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Resonance Brillouin Scattering in Cadmium Sulfide†

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A weak resonant enhancement of the Brillouin-scattering cross section is observed as the fundamental absorption edge of cadmium sulfide is thermally tuned through the incident radiation at 5145 Å. The data are compared to light-scattering theory where the parameters are determined by optical absorption. In regions of high absorption, the spectral width of the Brillouin scattering is increased due to the optical wave-vector spread; this provides an independent measurement of the absorption.

I. INTRODUCTION

A weak resonant enhancement of the Brillouin-scattering cross section is observed as the fundamental absorption edge of cadmium sulfide is thermally tuned through the incident radiation at 5145 Å. This study complements earlier measurements by Tell, Worlock, and Martin[1] of the enhancement of the Pockel's electro-optic coefficients in CdS and ZnO. Here by back scattering from thermal phonons, the highly absorbing band-gap region can be approached more closely than with the low-acoustic-frequency small-angle-scattering technique used by Tell *et al.*[1] The resonant behavior for scattering from longitudinal acoustic (LA) waves propagating along either the *c* or *a* axis is essentially the same. This implies that the electro-optic contribution to the scattering from the piezoelectric field associated with the *c*-axis LA phonon[2] does not dominate the resonance effects the way that the polar fields associated with the LO phonons do in Raman scattering. When the measured Brillouin count rate is suitably corrected for the varying temperature and scattering volume, the cross section is found to increase roughly as the square root of the absorption. Between 100 and 300 °K the absorption increases by over three orders of magnitude. This resonance enhancement is characterized as weak since it is less than one would predict by Loudon's[3] theory assuming that the electron-hole-pair states responsible for the absorption are the intermediate virtual states of

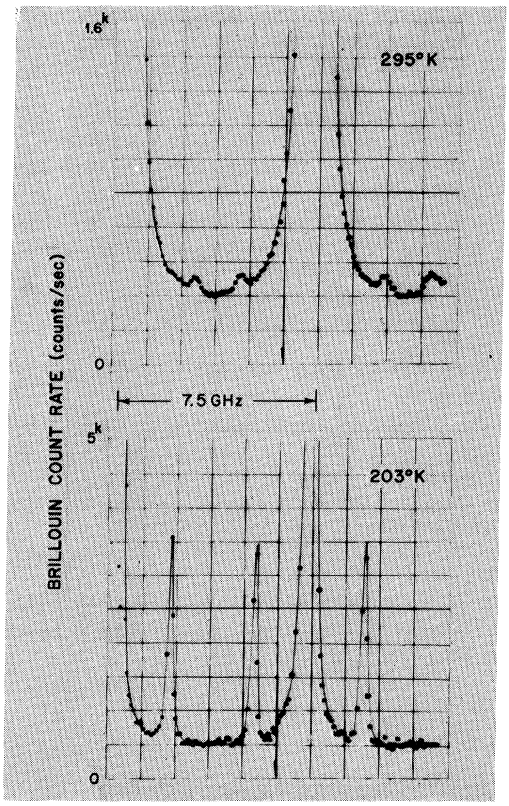

FIG. 1. Resonance Brillouin back-scattering spectra for 5145-Å light in CdS.

the scattering process.

The spectral resolution of the experiment is sufficient to observe for the first time a line broadening due to the absorption-induced optical wave-vector spread. Since the phonon frequency is linearly proportional to the wave-vector transfer, the wave-vector distribution is directly reflected in the excess frequency broadening. The absorption constants determined from this broadening are in satisfactory agreement with Dutton's[4] transmission measurements on thin platelets. However, the Brillouin determination shows somewhat higher absorptions and a systematic deviation from the Urbach exponential tail usually found in CdS.

