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<sup>2</sup>R. Loudon, J. Phys. (Paris) 26, 677 (1965), and Advan. Phys. 13, 423 (1964).

<sup>3</sup>A. K. Ganguly and J. L. Birman, Phys. Rev. 162, 806 (1967).

<sup>4</sup>R. C. C. Leite, T. C. Damen, and J. F. Scott, in Proceedings of the International Conference on Light Scattering Spectra of Solids, New York University, September, 1968, edited by G. B. Wright (to be published).

<sup>5</sup>As discussed in the text, we cannot distinguish free and bound excitons in this experiment.

<sup>6</sup>R. Loudon, J. Phys. (Paris) 26, 677 (1965).

<sup>7</sup>M. A. Nusimovici and J. L. Birman, Phys. Rev. 156, 925 (1967).

<sup>8</sup>R. C. C. Leite and J. F. Scott, Phys. Rev. Letters 22, 130 (1969).

<sup>9</sup>Present work. We find  $\omega_{LO} = 253 \text{ cm}^{-1}$ ,  $\omega_{2LO} = 500 \text{ cm}^{-1}$ . We have also been informed of similar observations in InSb (A. Pinczuk, private communication).

<sup>10</sup>P. J. Dean, Phys. Rev. 168, 889 (1968).

### MULTIPLE-PHONON-RESONANCE RAMAN EFFECT IN CdS\*

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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.<sup>1</sup> 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  $50 \mu$  in diameter. The  $180^\circ$  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  $5070 \text{ \AA}$  (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  $\omega_0$ , the  $k \approx 0$  LO-phonon frequency at  $304 \text{ cm}^{-1}$ .<sup>2</sup>

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 im-

purity concentration. The position of the emission peak seems consistent with what is known from absorption and emission of CdS<sup>3</sup>; 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-

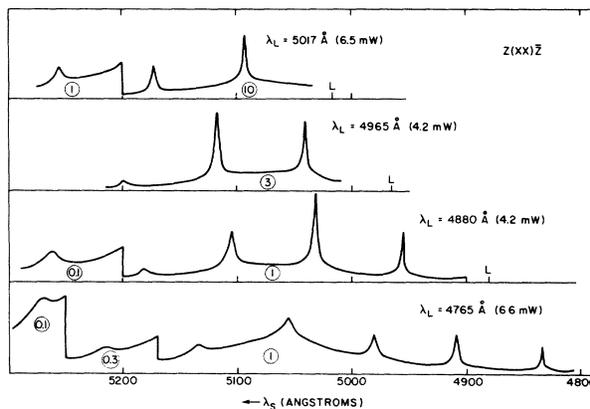


FIG. 1. Spectra of light back-scattered at room temperature from a CdS crystal for various wavelengths  $\lambda_L$  of incident laser light (also indicated by an "L" on the horizontal axes). The incident laser power is indicated in parentheses. The vertical axis represents electrometer current from 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  $z(xx)z$  notation is that of Ref. 2.

licas shifted by multiples of  $\omega_0$ . Scattering spectra for  $E \parallel c$  have also been taken. Results are similar to those shown in Fig. 1, except that both the fluorescent emission and the most intense Raman line peak at about 16 meV lower energy, as expected for the ( $n=1, B$ ) exciton.

The emission peak shifts to higher energy at lower temperatures, as may be seen in Fig. 2. The 25-meV separation between the  $A$  exciton and the emission peak reduces somewhat as the temperature is lowered.

The following facts characterize the data shown here and a considerable amount of additional data taken at temperatures between 112°K and room temperature.

(1) The multiple-phonon Raman spectrum closely follows the fluorescent emission. There is not a simple proportionality between the area under a given Raman line and the nearby emission intensity, but where there is no emission, there is no resonance Raman effect, and the most intense Raman line (in terms of integrated intensity) is the one closest to the emission peak and hence, approximately, closest to the exciton.

(2) The intensity of the entire scattered spectrum (Raman plus emission) increases as the laser frequency approaches the exciton frequency. This can be seen in Figs. 1 and 2. When  $\omega_L < \omega_{ex}$ , as is the case for  $\lambda_L = 5145 \text{ \AA}$ , the entire intensity falls off again. Because we do not have a continuously tunable laser, we are not sure exactly where the intensity peaks as a function of  $\omega_L$ ; it could be near  $\omega_{ex}$  but not exactly at it. There seem to be two broad resonances, one for  $\omega_L \approx \omega_{ex}$  and one for  $\omega_R \approx \omega_{ex}$ . There is no evidence for an intermediate frequency  $\omega'$ ,  $\omega_L > \omega' > \omega_R$ , also resonating with  $\omega_{ex}$ , as would be predicted by the cascade process illustrated in Fig. 3(a) of Ref. 1.

