Resonant and Forbidden Brillouin Scattering from Exciton States in Cadmium Sulfide

Zhengda Pan and James P. Wicksted
Department of Physics, Oklahoma State University, Stillwater, OK 74078
Received: 1991 February 14

New measurements are reported on the resonant enhancement and dispersion of allowed and forbidden Brillouin scattering processes from the A and B excitons in CdS. Experiments have been conducted by temperature tuning the exciton energies to a fixed laser wavelength. The most notable observation is the appearance of the forbidden transverse acoustic mode some 90 cm^{-1} below the A-exciton from a thin CdS platelet. The dispersion of the Brillouin shift as a function of temperature indicates that this mode results from an interaction with the free A-exciton state and not a bound exciton state. Measurements obtained from a bulk CdS sample are also discussed and compared with those of the platelet sample.

INTRODUCTION

Brillouin spectroscopy has previously been used to explore dipole-allowed exciton states of several II-VI semiconductors (1-2). In 1972, a theory was constructed concerning the resonant Brillouin scattering of acoustic phonons by coupled exciton-photon modes (exciton-polaritons) in dipole-allowed semiconductors (3). Predictions of this theory included resonant enhancement and dispersion of the Brillouin peaks and the appearance of additional Brillouin modes for laser energies above that of the exciton state. Experimental verification followed from several II-VI semiconductors such as CdS (4-7), CdSe (8), and ZnSe (9). However, several questions remain unanswered such as the effects of impurities and dopants on the resonant scattering of acoustic phonons by exciton-polariton modes, at what energy below the exciton state does the piezoelectric property of the material become important in the resonant scattering of transverse acoustic phonons, and how surface preparation of the sample affects the Brillouin spectrum.

In an initial effort to address these questions, Brillouin scattering experiments have been conducted from CdS as a function of temperature. This technique, which is similar to that used in Refs. 5 and 6, allowed us to study the effects of both the A and B excitons on the Brillouin spectra by temperature tuning these states to a fixed laser wavelength. In particular, lines at 488 nm and 514.5 nm of a single-mode argon-ion laser were used. The CdS single crystals studied consisted of a bulk, mechanically polished sample and a thin, unpolished platelet.

EXPERIMENTAL METHODS

Brillouin scattering experiments were performed in a backscattering configuration. A Spectra Physics model 2020 argon-ion laser provided single-line excitation at wavelengths of 514.5 and 488 nm. The incident light was directed normal to plane surfaces of the crystals containing the c-axis and was polarized either parallel or perpendicular to the c-axis; the former polarization allows interaction with the B exciton while the latter allows interaction with both the A and B excitons. An incident laser power of 15 mW was used to minimize local heating of the samples. The samples were attached to a copper mount via a conductive vacuum mixture and placed inside a Janis Supervaritemp helium dewar (Model 8DT). The temperature was measured with a silicon diode attached to the sample mount with an accuracy of 0.5 K and a control capability of ±0.1 K.

Light scattered from the samples was analyzed using a Burleigh model RC-110 triple-pass Fabry-Perot interferometer which has a finesse of 55 with a contrast of about $1x10^6$. The free spectral ranges varied from 92.58 GHz to 127.11 GHz. The scattered light also passed through a 1-nm bandwidth laser interference filter which removed most of the sample luminescence.

A Burleigh model DAS-10 stabilization system maintained the alignment of the interferometer. This was accomplished by splitting and attenuating part of the laser light (reference beam) and recombining it with the light scattered from the sample. The intense Rayleigh light was prevented from entering, the Fabry-Perot instrument by an electronic

shutter. The DAS-10 system provided adjustable bias voltages to the interferometer's three piezoelectric stacks to minimize the intensity of the reference beam as it passed through the interferometer. Photoelectric counts from an ITT FW130 photomultiplier tube were multiscaled into a Canberra Model 3502 multichannel analyzer and then analyzed on an IBM XT computer.

Two samples were used in the Brillouin scattering measurements. The first was a parallelepiped (1 x 0.5 x 0.2 cm^3), mechanically polished and supplied by Eagle-Picher. The temperature studies performed on this sample were from 80 K to room temperature using the 514.5-nm laser light. The second sample was a 200-μm-thick platelet obtained from Prof. Herman Cummins of the City University of New York. Temperature studies conducted on this sample were from 10 K to 100 K using the 488-nm laser light. No measurements could be obtained from the first sample under laser excitation of 488 nm.

EXPERIMENTAL RESULTS

The most interesting results were obtained from the thin CdS platelet. Figures 1 and 2 show spectra at temperatures of 35 K and 65 K, respectively, with polarization perpendicular to the c-axis. These temperatures correspond to energies of 75 cm^{-1} and 40 cm^{-1} below the A exciton (10). At the lower temperature, very strong longitudinal acoustic (LA) phonon modes and weak transverse acoustic (TA) phonon modes are observed on both the Stokes (energy loss) and anti-Stokes (energy gain) sides of the central peak. The central peak corresponds to the laser frequency. Brillouin shifts (in GHz) of the two phonon peaks are determined with respect to the central line. At the higher temperature, the transverse peak is no longer observed while the longitudinal mode has decreased in intensity. A dramatic increase in the background is also evident. Dispersion of the longitudinal mode is observed between these two temperature spectra. For incident light polarized parallel to the c-axis, a longitudinal phonon is observed from 10 K to 100 K, attaining its maximum intensity between 50-55 K. The dispersion as a function of temperature is shown in Fig. 3(A) for the longitudinal Stokes mode for polarization perpendicular and parallel to the c-axis of the crystal. A similar plot is given

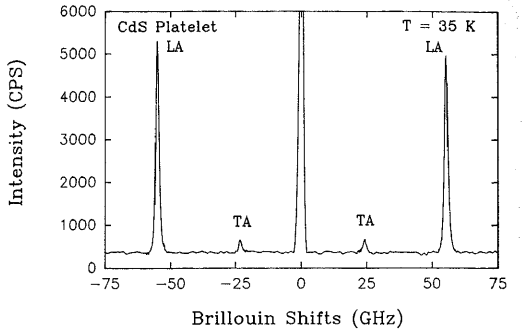

Figure 1. Observed Brillouin shifts of the LA and TA modes at 35 K with λ = 488 nm and the electric field perpendicular to c-axis. CPS = counts/second.

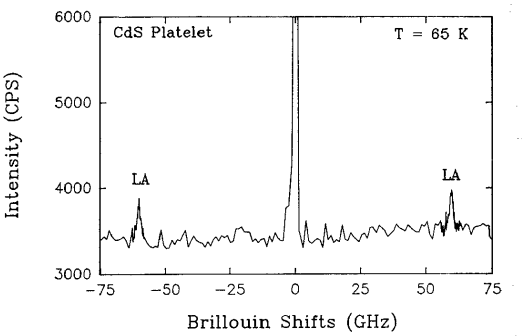

Figure 2. Observed Brillouin shifts at 65 K; parameters as in Fig. 1. TA mode is not seen.

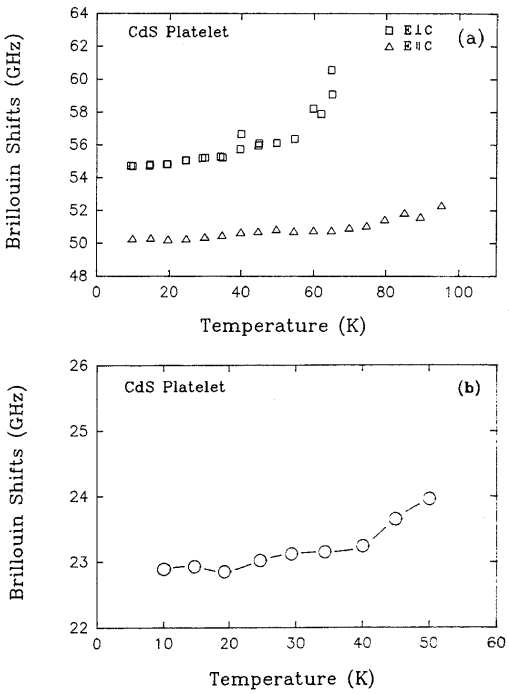

Figure 3. Brillouin shifts as a function of temperature with λ = 488 nm; (A) LA mode and (B) TA mode.

for the transverse mode in Fig. 3(B). The transverse phonon was only observed with polarization perpendicular to the c-axis.

The data obtained from the mechanically polished bulk sample were consistent with the results reported in Ref. 5. With the incident laser light (514.5 nm) polarized perpendicular to the c-axis of the crystal, the longitudinal Brillouin peaks increased in intensity as the temperature on the sample increased from 80 K, reaching a maximum at approximately 200 K. The intensity then decreased above 210 K while the background increased owing to phonon-assisted absorption. No peak could be observed above 250 K. The dispersion of the Brillouin shift was most noticeable in the temperature range 140-230 K, where it increased by ~2.5 GHz. For parallel polarization of the incident light, Brillouin spectra of the longitudinal mode could be obtained up to room temperature, reaching an intensity maximum at about 220 K. A small dispersion of about 2.5 GHz in the Brillouin shift was observed. No transverse phonon was observed in either polarization from this bulk sample.

DISCUSSION

The spectra observed from the CdS platelet is very similar to that previously reported (6). For the perpendicular polarization (resonant scattering with the A exciton), both the resonant enhancement and frequency dispersion of the longitudinal mode were observed as the temperature of the sample was increased from 10 K to 65 K. No evidence of the longitudinal mode was seen for temperatures above 65 K; at this higher temperature phonon-assisted absorption causes a large increase in background (6). For the parallel polarization (resonant scattering with the B exciton), resonant enhancement is also observed along with a small frequency dispersion of the longitudinal phonon. However, the previous study (6) did not observe the transverse phonon mode.

In this work, the transverse mode was first observed at 10 K. It increased in intensity as the temperature was raised to 35 K; above 35 K, it decreased in intensity and was not observed above 50 K. There appears to be dispersion of approximately 1 GHz associated with this mode from 20 K to 50 K.

The transverse phonon mode is normally forbidden by crystal symmetry for the backscattering configuration used. However, previous studies on CdS have observed this mode near an exciton resonance due to piezoelectric coupling of the phonon with the longitudinal electric field associated with the exciton (11). These measurements were conducted at low temperature whereby resonance was obtained by changing the energy of the laser. However, the observation of the forbidden transverse phonon was obtained for laser energies within 50 cm^{-1} of the exciton state (7). In our present study where resonance is obtained by temperature tuning the exciton state to a fixed laser energy, the onset of this mode occurs at a temperature of 10 K, which corresponds to an energy of ~90 cm^{-1} below the A exciton for the laser wavelength λ = 488 nm.

There are two possible explanations for the appearance of the transverse phonon mode. The first is that the CdS platelet studied is a very pure sample. Such samples allow very strong coupling between phonons and excitons through either the deformation potential interaction or, as previously discussed, the piezoelectric interaction. The resonant cross-section of this latter interaction depends both on the e_{15} piezoelectric constant and the wavevector of the transverse phonon. Thus, both the resonant dispersion and enhancement of this phonon should be wavevector dependent. There appears to be some increase of the Brillouin shift of the transverse phonon over the temperature range where this mode was observed (Fig. 3(B)), indicating that the phonon probably results from the piezoelectric interaction with the A exciton since only free exciton states (with finite effective masses) can yield resonant dispersion of acoustic phonons through their exciton-polariton dispersion.

A second explanation is that the transverse phonon results from resonant scattering from a bound exciton. Such bound excitons can occur in II-VI semiconductors (12) and resonant scattering via these states has been reported (8). For example, resonant scattering of a transverse acoustic phonon has been observed from the I_{2B} bound exciton in CdS (13). This bound exciton results from the B exciton becoming bound to a neutral donor atom in the crystal. A similar bound exciton, known as I_2, exists some 40 cm^{-1} below the A exciton in CdS at low temperatures (10 K). As in the case of the free A exciton, the I_2-bound exciton is active only for light polarized perpendicular to the c-axis. The

transverse phonon is observed only for incident laser light polarized perpendicular to the c-axis. Unlike the free A and B excitons, the bound exciton shows no dispersive behavior. Thus, the Brillouin shifts of the transverse phonons should not show resonant dispersion as a function of temperature since the phonon wavevector is determined by the bound exciton radius rather than by the polariton wavevector resulting from the coupled exciton-polariton mode.