II. EXPERIMENTAL RESULTS

Brillouin spectra obtained by back scattering of a single-mode 5145-Å argon-laser line (~40 mW) from LA phonons in CdS are shown in Fig. 1. A multiscanned confocal spherical interferometer with free spectral range of 7.5 GHz is used in conjunction with a multichannel analyzer for signal averaging and drift compensation.[5] The CdS sample is a $2\times2\times1$-cm^3 nominally pure (resistivity ~15 Ω cm at 300 °K) crystal grown by Harshaw and cut with c and a axes at Brewster's angle from the square dimensions. The crystal is mounted on a cold-finger Dewar with temperature measured by a thermocouple embedded in the mounting bracket.

The traces of Fig. 1 show that the Brillouin count rate drops dramatically as the temperature increases. At the same time the optical absorption α_0 increases because of the temperature dependence of the band gap. Dutton[4] gives for this energy gap

$$E_g(T) = (20840 - 3.82T)\ \text{cm}^{-1}\ , \qquad (1)$$

taken from the frequency at which $\alpha_0 = 10^4$ cm^{-1} as measured by transmission of thin platelets. The Brillouin-scattering linewidth also increases with temperature, as seen in Fig. 1. The excess broadening $\delta\nu_0$ after the instrumental and phonon lifetime widths are subtracted out is caused by the absorption-induced optical wave-vector spread,[2]

$$\delta(k_i + k_s) = 2\alpha_0 = \pi\delta\nu_0/v_j\ . \qquad (2)$$

Here $\delta\nu_0$ is the full width at half-maximum and v_j is the sound velocity; the subscripts i and s correspond to the incident and scattered light. The phonon damping width is known from higher-resolution Brillouin scattering with 6328-Å light[6] for which CdS is transparent. Above 250 °K the excess width becomes measurable and yields an *in situo* value of α_0. Below 220 °K the sample transmits measurable 5145-Å light, so the absorption can be obtained directly.

The square root of α_0, measured by these methods, is plotted in Fig. 2. Also plotted is the absorption interpolated from Dutton's data[4] according to his Urbach exponential-tail formula. The low-temperature background absorption is consistent with the data of Thomas *et al.*[7] and falls outside the range of applicability of the Urbach behavior. For high absorptions, the measurements are in reasonable agreement with Dutton allowing for possible sample and surface preparation variation. However, systematic deviations of the Brillouin measurements may be expected due to laser-induced local heating and carrier concentration which tend to raise the effective absorption of both light and sound.[6] The scale labeled "frequency below the gap" is obtained from Eq. (1) and $\bar{\omega}_i = 19435$ cm^{-1}.

The Brillouin cross section defined as the scattering efficiency per unit length per unit solid angle is given by[5]

$$\sigma_B = \frac{\partial^2 S_j(\omega_i)}{\partial L\,\partial\Omega} = \frac{\pi^2}{\lambda_i^4}\frac{kT}{\rho v_j^2}(\epsilon^2 p)^2\ . \qquad (3)$$

Here j corresponds to the acoustic mode, ρ is the density, and $(\epsilon^2 p)$ is the contraction of the dielectric and Pockel's tensors for the particular scattering geometry. Because of the optical absorption, the measured back-scattered Brillouin count rate I_s in a sample of length L is related to

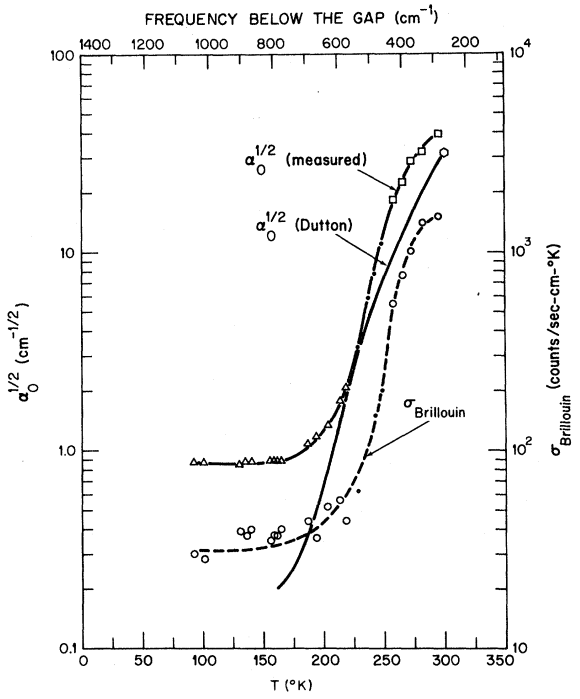

FIG. 2. Optical absorption and resonance Brillouin cross section in CdS. △ measured by transmission; □ measured by linewidth; ● interpolated; ○ measured by Dutton; ○ Brillouin cross section from measured count rate and absorption.

