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Observation of Forbidden Brillouin Scattering near an Exciton Resonance

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We have observed resonant Brillouin scattering by TA phonons near the *A* exciton of CdS in a usually forbidden backscattering configuration. This effect, attributed to electron-phonon piezoelectric coupling, is equivalent to the Fröhlich-interaction–induced forbidden LO scattering. A numerical estimate of the scattering strength of the forbidden TA scattering accounts for the intensity of the observed lines.

Fröhlich-interaction–induced resonant forbidden Raman scattering by *longitudinal* optical phonons has been extensively investigated in semiconductors.[1] In this Letter we show that a similar effect exists for *transverse* acoustic phonons and we present, for the first time to our knowledge, experimental evidence of resonant forbidden Brillouin scattering. The macroscopic electric field required for the Fröhlich interaction is, in this case, produced by the strain-induced longitudinal piezoelectric polarization, i.e., by the piezoelectric coupling between TA and LO modes. Surface electric field or impurity-induced forbidden scattering can be ruled out since it would not conserve the vector $\vec{q}$ thus leading to broad structures in scattering by acoustic phonons.

Our measurements were performed in the regime of resonant polariton scattering discussed by Brenig, Zeyher, and Birman[2] and experimentally observed for allowed LA scattering by Ulbrich and Weisbuch[3] in GaAs, and by Winterling and Koteles[4] in CdS. Our samples were vapor-grown single-crystal CdS platelets with smooth, unpolished surfaces and a thickness of $\sim 10^{-2}$ cm. The Brillouin spectra were excited by the focused beam of a tunable narrow-band ($\lesssim 0.4$ cm^{-1}) cw dye laser (Coumarin 102) with the sample at $T \sim 6$ K. The incident power density was of the order of 1 W/cm^2. Both the incident and the backscattered light propagated with $\vec{k}$ perpendicular to the hexagonal c axis and their electric fields were also perpendicular to c. Thus the scattering wave vector $\vec{q}$ was perpendicular to the c axis and, consequently, the scattering phonons are either purely longitudinal or purely transverse. The backscattered light was spectrally analyzed with a double-grating monochromator. The combined spectrometer and dye-laser width was 0.7 cm^{-1}.

The principle of resonant polariton (back-) scattering is illustrated in Fig. 1(a). The exciton-polariton dispersion relation of CdS in the vicinity of the *A* exciton was obtained from the dielectric function[6] with the parameters given in Fig. 1. Contrary to the ordinary picture of resonant scattering which involves *virtual* excitons as intermediate states, polariton scattering takes place between two real polariton states. The allowed LA backscattering, indicated by the dashed lines in Fig. 1(a), is that reported in Ref. 4 and shown also in Fig. 2.

The corresponding backscattering by TA phonons is, for $q \rightarrow 0$, forbidden by symmetry. The shear strains in this case modulate only that component of the optical-frequency dipole moment which is parallel to the $\vec{q}$ of the TA phonon and which, consequently, cannot radiate in the backward ($\vec{q}$) direction. This argument applies equally to deformation-potential coupling and to coupling through the first-order electro-optic effect.

Strong resonant forbidden LO Raman scattering[1] has been observed in CdS. It is induced by the macroscopic longitudinal electric field of the LO phonon through the Frölich interaction. Since the slow TA phonon also has a *longitudinal* electric field (piezoelectric effect), as one sees from an inspection of the piezoelectric tensor, resonant forbidden TA scattering in analogy to the forbidden LO scattering should take place. We

