more exact calculations of the Fermi-surface properties in the EZS for those superconductors for which bulk tunneling data are available, i.e., gallium, tin, niobium, tantalum, rhenium, and lead.

We wish to thank Professor J. H. Wood, Professor M. L. A. MacVicar, and Professor W. N. Mathews, Jr., for discussion. We are particularly grateful to Professor Sasaki and Professor Yoshihiro for discussions regarding their data which took place during the Twelfth International Conference of Low Temperature Physics in Kyoto, Japan, 1970.

*Work supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-3665.

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Bound Exciton Resonance in Raman Cross Sections in CdS

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(Received 7 September 1971)

We present the first direct and conclusive evidence of bound exciton resonance in phonon Raman scattering from solids. The observed enhancement in the 1LO scattering cross section at the I_1 bound exciton in CdS is a factor of ~30 for the sample with the highest impurity content. In contrast to 1LO, the 2LO scattering cross section shows no enhancement near bound excitons. An explanation of this behavior is suggested.

Various authors have invoked resonance with excitons bound to impurities (bound excitons) in a solid to explain their Raman scattering observations.[1-7] However, their arguments have been based on selection rules,[1,3,5] effects of momentum transfer,[4,6] or similar indirect evidence. By using a continuously tunable dye laser, we have obtained the first direct cross-section measurements which conclusively prove the importance of bound-exciton intermediate states in Raman scattering. We describe and discuss these results in this Letter.

Raman spectra were obtained by using a flash-lamp-pumped, pulsed dye laser.[8] Using the esculin dye dissolved in methanol, the dye laser could be continuously tuned from ~4600 to 4950 Å with a resolution of ~1 Å. With peak power ~1 kW and repetition rate ~10 pulses per sec (average power ~10 mW), a fairly good signal-to-noise ratio was obtained for the 1LO and 2LO Raman spectra. A double spectrometer and a boxcar integrator were used for analyzing and detecting the Raman spectra. High-optical-quality platelets (~50–100 μm thick) of CdS were used. CdS was chosen because its luminescence[9] and Raman spectra[10] are well known. All measurements were performed at 6°K to avoid thermal broadening. One of the problems encountered at this temperature and high laser peak power was the strong luminescence from CdS in the spectral region of interest. This was alleviated by making the laser spot at the sample relatively large (>1 mm diam) and using the geometry shown in Fig. 1(a). In spite of these, the spectra for dye-laser wavelengths shorter than 4865 Å could not be obtained because of strong luminescence.

We have studied three different samples. Sample 1, an I_1-rich sample, had a large number ($\sim 5\times10^{17}$ cm^{-3}) of impurities giving rise to strong I_1 and I_2 bound-exciton luminescence.[11] Sample 2 had strong I_2 but weak I_1 luminescence whereas sample 3 was "pure," having intermediate strength I_2 luminescence and no I_1 luminescence. Since the exact impurity densities were unknown, the strengths of I_1 and I_2 luminescence obtained with the 4765-Å line of the Ar^+ laser were used as a rough indication of relative densities.

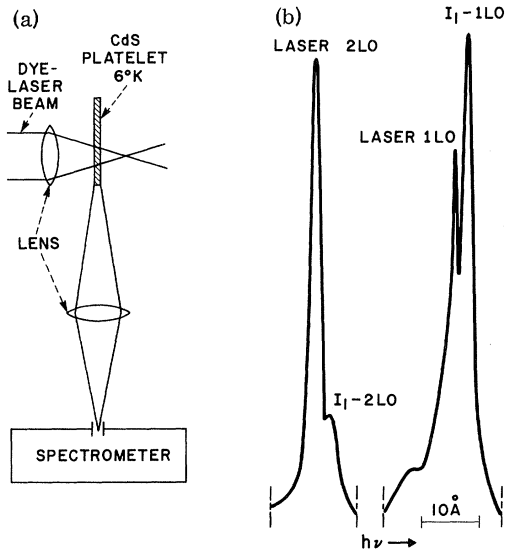

FIG. 1. (a) Experimental geometry. (b) An experimental trace of the 1LO and 2LO Raman scattering obtained in the $Y(X_Y^X)Z$ geometry with dye laser at 4892 Å. Spectrometer resolution ≈ 2 Å.

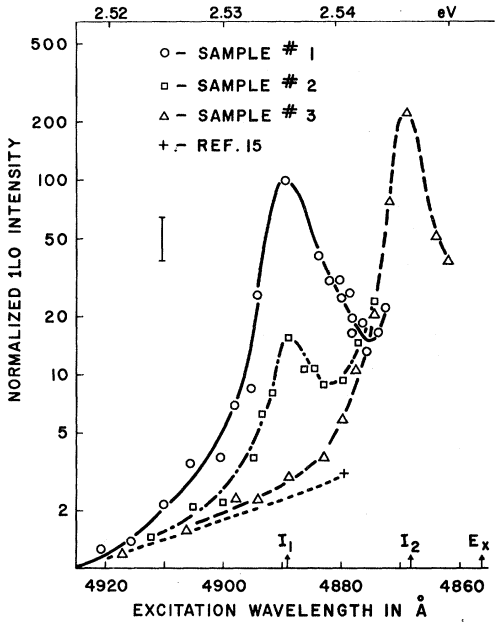

FIG. 2. Normalized Stokes 1LO scattering intensity as a function of the incident photon (dye-laser) energy for the three samples discussed in the text. The arrows indicate the positions of I_1 and I_2 lines in luminescence. The intensity *at* the I_1 (I_2) energy is a combination of Raman scattering and the LO sideband of I_1 (I_2) luminescence. For samples 1 and 2, the I_2 luminescence was so strong that no data could be obtained for $\lambda < 4870$ Å. It was found that the ratio of intensities, 1LO/2LO, at 4925 Å was the same for all three samples. Since the 2LO cross section was found to be independent of impurity content (see text), it can be deduced that the 1LO cross section was the same for all three samples at 4925 Å. We have therefore set the normalized 1LO intensity to 1 for all three samples at 4925 Å. E_x indicates the position of the free exciton. The vertical bar indicates approximate error limits for experimental points.