CONCLUSIONS

By temperature tuning the A and B exciton states toward a fixed laser frequency, we have observed the expected resonant enhancement and dispersion of the longitudinal acoustic phonon, in addition to the forbidden transverse acoustic phonon. Since this latter phonon shows some dispersion, we feel it is coupled to the free A exciton resonance and not to the I_2-bound exciton. This implies that the piezoelectric interaction between the exciton and phonon is already important some 90 cm^{-1} below the exciton resonance and that this sample has a much stronger free exciton than bound exciton content. As reported (6), the sample quality and preparation are important factors in the observation of resonant Brillouin scattering. No low-temperature Brillouin scattering was observed from the mechanically polished bulk sample with laser excitation of 488 nm whereas the pristine platelet showed very strong scattering. Although no defect characterization has been conducted from either sample, one expects that the CdS platelet will show very strong free A exciton luminescence with small amounts of the bound exciton luminescence.

ACKNOWLEDGEMENTS,

The authors thank Professor Herman Z. Cummins of the Department of Physics at the City College of New York for generously providing the CdS platelet. This research was funded by the Defense Advanced Research Projects Agency under Contract No. MDA972-89-K-0001.

REFERENCES

1. Birman, J.L., Electrodynamics and Non-Local Optical Effects Mediated by Exciton Polaritons, In *Excitons* (Rashda, E., and Sturge, M., Eds.), North-Holland Press, Amsterdam (1982) pp. 27-82.
2. Koteles, E.S., Investigations of Exciton-Polariton Dispersion using Laser Techniques, In *Excitons* (Rashda, E., and Sturge, M., Eds.), North-Holland Press, Amsterdam (1982) pp. 83-140.
3. Brenig, W., Zeyher, R., and Birman, J.L., Spatial Dispersion Effects in Resonant Polariton Scattering. II. Resonant Brillouin Scattering. *Phys. Rev.* **B6**, 4617-4622 (1972).
4. Winterling, G., and Koteles, E.S., Resonant Brillouin Scattering Near the A Exciton in CdS. *Solid State Commun.* **27**, 95-98 (1977).
5. Pine, A.S., Resonance Brillouin Scattering in Cadmium Sulfide. *Phys. Rev.* **B5**, 3003-3007 (1972).
6. Bruce, R.H., and Cummins, H.Z., Resonant Dispersion of the Brillouin Shift in CdS. *Phys. Rev.* **B16**, 4462-4465 (1977).
7. Wicksted, J., Matsushita, M., Cummins, H.Z., Shigenari, T., and Lu, X.Z., Resonant Brillouin Scattering in CdS. I. Experiment. *Phys. Rev.* **B29**, 3350-3361 (1984).
8. Herman, C., and Yu, P.Y., Resonant Brillouin Scattering Via Free and Bound Excitons in CdSe. *Solid State Commun.* **28**, 313-316 (1978).
9. Sermage, B., and Fishman, G., Resonant Brillouin Scattering of Polaritons in ZnSe: Heavy and Light Excitons. *Phys. Rev. Lett.* **43**, 1043 -1046 (1979).
10. See Ref. 6, Fig. 3 for the correlation of sample temperature with the energy difference (in cm^{-1}) between the exciton states and the 488-nm photon.
11 Winterling, G., Koteles, E.S., and Cardona, M., Observation of Forbidden Brillouin Scattering near an Exciton Resonance. *Phys. Rev. Lett.* **39**, 1286-1289 (1977).
12. Thomas, D.G., and Hopfield, J.J., Optical Properties of Bound Exciton Complexes in Cadmium Sulfide. *Phys. Rev.* **128**, 2135-2148 (1962).
13. Wicksted, J., Matsushita, M., and Cummins, H.Z., High Resolution Resonant Brillouin Scattering of Exciton-Polaritons in Cadmium Sulphide. *Solid State Commun*. **38**, 777-781 (1981).