the incident intensity I_0, according to Loudon, [8] by

$$I_s/I_0 = \sigma_B(1 - e^{-2\alpha_0 L})/2\alpha_0 \quad . \tag{4}$$

For transparent samples, then, $I_s/I_0 \sim \sigma_B L$, whereas for opaque samples $I_s/I_0 \sim \sigma_B/2\alpha_0$. In the latter case, if $\sigma_B \propto \alpha_0$ (or α_0^2) then the measured count rate would be independent of (or proportional to) the absorption. Such behavior will be shown to correspond to Loudon's theory[3] with interband (or intraband) electron-phonon matrix elements. From Fig. 1 it is obvious that such a strong resonance is not observed. The Brillouin cross section, corrected for the linear temperature dependence of (3) and the absorption according to (4), is also plotted in Fig. 2. There it is seen that the cross section is roughly proportional to $\alpha_0^{1/2}$. The data plotted are for scattering from the LA phonon along the c axis via the electro-optic tensor component p_{13}. Similar results are obtained from the a-axis LA phonon via the coefficients p_{21} or p_{31}. Since the optical absorption is greater for the ordinary ray than the extraordinary ray[4] at a given temperature, the scattered count rate for the former polarization is less than the latter.

III. INTERPRETATION

Several models of varying sophistication exist to explain the frequency dependence of Brillouin scattering. The simplest of these assumes that the light couples only to the density fluctuations accompanying the LA phonon. Then the Pockel's coefficient may be obtained from the Lorentz-Lorenz law[9]:

$$(\epsilon^2 p) \sim \tfrac{1}{3}(\epsilon - 1)(\epsilon + 2) \quad . \tag{5}$$

This approximation works remarkably well for transparent liquids and solids where ϵ is real and equal to the square of the refractive index $n(\omega)$. However, in the resonance region of CdS (~5145 Å), $n(\omega)$ increases by only ~8.5% over the temperature range studied.[10] Thus the observed effect is greatly underestimated by this approximation.

A more detailed microscopic formulation of the light-scattering problem in solids has been given by Loudon.[3] He obtained

$$\sigma_B = \left(\frac{e}{\hbar mc}\right)^4 \frac{kT}{2\rho v_j^2} \frac{\omega_s}{\omega_i} |R_{is}^{jq}|^2 \quad , \tag{6a}$$

$$R_{is}^{jq} = \frac{1}{V} \sum_{\mu\mu' k} \frac{\langle 0|p_i|\mu k\rangle \chi_{\mu\mu'}^{jq} \langle \mu' k|p_s|0\rangle}{(\omega_{\mu k} - \omega_i)(\omega_{\mu' k} - \omega_s)} \quad . \tag{6b}$$

This is a perturbation-theory description of a process whereby a photon $(\omega_i, \vec{k}_i)$ incident on a crystal in ground state $|0\rangle$ creates a virtual electron-hole pair in band μ with wave vector k. The electron or hole then interacts with the phonon via the deformation potential $\chi_{\mu\mu'}^{jq}$, possibly changing its state to μ', and subsequently recombines emitting a shifted scattered photon $(\omega_s, \vec{k}_s)$. Over-all frequency $\omega_s = \omega_i \pm \omega_j$ and wave vector $\vec{k}_s = \vec{k}_i \pm \vec{q}$ are conserved. The phonon frequency and wave vector are related by $\omega_j = v_j q$. The photon and phonon wave vectors are neglected in comparison with those of the electron-hole pair (vertical transitions). Here V is the crystal volume, $\langle|p|\rangle$ is the momentum matrix element, and $\hbar\omega_{\mu k}$ is the energy of the pair state above $|0\rangle$. This definition of the deformation potential is related to Loudon's by $\chi = qa\Xi$. The resonance effects arise from the denominator of (6b) as the incident frequency approaches the excited electronic states of the medium. Antiresonance terms are omitted. In the present experiment $\omega_{\mu k}$ is varied by changing the temperature according to (1).

