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Resonant dispersion of the Brillouin shift in CdS†

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Resonant dispersion of the Brillouin shift in CdS has been observed with a high-resolution triple-pass Fabry-Perot interferometer. Tuning of the *A* exciton relative to the 4880-Å argon laser line was accomplished by varying the temperature. Reflectance spectra were also measured at different temperatures, and optical constants deduced from them predict Brillouin shifts which are consistent with those observed.

INTRODUCTION

Although resonant Raman scattering in semiconducting crystals has been the subject of extensive experimental and theoretical study during the past decade, there has been relatively little work on the closely related problem of resonant Brillouin scattering. In 1971, Pine studied the Brillouin spectrum of CdS as a function of temperature.[1] As the temperature was increased, thereby lowering the frequency of the *A* exciton towards the laser frequency, he observed strong resonance enhancement of the LA Brillouin cross section. No resonance effects were observed in the Brillouin-*shift* measurements, however, since the exciton frequency did not come sufficiently close to the frequency of the 6328-Å laser line.

In 1972, Brenig, Zeyher, and Birman reported a theoretical analysis of resonant Brillouin scattering in crystals exhibiting spatial dispersion which included exciton polaritons as intermediate states in the scattering process.[2] They found that (i) there should be a rapid increase in the Brillouin shift as resonance is approached from below; (ii) when the laser frequency is slightly above the exciton frequency several new Brillouin components should appear due to the participation of both branches of the exciton polariton as intermediate states; and (iii) the cross sections for the Brillouin components should be strongly frequency dependent and should also depend on the additional boundary conditions (ABC's).

Despite the importance of these predictions, experimental verification was not quickly obtained, primarily because of the severe experimental problems associated with measuring very small frequency shifts (~1 cm^{-1}) in absorbing crystals. Furthermore, if one takes the most straightforward approach to the experiment by using a tunable dye laser, there is additional experimental difficulty at least with Rhodamine 6G, due to the dye fluorescence which produces an intense background near the laser line.

Several months ago, Ulbrich and Weisbuch reported the first experimental observation of the effects predicted by Brenig *et al.* in the Brillouin spectrum of gallium arsenide.[3] They employed a tunable near-infrared dye laser as the exciting source and observed the scattered light with a double-grating spectrometer. Very recently, Winterling and Koteles have obtained similar results for CdS, also employing a tunable dye laser and a double-grating spectrometer.[4] Although these two experiments have succeeded in uncovering many of the most significant features of resonant Brillouin scattering, they were both somewhat limited by the relatively low resolution of the grating spectrometer. Much-higher-resolution Brillouin spectra can be obtained with a Fabry-Perot interferometer than with a grating spectrometer, and the difficulties associated with studying opaque materials can now be largely overcome by using the high-contrast multipass scheme developed by Sandercock.[5]

We have employed a triple-pass Fabry-Perot interferometer to study resonant Brillouin scattering in CdS crystals obtained from several sources, and have also performed reflection, luminescence, and absorption experiments on these samples in order to obtain a self-consistent description of their optical properties. In this paper we present our observations of resonant dispersion in the Brillouin shift. A preliminary report on this work was presented previously.[6] In the Brillouin experiments we used the 4880-Å line of a single-mode argon laser which lies 12.4 meV (100 cm^{-1}) below the *A* exciton in CdS at 4.2 °K both because of its extreme narrowness and because it has essentially no fluorescence background. Experiments were performed on platelets obtained from Wright-Patterson, General Motors (GM), and the University of Delaware, and on bulk crystals purchased from Eagle-Picher and Cleveland Crystals.

In one series of experiments we attempted to observe the Brillouin spectrum at 4.2 °K while tuning the *A* exciton through resonance with the 4880-Å laser line by applying uniaxial stress.[7] We found, however, that the stress produced an enormous increase in luminescence which overwhelmed the Brillouin signal making this approach unworkable. All subsequent experiments were performed with CdS platelets which the reflectivity measurements show to have much sharper excitons than the bulk samples. The approach followed in these experiments was an extension of that employed by Pine in that the exciton was thermally tuned while the laser frequency remained constant. The *A* exciton in CdS should reach resonance with the 4880-Å argon laser line at approximately 90 °K.