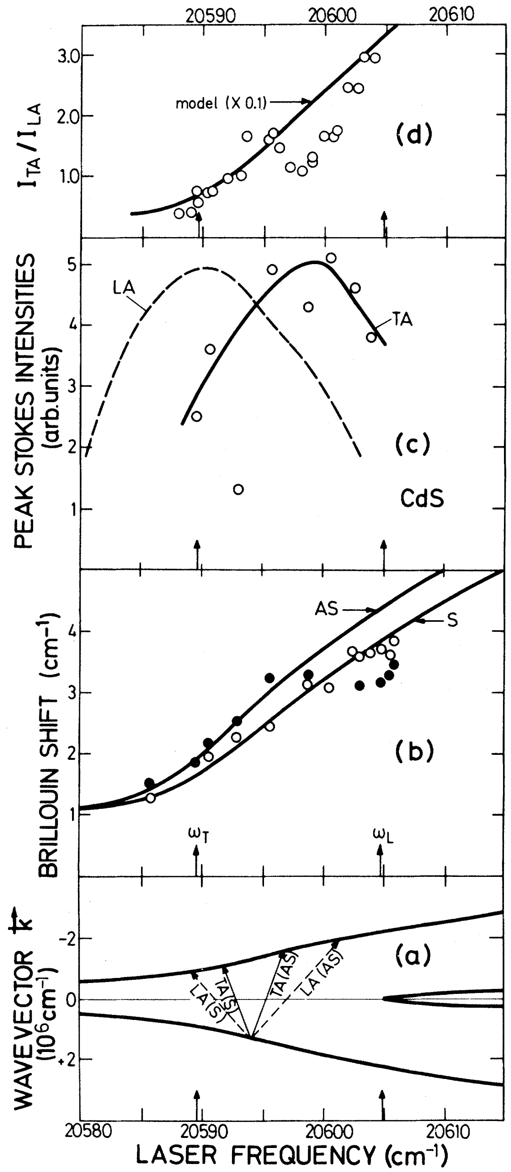

FIG. 1. (a) Polariton dispersion for incoming (+ k) and outgoing (− k) waves calculated with the parameters given in (b): ϵ_0 is the background dielectric constant; m is the exciton mass; ω_L is the longitudinal exciton frequency, and ω_{LT} is the longitudinal-transverse exciton splitting (see Ref. 5). (b) Theoretical curves of Stokes (S) and anti-Stokes (AS) shifts due to scattering by TA phonons with velocity v. The open and filled circles are the measured Stokes and anti-Stokes shifts, respectively. Here, $\omega_L = 20\,604.9\ \mathrm{cm}^{-1}$, $\omega_{LT} = 15.3\ \mathrm{cm}^{-1}$, $\epsilon_0 = 8$, $m = 0.94m_e$, $\nu = 1.763 \times 10^5\ \mathrm{cm\ R}^{-1}$. (c) Measured TA (circles) and LA (dashed curve) peak Stokes intensities; the solid curve is a guide to the eye. (d) Ratio of the measured TA to LA peak intensities (circles) and the model estimate [Eq. (6)] of the corresponding ratio of the scattering efficiencies.

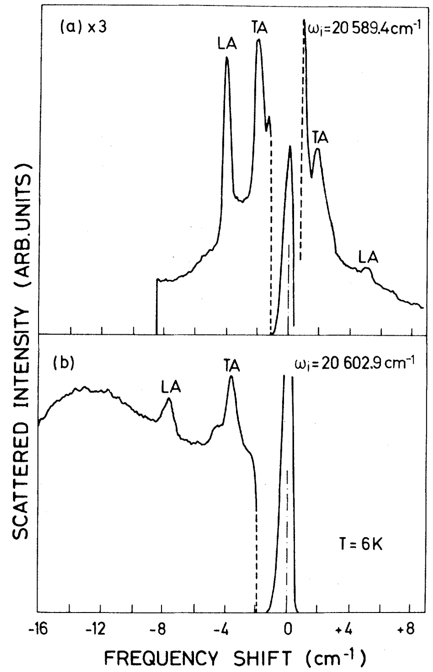

FIG. 2. Experimental traces at two incident frequencies ω_i; the elastically scattered laser light has been attenuated by inserting neutral density filters.

identify the lines labeled as TA in Fig. 2 with this scattering. The reasons for this identification are the following:

(1) The observed Brillouin shifts of the Stokes and anti-Stokes lines, shown in Fig. 1(b), agree with the shifts calculated on the basis of the exciton-polariton dispersion relation[7] using a TA velocity,[8] $v = 1.76 \times 10^5\ \mathrm{cm\ s}^{-1}$.

