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MULTIPLE-PHONON RESONANT RAMAN SCATTERING IN CdS

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(Received 15 January 1969)

We have observed nth order ($n=1,2,\cdots,9$) Raman scattering in CdS under conditions of resonance between the laser frequency and the band gap or the associated exciton states. The frequency spectrum of these higher order processes demonstrates that the phonons involved are localized within a small volume of k space centered at Γ. We believe that such spectral features are characteristic of direct-gap resonant scattering, and the kinematics of their production is discussed.

Different theories of lattice Raman scattering[1-3] have as a common feature terms in the expressions for cross sections which diverge or become very large. This is expressed analytically by the existence of second-order zeroes in the energy denominators of the Raman tensor components. The number of zeroes depends upon the order of the scattering process (i.e., the number of phonons created or annihilated) and upon the kinematic details of the process (such as whether several phonons are produced simultaneously); according to the theory of Birman and Ganguly,[3] for any scattering process which proceeds via electron-photon, electron-lattice interaction, there are at least two such second-order poles present. The first of these poles occurs when the incident photon energy equals the energy of an optical transition in the lattice (e.g., the band gap E_g or an exciton level E_g-R/n^2). In a recent paper[4] we experimentally demonstrated the existence of this pole in CdS for both first- and second-order scattering below the band gap. We showed that the pole was second order and that the resonant state was the first exciton level.[5] The second pole occurs when the scattered-photon energy is equal to that of the optical transition in question. This Letter presents the first experimental evidence for the existence of resonance at the scattered-photon energy. The data consist of intensity measurements of nth order scattering features ($n=1,2,\cdots,9$) in CdS as a function of temperature (hence E_g) and laser frequency, for laser frequencies above the band gap. These observations are the first known to the authors of Raman processes higher than fourth.

The data analyzed in the present paper were acquired by reflection scattering from the surface of a single crystal of CdS. An argon laser emitting ~100 mW was used as the exciting source and detection was by means of a cooled FW130 photomultiplier, a Keithley 610B electrometer, and a Spex double monochromator. Many geometries were examined, and the results presented here are essentially independent of scattering geometry and were corrected for absorption by means of Loudon's formula.[6]

Figure 1 shows the spectrum obtained from a relatively pure CdS crystal with 4579-Å excitation. Significant features of the spectrum are the following: (1) The multiphonon lines are shifted by energies which are approximately 1% less than exact multiples of the first-order LO phonon line at ~305 cm^{-1}; (2) these features remain linelike and have widths not much larger than that of the first-order line (e.g., $\lambda_{2\,\mathrm{LO}} \approx 1.3\lambda_{1\,\mathrm{LO}}$); (3) all processes higher than second disappear when the laser frequency is far below the gap $E_g/\hbar$.

We believe that the features observed above may be assigned as due to near zone-center phonons. The evidence for this consists of the following:

(1) Phonon dispersion curves have been calcu-

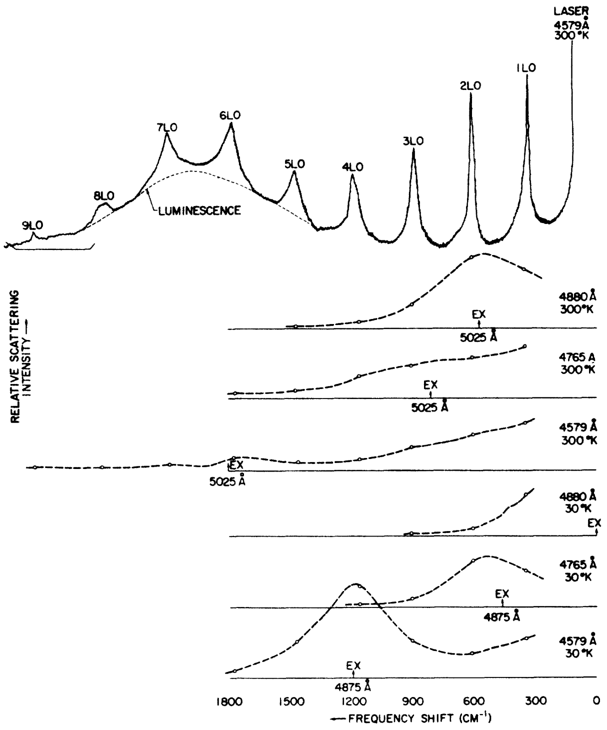

FIG. 1. Top trace: Uncorrected spectrum of CdS at ~300°K with excitation at 4579 Å. Below: Corrected intensities of multiphonon scattering features in CdS as a function of temperature and laser frequency. The arrow indicates the approximate energy of the $n=1$ free and I_2, I_5 bound excitons.

lated[7] for CdS and show no critical-point frequencies near 300 cm^{-1}, and, in fact, no phonon frequencies as high as 300 cm^{-1} except very near Γ.

(2) We have also observed scattering features at almost exactly twice the frequencies of first order lines in ZnTe, InAs,[8] and ZnSe,[9] when the laser frequency was very near that of a direct gap. It would require an extremely unlikely coincidence for all these materials to have phonon frequencies the same at Γ and some other critical point.

On the basis of Nusimovici's and Birman's calculations[7] we can say that the phonons contributing to our scattering features have $K \lesssim 10^7$ cm^{-1}. A related phonomenon has recently been reported in luminescence studies in GaP.[10] There sidebands involving multiples of zone-center LO phonons are observed. Both experiments suggest that the Fröhlich interaction between electrons and phonons is small for large wave-vector phonons.