BRILLOUIN-SCATTERING EXPERIMENTS

Brillouin-scattering measurements were performed in backscattering geometry with 4880-Å light from a single-mode argon-ion laser incident normal to a plane surface of the crystal containing the *C* axis. The incident light could be polarized either parallel to the *C* axis allowing interaction with the *B* exciton or perpendicular to the *C* axis allowing interaction with both the *A* and *B* excitons. When the crystal was highly absorbing, only 10 mW of laser light (corresponding to approximately 3 W/cm^2) was used to minimize local heating. The crystal was attached to the cold finger of an Air Products Cryotip Dewar with a small amount of vacuum grease. The temperature was measured with a thermocouple embedded in the base of the cold finger with an accuracy of 0.5 °K and could be controlled to within ±0.1 °K.

A Tropel model 350 piezoelectrically scanned plane Fabry-Perot interferometer equipped with corner-cube prisms for triple-pass operation was used to analyze the scattered light which also traversed a 12-Å bandwidth laser filter that served to remove most of the fluorescence. The interferometer has a working finesse of 50 and contrast of 3×10^6. The free spectral range was 16.8 or 13.8 GHz for measurements with the polarization of the incident light perpendicular or parallel to the *C* axis, respectively.

Photoelectric counts were multiscaled into a PDP-8E minicomputer operating as a multichannel analyzer with its address sweep triggered by the Tropel ramp generator. The minicomputer also provided adjustable bias voltages to two of the interferometer's piezoelectric stacks through programmable power supplies. During a run, the computer operating program interrupted data acquisition periodically and automatically adjusted the bias voltages to maintain alignment of the interferometer. Simultaneously a delay in the multiscaling subroutine was adjusted to compensate for thermal drifts in the interferometer. With this system, data could be collected continuously for several hours without noticeable degradation of the finesse.

Brillouin spectra were measured for many of the CdS crystals, but the best results were obtained with the GM platelets which gave the largest resonant enhancement of the Brillouin cross section with a minimum of fluorescence. The measurements were performed on as-grown optically smooth surfaces since it was found that polishing drastically reduces the resonant enhancement.

Luminescence measurements on samples from different sources gave widely varying intensities, particularly for the I_1 and I_2 lines. The GM platelets gave remarkably little impurity luminescence even at helium temperatures. The *A* exciton in the Wright-Patterson samples was as sharp or sharper than in the GM samples as seen in reflection spectra, but these samples tended to show strong I_2 luminescence at low temperatures.

Brillouin-scattering results obtained with a GM platelet are shown in Figs. 1 and 2. Figure 1 shows four representative spectra with $\vec{E}\perp\vec{C}$ obtained at 10, 30, 50, and 65 °K. The positions of the LA Brillouin components corresponding to the central Rayleigh line are indicated by the arrows. The

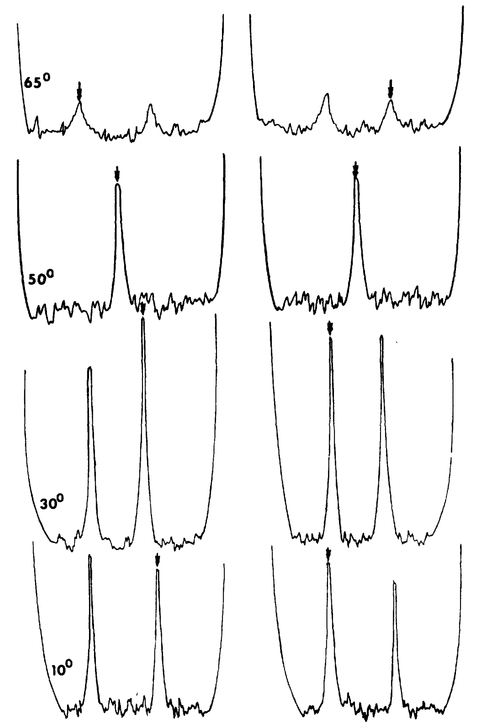

FIG. 1. Representative Brillouin spectra of GM CdS platelet at 10, 30, 50, and 65 °K, backscattered 4880-Å light with $\vec{k}_0\perp\vec{C}$ and $\vec{E}_0\perp\vec{C}$. The arrows indicate the Stokes and anti-Stokes Brillouin components corresponding to the central Rayleigh line.