(2) The TA lines[9] are observed only in the $\vec{E}_s \parallel \vec{E}_i \perp c$ polarization. The parallel-parallel ($\vec{E}_s \parallel \vec{E}_i$) selection rule is characteristic of Fröhlich-interaction-induced intraband scattering as shown in forbidden LO scattering.[1] The $\vec{E}_i \perp c$ selection rule is simply related to the polarization properties of the A exciton. On the other hand, allowed TA scattering (at any scattering angle $\theta \neq 180°$) is only observable for $\vec{E}_s \perp \vec{E}_i$.

(3) The peak TA intensity is found at a larger incident photon frequency ω_i than the peak LA intensity [see Fig. 1(c)]. This upshift of the resonance maximum can be explained by the additional q^2 dependence of the forbidden TA scattering in comparison to the allowed LA one.

(4) Additional evidence for the Fröhlich mechanism originates from an estimate of the efficiency of the forbidden TA scattering. Since a measure-

ment of the absolute efficiency is very difficult we restrict ourselves here to the ratios of the TA to the LA and of the TA to the forbidden LO scattering efficiencies, as discussed below.

The Brillouin efficiencies of polariton scattering have been calculated for deformation-potential coupling[2] (allowed LA in our case) but not for the Fröhlich-interaction-induced forbidden case. The efficiencies are found to depend rather critically on the additional surface boundary conditions.

For the purpose of the present Letter we use a simple heuristic treatment of the polarizability theory[10] which is expected to provide the correct order of magnitude for the scattering efficiencies. Within this theory the Stokes-allowed LA efficiency is

$$\sigma_{\rm LA} = {\rm const}|d\chi/d\omega|^2 C_2^2 |\langle(n_{\rm LA}+1)|s_{\rm LA}|n_{\rm LA}\rangle|^2, \quad (1)$$

where const is proportional to ω^4, χ is the electrical susceptibility, $C_2 = 4.5$ eV is a deformation potential defined by Langer *et al.*[11] $s_{\rm LA}$ is the strain amplitude and $n_{\rm LA}$ is the thermal occupation number of the LA phonons. In the immediate vicinity of a resonance, the derivative in Eq. (1) must be replaced by the corresponding ratio of finite differences.[12]

Within the spirit of the polarizability theory the Fröhlich-interaction–induced LO and TA strengths, as *forbidden* effects, should be proportional to the square of the *second* derivative of χ. For one-electron transitions between parabolic bands, the following expression has been found to hold[13]:

$$\sigma_{\rm LO,\,TA} = {\rm const}\left[\frac{(m_h - m_e)}{12 m_h m_e}\left(\frac{d^2\chi}{d\omega^2}\right)\right]^2 q^2 |\langle n+1|E_F|n\rangle_{\rm LO,\,TA}|^2, \quad (2)$$

where m_e and m_h are the electron and hole masses, respectively, and E_F is the longitudinal electric field associated with the LO or TA phonon. Equation (2) should remain approximately valid for excitonic transitions, provided that one uses for χ the experimental susceptibility which includes exciton effects.

Since we are near or at the maximum of the resonance, the second derivative must be replaced by the corresponding ratio of finite differences. Thus, in Eq. (2) we can replace

$$d^2\chi/d\omega^2 \simeq \Omega^{-1} d\chi/d\omega, \quad (3)$$

where Ω is a characteristic energy; for LO scattering, $\Omega \simeq \omega_{\rm LO} = 306\ {\rm cm}^{-1}$. In TA scattering $\omega_{\rm TA}$ is smaller than the width of the exciton resonance which is broadened by the exciton-photon interaction. Therefore, in order to take polariton effects approximately into account, we use, for TA scattering, $\Omega \simeq$ L-T splitting of the exciton which is equal to $\omega_{\rm LT} = 15.3\ {\rm cm}^{-1}$ ($\omega_{\rm LO} \gg \omega_{\rm LT} > \omega_{\rm TA}$). Hence, the ratio of the TA to LO Stokes scattering efficiencies is