Taken by itself, Loudon's theory contains enough flexibility in the band parameters of (6b) to explain the resonance Brillouin data presented here. However, many of these parameters are specified by the optical absorption, and it is felt that the details of the theory are less important than the relationship between the scattering cross section and the absorption. The absorption is given by[11]

$$\alpha_0(\omega) = \frac{2\pi e^2 \omega}{\hbar m^2 c n(\omega)} \frac{1}{V} \sum_{\mu k} \frac{|\langle 0|p|\mu k\rangle|^2 (\gamma_{\mu k}/\omega_{\mu k}^2)}{(\omega_{\mu k} - \omega)^2 + \gamma_{\mu k}^2} \quad . \tag{7}$$

Here $\gamma_{\mu k}$ is the electronic damping and $n(\omega)$ varies slowly over the frequency range of interest. Again the major frequency dependence comes from the resonance denominator. It is clear from (6b) and (7) that if $(\omega_{\mu k}-\omega)\gg\omega_j$ or $\gamma_{\mu k}$, then $\sigma_B\propto\alpha_0^2$ if also $\chi^{jq}_{\mu\mu}\neq 0$ (intraband scattering allowed), or $\sigma_B\propto\alpha_0$ if $\chi^{jq}_{\mu\mu}=0$ (interband contribution). This is demonstrated below for a specific band model. These approximations are pertinent to this experiment, but the theory does not well represent the $\sigma_B\propto\alpha_0^{1/2}$ results.

Loudon has shown[3] that for spherical parabolic bands the factor R does not diverge as the band gap is approached. He takes the most resonant case $\chi^{jq}_{\mu\mu}\neq 0$ and assumes

$$\omega_{\mu k}=\omega_{\mu',k}=\omega_\mu+\hbar k^2/2m_\mu$$

out to the Brillouin zone edge k_m and wave-vector-independent matrix elements. Then with the prescription

$$\frac{1}{V}\sum_k \rightarrow \frac{2}{(2\pi)^2}\int_0^{k_m} k^2\,dk \quad ,$$

Eq. (6b) becomes

$$R_{is}=\frac{2}{(2\pi)^2}\sum_\mu\left(\frac{2m_\mu}{\hbar}\right)^{3/2}\frac{p_{0\mu}\chi^{jq}_{\mu\mu}p_{\mu 0}}{\omega_j}I_\mu \quad , \tag{8a}$$

$$I_\mu=(\omega_\mu-\omega_s)^{1/2}\tan^{-1}[\Delta\omega_\mu/(\omega_\mu-\omega_s)]^{1/2} - (\omega_\mu-\omega_i)^{1/2}\tan^{-1}[\Delta\omega_\mu/(\omega_\mu-\omega_i)]^{1/2} \quad , \tag{8b}$$

where $\Delta\omega_\mu=\hbar k_m^2/2m_\mu$. Loudon's form for I_μ when $\Delta\omega_\mu\gg(\omega_\mu-\omega_{i,s})$ is

$$I_\mu\simeq(\omega_\mu-\omega_s)^{1/2}-(\omega_\mu-\omega_i)^{1/2} \quad , \tag{8c}$$

which is finite at the gap and when $(\omega_\mu-\omega_{i,s})\gg\omega_j$ reduces to

$$I_\mu\simeq\tfrac{1}{2}\omega_j/(\omega_\mu-\omega_i)^{1/2} \quad . \tag{8d}$$

In the opposite limit when $\Delta\omega_\mu\ll(\omega_\mu-\omega_{i,s})$, then

$$I_\mu\simeq\tfrac{1}{3}\omega_j(\Delta\omega_\mu)^{3/2}/(\omega_\mu-\omega_i)(\omega_\mu-\omega_s) \quad . \tag{8e}$$

Thus, far from resonance the apparent divergence in (8e) is greater than actually occurs near resonance as in (8d) or (8c).