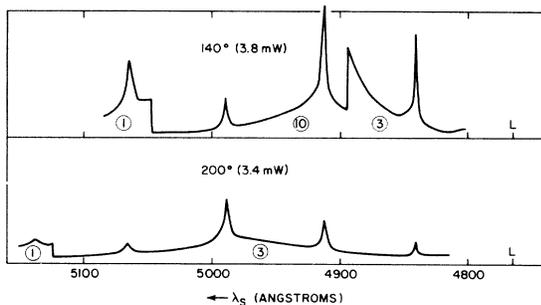


FIG. 2. The scattered light spectrum at two different temperatures for 4965-Å laser excitation. The remarks in the caption for Fig. 1 apply here also.

(3) The selection rules for this resonance Raman effect are not the usual rules of Loudon.<sup>4</sup> The ordinary prediction is that for back scattering of light propagating along the  $z$  ( $c$ ) axis, there are interactions with  $A_1$ -LO phonons with a dynamic polarizability tensor  $\Delta\alpha$  having nonzero components  $\Delta\alpha_{xx} = \Delta\alpha_{yy}$ , and  $\Delta\alpha_{zz}$ . Hence one should see LO phonons in a  $z(xx)\bar{z}$  experiment, and we do. For back scattering along the  $x$  axis ( $\perp c$ ), the LO phonons have  $E_1$  symmetry and usual selection rule gives  $\Delta\alpha_{xz} = \Delta\alpha_{zx}$  as the only nonzero components of  $\Delta\alpha$ . Thus there should be no coupling to a single LO phonon in an  $x(yy)\bar{x}$  experiment. Figure 2 shows that there is indeed such coupling. It is about as strong as that in a  $z(xx)\bar{z}$  experiment. Far below resonance, say for  $\lambda_L = 5462 \text{ \AA}$ , the usual Loudon selection rules apply; several different  $k \approx 0$  phonons are then seen in first order in an  $x(yy)\bar{x}$  experiment, but no first-order LO phonon.

(4) We have studied the depolarized light scattered in geometries such as  $x(yz)\bar{x}$  and  $x(zx)\bar{x}$ . The combined (fluorescence plus Raman) spectrum is asymmetric, i.e., the  $yz$  and  $zy$  results are not equivalent. These spectra are evidence that interband ( $A \leftrightarrow B$ ) exciton processes are important; nevertheless we would like to ignore such processes in a first approximate discussion of this effect.

Apart from these  $A \leftrightarrow B$  interband effects and apart from shifts in the emission peak due to  $A \leftrightarrow B$  energy difference, our results show that the resonance Raman tensor  $\Delta\alpha$  couples to LO phonons, regardless of their direction of propagation, even in first order, and has diagonal components  $\Delta\alpha_{\perp\perp}$  along axes perpendicular to the propagation direction of the photon. As pointed out by Kleinman,<sup>5</sup> such would be the form of the Raman tensor for light in a dielectric continuum interacting with a longitudinal polarization wave. This is what one would expect if the interaction with LO phonons is via the orbital part of a large-radius Wannier exciton. Then continuum polarization effects would dominate over the short-range forces which usually determine the symmetries of the scattering tensor.

The above considerations suggest strongly that the resonance Raman effect of LO phonons goes through an exciton as an intermediate state.<sup>6</sup> Assume a single exciton band for simplicity; multiple bands may be treated by the methods of Seigall and Mahan.<sup>7</sup> Consider the three processes shown in Fig. 3 of Ref. 1. Our data suggest broad resonances at  $\omega_L \approx \omega_{ex}$  and  $\omega_R \approx \omega_{ex}$  with no oth-

er resonances at intermediate frequencies between  $\omega_L$  and  $\omega_R$ . This seems to rule out the cascade process in Fig. 3(a).<sup>8</sup> The remaining processes, (b) and (c), will have resonance factors in perturbation theory of the form  $(\omega_L - \omega_{ex}^0)^{-1}(\omega_R - \omega_{ex}^0)^{-1}$  that describe the propagation of the exciton just after creation and just before annihilation. Absorption and emission data indicate a strong broadening of the exciton line due to phonon interactions. