The sample was taken at 5 °K. Curve (a): case (i), $\partial n_e/\partial\omega = 3.5\times10^{-4}$ cm; curve (b): case (ii), $\partial n_0/\partial\omega = 5.6\times10^{-4}$ cm.

is the same as curve (a) of Fig. 2. We see that the agreement between observed and calculated plasmariton frequencies is reasonably good, considering that the plasmariton scattered lines are rather broad (Fig. 1).

Figure 4 presents the results for the 4965-Å laser line. The solid curves are computed while the points are experimental. One can see that the agreement between the two is good.

One point of interest is comparison between the 5145- and 4965-Å data. Comparing the values of $n_0 - n_e$ at 5145 and 4965 Å (captions of Figs. 2 and 4), one notices that CdS has passed through its "isotropic wavelength" between these wavelengths, i.e., CdS, which is a positive birefringent crystal at 5145 Å, has become a negative birefringent crystal at 4965 Å. One may therefore expect that the polariton frequencies for case (ii) will be smaller than those for case (i) at 4965 Å, exactly opposite of what happens at 5145 Å. This expectation is experimentally as well as theoretically verified, as can be seen from Fig. 4.

V. SUMMARY AND CONCLUSIONS

We have presented experimental results on light scattering from polaritons and plasmaritons in CdS. We have also computed the dispersion curves for these excitations. We find that there is a good agreement between experimental and computed results. The analysis of the data is complicated by the fact that CdS is birefringent, that its birefringence changes sign in the region of interest, and that resonance effects must be considered. We have demonstrated the effects of these factors on the dispersion relations of polaritons and plasmaritons.

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