The optical absorption may be evaluated similarly by assuming a k-independent damping and neglecting the k dependence of the $\omega_{\mu k}^{-2}$ factor:

$$\alpha_0(\omega)=\frac{2\pi e^2\omega}{\hbar m^2 cn(\omega)}\sum_\mu\left(\frac{2m_\mu}{\hbar}\right)^{3/2}\frac{|p_{0\mu}|^2}{\omega_\mu^2}\,\mathrm{Im}(J_\mu) \quad , \tag{9a}$$

$$J_\mu=(\omega_\mu-\omega+i\gamma_\mu)^{1/2}\tan^{-1}[\Delta\omega_\mu/(\omega_\mu-\omega+i\gamma_\mu)]^{1/2} \quad . \tag{9b}$$

Here, above the gap for $\Delta\omega_\mu\gg(\omega-\omega_\mu)\gg\gamma_\mu$, the familiar direct gap threshold independent of damping is obtained,

$$\mathrm{Im}\{J_\mu\}\simeq\tfrac{1}{2}\pi(\omega-\omega_\mu)^{1/2} \quad . \tag{9c}$$

Below the gap for $\Delta\omega_\mu\gg(\omega_\mu-\omega)\gg\gamma_\mu$

$$\mathrm{Im}\{J_\mu\}\simeq\tfrac{1}{4}\pi\gamma_\mu/(\omega_\mu-\omega)^{1/2} \quad ; \tag{9d}$$

or, for $(\omega_\mu-\omega)\gg\Delta\omega_\mu,\ \gamma_\mu$,

$$\mathrm{Im}\{J_\mu\}\simeq\tfrac{1}{3}\gamma_\mu(\Delta\omega_\mu)^{3/2}/(\omega_\mu-\omega)^2 \quad . \tag{9e}$$

Since the resonance behavior of the light-scattering cross section and the optical absorption is dominated by the factors I_μ and $\mathrm{Im}\{J_\mu\}$, it is seen by comparing (8d) and (8e) with (9d) and (9e) that R^{jq}_{is} tracks α_0 below the gap. In both cases the rate of increase with $(\omega_\mu-\omega)^{-1}$ slows markedly as the gap is approached. Thus for this specific model with allowed intraband electron-phonon scattering, $\sigma_B\propto\alpha_0^2$ as previously indicated.

More recently, Burstein *et al.*[2] have extended Loudon's theory of resonance Brillouin scattering to excitonic insulators. They treat the strongly coupled light and quasilocalized electron-hole pair as a polariton and consider the scattering of polaritons by phonons. Their expression for the scattering efficiency may be written

$$\sigma_B=\left(\frac{\omega_s}{2\pi\hbar}\right)^2\frac{kT}{2\rho v_j^2}\frac{|M^{jq}_{is}|^2}{v_p^2(\omega_s)v_g(\omega_s)v_g(\omega_i)} \quad , \tag{10a}$$

$$M_{is}=\frac{1}{2}\sum_{\mu\mu'}\left(1+\frac{\omega_\mu\omega_{\mu'}}{\omega_s\omega_i}\right)s_\mu^{1/2}(\omega_i)\chi^{jq}_{\mu\mu'}s_{\mu'}^{1/2}(\omega_s) \quad , \tag{10b}$$

where $v_p(\omega)$ and $v_g(\omega)$ are the phase and group velocities of the polariton at frequency ω and $s_\mu(\omega)$ is the exciton strength of the polariton. These are given by