An experimental trace of 1LO and 2LO Raman scattering for incident laser frequency close to the I_1 bound exciton is shown in Fig. 1(b) for the I_1-rich sample (No. 1). Since the LO-phonon sidebands of the I_1 bound exciton are very strong,[9] the problem of distinguishing Raman scattering from the 1LO sideband of I_1 luminescence (and its acoustic wing)[9] is most acute in the case of the I_1-rich sample. Figure 1(b) shows that Raman intensities can be measured with fairly good accuracy even in this unfavorable case.

Spectra similar to the one shown in Fig. 1(b) were obtained for all the three samples at several wavelengths between 4925 and 4865 Å. The intensity of the 1LO Stokes line was normalized to the incident laser intensity at each wavelength. This normalized 1LO intensity for $Y(X_Y^X)Z$ geometry[12] is plotted in Fig. 2 as a function of the incident photon (laser) energy. The position of the I_1 and I_2 luminescence peaks are indicated by arrows on the figure. The data[13] in Fig. 2 clearly show the large enhancement of the 1LO scattering cross section when the incident photon energy is close to the I_1 and the I_2 bound-exciton energy. This provides direct and conclusive evidence that resonance of the incident photon energy with the bound excitons leads to a large increase in the 1LO scattering cross section. This large enhancement is possible in spite of the small densities ($\sim 5\times10^{17}$ cm^{-3}) of bound excitons because the bound excitons have large oscillator strengths (~10) in CdS.[1,4] The linewidth of 1LO scattering was instrument limited, so that its predicted broadening[14] near bound-exciton resonance could not be verified experimentally.

From Fig. 2 we can also see that the enhancement at the energy of I_1 decreases with the decrease in the I_1 impurity content (i.e., going from sample 1 to sample 3). Also the 1LO scattering cross section for the 4880-Å line of the Ar^+ laser is larger for sample 1 than sample 3. These observations provide additional evidence in favor of bound exciton resonance. Note also that comparison of various curves in Fig. 2 shows that the range of dominance of the I_1 bound-exciton contribution over the background (presumably due to the free exciton[15]) is about ±15 meV for the I_1-rich sample (No. 1) and even smaller for the oth-

ers. Thus it seems unlikely that the influence of the I_1 bound exciton will be significant for data taken with the 4965-Å line (≈ 40 meV from the I_1 bound exciton) of the Ar^+ laser, except at very high impurity density.

The most surprising feature of the data is that the 2LO intensity does not show any resonance enhancement in the vicinity of the I_1 or the I_2 bound exciton. The 2LO intensity increases monotonically with increasing incident photon energy, roughly in agreement with the data obtained previously using discrete Ar^+ laser lines.[16] We suggest the following as a possible explanation. The matrix element $M(q)$ for the exciton-LO interaction is zero for $q=0$, increases with q until it reaches a maximum near $qa_0 \sim 1$, and then decreases slowly with further increase in q. Here a_0 is the exciton radius (~ 30 Å in CdS). A plot of this matrix element is given in Fig. 1 of Ref. 14. From this it can be seen that the free-exciton contribution to 1LO scattering ($q \approx 5\times 10^5$ cm^{-1}, $qa_0 \approx 0.15$) is small. However, the free-exciton contribution to the 2LO scattering is large because phonons with $q \sim 1/a_0$ can participate in 2LO scattering. Therefore, the bound-exciton contribution may be significantly larger than the free-exciton contribution for the 1LO scattering but considerably smaller than the free-exciton contribution for the 2LO scattering. A deeper bound exciton may give observable increase in the 2LO scattering for incident photon energy close to the bound exciton.

In conclusion, we have presented direct and conclusive evidence that bound excitons give a large enhancement in the 1LO scattering cross section in CdS. The range of photon energy over which the bound exciton dominates the cross section depends on the concentration of the impurity binding the exciton. We also find that the 2LO scattering cross section shows no reasonant enhancement near bound excitons.

We thank Professor P. A. Wolff and Dr. R. M. Martin for discussions, Dr. J. P. Gordon and Dr. J. F. Scott for helpful comments on the manuscript, and Dr. B. G. Huth for advice on dye lasers.

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[12]It is known (Ref. 9) that absorption at I_1 and I_2 bound excitons is ~ 20 times stronger for light polarized perpendicular to the c axis than for light polarized parallel. Hence the bound excitons are not expected to contribute strongly in the $X(ZZ)Y$ geometry which we did not investigate experimentally.

[13]The data have not been corrected for absorption because (1), since we have restricted ourselves to $\lambda > 4865$ Å, the maximum correction due to changes in absorption is less than a factor of 2; and (2), since absorption is larger at bound excitons, the corrections would merely accentuate the enhancement. No significant change in the shape of the curve in Fig. 2 is expected.

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