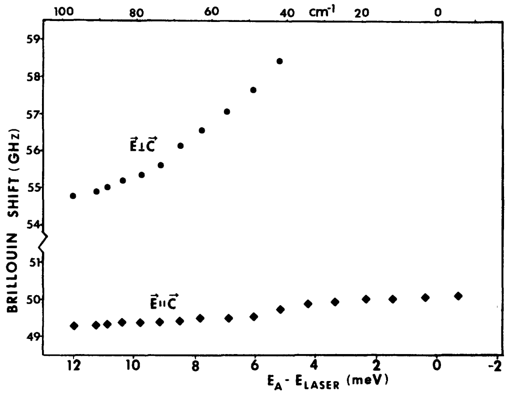

FIG. 2. Observed Brillouin shifts for $\vec{E}_0 \perp \vec{C}$ and $\vec{E}_0 \parallel \vec{C}$ plotted against the difference between the A exciton and laser frequencies.

Brillouin shifts, whose precision is at least 0.3%, are plotted in Fig. 2 as a function of the energy difference between the A exciton and laser frequencies. The strong dispersion in the $\vec{E} \perp \vec{C}$ Brillouin shift must be due to the A exciton since in this range there is very little change in the Brillouin shifts for $\vec{E} \parallel \vec{C}$. The Brillouin cross sections were not studied extensively, but were observed to exhibit essentially the same behavior reported by Pine.[1]

REFLECTANCE SPECTRA

Reflectance measurements were performed with conventional optics. Light from a white light source was focused on the sample perpendicular to the C axis at less than 5° from normal incidence and reflected light was analyzed by a double-grating spectrometer. We used fully digital photon-counting methods to measure both the reflected spectrum and the lamp spectrum. The ratio of these spectra then gave the reflectance which was normalized to 21% at 5000 Å where the crystal is transparent and R is known from independent refractive-index measurements.[8] The digital files of absolute reflectance were subsequently used for least-squares-fitting analysis to obtain optimum parameters for different theoretical functions.

One surprising observation was that the sharp spike which is sometimes seen on the high-frequency side of the A exciton tended to disappear with repeated temperature cycling between 300 and 4.2 °K. Computer simulations suggest that this is due to an increase in the A exciton damping Γ_A from less than 0.1 (where a sharp spike should occur) to 0.3 meV or more which is sufficient to eliminate the spike.[9]

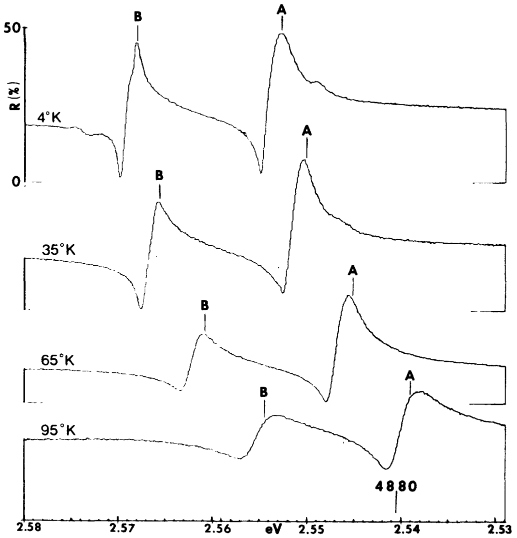

FIG. 3. Reflectance spectra of GM CdS platelet with $\vec{E} \perp \vec{C}$ at 4.2, 35, 65, and 95 °K. The arrows indicate the positions of the A and B excitons found from computer fits. The position of the 4880-Å argon laser line is also indicated.

Reflectance spectra at 4.2, 35, 65, and 95 °K are shown in Fig. 3. The energies of the A and B excitons deduced from computer fits are indicated in Fig. 3 along with that of the 4880-Å argon laser line. Those spectra are from a GM platelet similar to the one used in the Brillouin-scattering experiments.