In our previous work below the gap we reported[4] the saturation of TO-phonon intensities. Figure 1 shows that above the gap no TO-phonon scattering is observed. Since TO intensities remain comparable to LO intensities for laser frequencies $3\omega_{\text{LO}}$ or more below the bandgap, we conclude that the mechanisms of Raman scattering above and below the band gap are basically different.

Figure 1 shows the relative intensities of the multiphonon processes for different temperatures and laser frequencies. The most obvious feature of these data plots is that scattering is enhanced when the scattered -photon frequency coincides with that of the exciton. This scattered-photon resonance is further substantiated by our observation in ZnSe of nonthermal-equilibrium ratios of Stokes and anti-Stokes intensities. Our data are not sufficient to enable us to distinguish between resonance with the free exciton and with the I_2 and I_5 bound excitons. (These I_2 and I_5 bound excitons were shown to be present in our CdS sample by means of low-temperature luminescence experiments.) This demonstration of exciton resonance further supports the theory of Ganguly and Birman,[3] initially substantiated by our previous work[4]; however, the important question of whether the excitons are free or bound remains unanswered.

In a prior paper we considered alternative kinematical schemes for resonant multiphonon light scattering in CdS.[4] A true iterative process with electron-hole recombination can be ruled out on the basis of intensity. The two basic processes which remain (ignoring hybrid mechanisms) are (1) virtual absorption of the incident photon followed by simultaneous emission of n phonons via a single electron-lattice interaction (one vertex of a Feynman diagram), and then subsequent emission of the scattered photon; or (2) virtual absorption of an incident photon, followed by emission of n phonons through successive electron-lattice interactions. While the latter mechanism is more amenable to theoretical treatment via iteration of existing perturbation calculations,[3] neither alternative has yet been considered in any detailed theory, and the choice between them must be postponed.

It is a pleasure to acknowledge discussions with Dr. J. M. Worlock, Dr. J. J. Hopfield, Dr. A. K. Ganguly, Dr. J. L. Birman, and Dr. J. P. Gordon.

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MULTIPLE-PHONON-RESONANCE RAMAN EFFECT IN CdS*

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(Received 23 January 1969)

Data are presented that tie the multiple-phonon-resonance Raman effect in CdS to the fluorescent-emission spectrum. The one-phonon selection rules differ from those of the ordinary Raman effect. A possible theoretical approach to this effect is suggested.

Multiple-LO-phonon structure was observed by Leite and Porto in the Raman scattering spectrum of CdS at room temperature for exciting light in the region of the fundamental absorption edge.[1] This paper presents several new experimental aspects of this phenomenon and suggests a way of looking at the theory of the effect.

Light incident normal to the polished surface of a CdS single crystal was focused to a spot about 50 μ in diameter. The 180° back-scattered light was analyzed with the usual combination of a double-grating monochromator and photomultiplier. We found that in the region of strong absorption necessary for the resonance Raman effect the laser power had to be limited to less than about 20 mW to avoid sample-heating effects.

The scattered light spectrum shows a mixture of fluorescent emission and Raman scattering. In the room-temperature spectra of Fig. 1, the peak of the broad fluorescent emission is at about 5070 Å (2.447 eV), independent of the wavelength of the exciting light. The superimposed sharp lines represent Raman scattering of the incident light; the frequency separation $\omega_L - \omega_R$ is an integral multiple of ω_0, the $k \approx 0$ LO-phonon frequency at 304 cm^{-1}.[2]

The observed fluorescent emission is believed to be intrinsic and hence not caused by recombination of excited electron-hole pairs at impurity centers. The photon-created carrier density estimated from the light intensity was several orders of magnitude larger than the estimated impurity concentration. The position of the emission peak seems consistent with what is known from absorption and emission of CdS[3]; at room temperature it is about 25 meV below the position of the $(n=1, A)$ exciton ($E \perp c$ axis). This is to be expected if the emission is composed of an unresolved superposition of this exciton line plus rep-

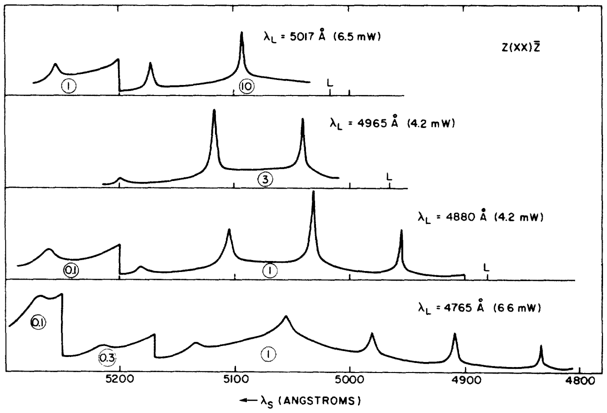

FIG. 1. Spectra of light back-scattered at room temperature from a CdS crystal for various wavelengths λ_L of incident laser light (also indicated by an "L" on the horizontal axes). The incident laser power is indicated in parentheses. The vertical axis represents electrometer current from the photomultiplier; the circled numbers give the full-scale reading in nanoamperes. The combined response of monochromator plus photomultiplier is flat in this region—the current is directly proportional to the light intensity. The $z(xx)\bar{z}$ notation is that of Ref. 2.