$$\frac{v_p(\omega)v_g(\omega)}{c^2}=\left(1+\sum_{\mu'}\frac{4\pi\beta_{\mu'}\omega_{\mu'}^4}{(\omega_{\mu'}^2-\omega^2)^2}\right)^{-1} \quad , \tag{11a}$$

$$s_\mu(\omega)=\frac{4\pi\beta_\mu\omega_\mu^3\omega}{(\omega_\mu^2-\omega^2)^2}\left(\frac{v_p(\omega)v_g(\omega)}{c^2}\right) \quad , \tag{11b}$$

where the oscillator strength β_μ may be written in terms of the momentum matrix elements as

$$\beta_\mu=\left(\frac{2e^2N}{m^2\hbar V}\right)\frac{|p_{0\mu}|^2}{\omega_\mu^3} \quad . \tag{11c}$$

Loudon's band theory[3] in the limit of narrow dispersionless bands (such that $\sum_k\rightarrow N$) reduces to this polariton theory apart from a factor $v_p(\omega_i)/v_p(\omega_s)$ which is always close to unity. Therefore there is no distinct difference in resonance behavior between the two theoretical approaches. On the other hand if one considers the electron-phonon coupling via the electric field accompanying a polar or piezoelectric phonon, then it is useful to distinguish between exciton and band states. This gives rise to the electro-optical contribution to the

light scattering which is usually dominated by excitonic intermediaries. The relative resonant Raman scattering of longitudinal-optic (LO) and transverse-optic (TO) phonons in CdS attests to this.[12] However, Burstein *et al.*[2] show that the piezoelectric field strength of the LA phonon in CdS is only a few percent that of the field of the LO phonon, so the electro-optic Brillouin-scattering terms are not expected to be large. Experimentally one observes the same resonance-scattering effects from LA phonons along either the piezoinactive a axis or the piezoactive c axis, affirming this expectation.

It should be mentioned here that the strong overtone lines observed in resonance Raman scattering[13,14] are not expected (and not observed) in Brillouin scattering for two reasons. First, because of the linear dispersion of the acoustic waves there is a very low density of states in the two-phonon spectrum near $2\omega_j$. Second, the restriction to $q \sim 0$ for the multiple LO scattering arises from the Fröhlich electron-phonon interaction ($\propto 1/q$) involved in the electrooptic scattering.[15] On the other hand the piezoelectric interaction is independent of q which removes this restriction and accounts for the weakness of the electro-optic Brillouin scattering in the first place.

In summary, the theories of Brillouin scattering presented here do not explain the resonance data unless the states responsible for the absorption are decoupled from those giving rise to the scattering. In a real crystal this may indeed be the case since even the theory of absorption in the Urbach-tail region is more complex than indicated in (7).

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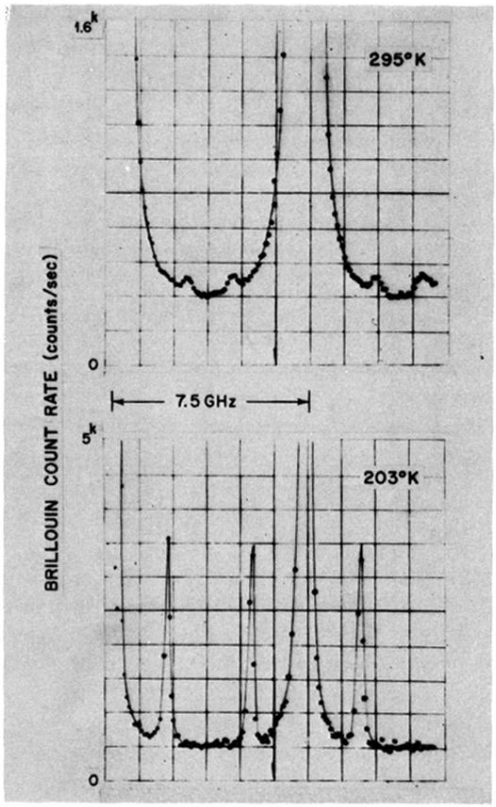

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