The complete set of reflectance spectra (4.2, 20, 35, 50, 65, 80, 95 °K) was analyzed twice using a nonlinear least-squares computer program. First, we fit the spectra to a two classical oscillator function with seven parameters. Then we reanalyzed the data following Hopfield and Thomas including both spatial dispersion of the A exciton and a dead layer[10]; the B exciton was also included as a classical oscillator. Comparison of the results of this nine-parameter spatial dispersion analysis with the two classical oscillator results gave essentially identical values for the energies of the excitons, but large differences in the A exciton damping as first found by Hopfield and Thomas.[10] The parameters found from these fits were plotted as functions of temperature, and smooth curves were drawn through the points. Values taken from the smooth curves were used to predict Brillouin shifts for comparison with the Brillouin-scattering data.

COMPARISON OF REFLECTANCE AND BRILLOUIN DATA

The Brillouin shift for scattering at $\theta = 180°$ (back scattering) when the laser frequency lies below that of the lowest exciton is given by

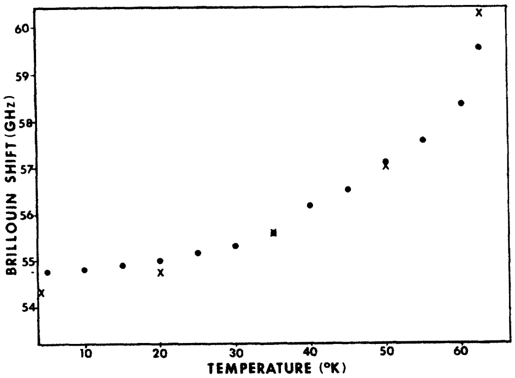

FIG. 4. Circles are observed Brillouin shifts as a function of temperature. Crosses show the Brillouin shifts predicted by Eq. (1) using the dielectric constant $\epsilon(\omega)$ obtained from the reflectivity measurements with spatial dispersion and the dead layer included.

$$\Delta\nu = 2\nu(v/c)\mathrm{Re}\sqrt{\epsilon} \,, \qquad (1)$$

where ν is the frequency of the incident light and ϵ is the complex dielectric constant. For the LA mode propagating along the A axis, the sound speed $v = 4.25\times10^5$ cm/sec which changes by less than 0.5% between 0 and 100 °K.[11]

The dielectric constant ϵ at the laser frequency was computed for each temperature using the parameters deduced from the reflectance analysis, and the corresponding Brillouin shifts could then be predicted from Eq. (1). In Fig. 4 we show the observed Brillouin shifts and the predicted Brillouin shifts using the dielectric constant including spatial dispersion and a dead layer for the A exciton and a classical oscillator B exciton. These predictions are seen to be in reasonable agreement with the observed Brillouin shifts.

Brillouin shifts were also computed using values of ϵ found from the two classical oscillator forms, and these were found to give a somewhat poorer agreement with the experimental shifts. Although this result suggests that the Brillouin shift may be sensitive to the presence of spatial dispersion even well below resonance, the difference in the two sets of predictions was probably too small to be significant.

CONCLUSIONS

We have shown that high-resolution interferometric Brillouin-scattering experiments can be extended sufficiently far into the excitonic resonance region to display resonant dispersion of the Brillouin shifts. We have also shown that the observed shifts are consistent with optical constants deduced from reflectance measurements.

We were, however, unable to definitely show the effects of spatial dispersion because the Brillouin signal decreased rapidly with increasing temperature, as previously noted by Pine,[1] preventing us from getting sufficiently close to resonance. From absorption measurements on CdS platelets, we conclude that this results from the onset of phonon-assisted absorption which increases more rapidly than the Brillouin cross section.

Future experiments should probably be carried out at 4.2 °K where phonon assisted absorption is negligible and direct absorption increases less rapidly than the predicted Brillouin cross sections[2] so that the Brillouin signal should increase rather than decrease as resonance is approached. This implies either the use of a tunable laser or of nonthermal means of tuning the exciton, e.g., employing a sequence of mixed CdS-CdSe crystals.

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