$$\frac{\sigma_{\rm TA}}{\sigma_{\rm LO}} \simeq \left(\frac{q_{\rm TA}\omega_{\rm LO}}{q_{\rm LO}\omega_{\rm LT}}\right)^2 \left[\frac{e_{15}^2}{\epsilon_0\epsilon_{11}c_{44}} \frac{\omega_{\rm TO}^2}{\omega_{\rm LO}^2 - \omega_{\rm TO}^2} \frac{\omega_{\rm TA}(n_{\rm TA}+1)}{\omega_{\rm LO}(n_{\rm LO}+1)}\right] \quad (4)$$

and the corresponding ratio of the TA to LA efficiencies is

$$\frac{\sigma_{\rm TA}}{\sigma_{\rm LA}} \simeq \left[\frac{m_h - m_e}{12 m_h m_e} \frac{e_{15}}{\epsilon_0\epsilon_{11}C_2\omega_{\rm LT}}\right]^2 q_{\rm TA}^2 \frac{\omega_{\rm LA}(n_{\rm TA}+1)}{\omega_{\rm TA}(n_{\rm LA}+1)} \quad (5)$$

with the shear elastic constant $c_{44} = 1.46\times10^{10}\ {\rm N\ m}^{-2}$,[8] the piezoelectric constant $e_{15} = d_{15}c_{44} = -0.208\ {\rm C\ m}^{-2}$,[14] the static dielectric constant $\epsilon_{11} = 9$ along an axis $\perp c$, the permittivity of free space $\epsilon_0 = 8.85\times10^{-12}\ {\rm C\ V}^{-1}\ {\rm m}^{-1}$ and the TO phonon frequency $\omega_{\rm TO} = 243\ {\rm cm}^{-1}$. By inserting $m_h = 0.7m$ and $m_e = 0.2m$ in Eq. (5) we obtain

$$\frac{\sigma_{\rm TA}}{\sigma_{\rm LA}} = 3.2\times10^4 q^2 (\text{in inverse Bohr radii})\left[\frac{n_{\rm TA}+1}{n_{\rm LA}+1}\right]. \quad (6)$$

This estimate, which is included in Fig. 1(d) as the solid curve, is ten times larger than the measured ratio of the Brillouin intensities. (The observed Brillouin linewidths are comparable to the instrumental width.) These values are considered to be in satisfactory agreement in view of the assumptions made and since the deviation is only a factor of $\sqrt{10} \simeq \pi$ in the scattering amplitude, the quantity calculated. The dip in the experimental ratio at 20 598 cm^{-1} is caused by the strong absorption of the TA Brillouin light at the exciton absorption peak.

The expression within the square brackets in Eq. (4) is equivalent to the ratio of the electric fields[15] $\langle E_{TA}^2\rangle/\langle E_{LO}^2\rangle$. This is calculated to be $\sim 10^{-3}$ at $T=6$ K; Eq. (4) then yields $\sigma_{TA}/\sigma_{LO}\simeq 1.5$ while our experiment gives a value of 6. This agreement demonstrates that in undoped CdS the resonant forbidden LO Raman scattering is induced by the Fröhlich interaction and not by impurities.[1]

Finally we comment on the possibility of observing forbidden TA scattering in a zinc-blende-type material, e.g., GaAs for which allowed LA backscattering has been observed from a (100) face.[3] TA phonons propagating in the (100) direction do not carry any longitudinal polarization and therefore forbidden Brillouin scattering should not be observable. For a (110) face, however, a TA phonon, polarized along the (001) axis, carries a longitudinal polarization field. In this configuration Eq. (5) still applies if C_2 is replaced by $a\simeq 9.6$ eV,[16] e_{15} is replaced by $e_{14}=0.12$ [C m^{-2}][17] and with $m_e=0.065m$, $m_h=0.6m$,[13] and $\epsilon_{stat}=12.95$. The smaller piezoelectric constant e_{14} of GaAs is overcompensated by the very small L-T splitting $\omega_{LT}\simeq 1$ cm^{-1}. Hence, forbidden TA backscattering induced by the longitudinal piezoelectric polarization should be observable from a (110) face.

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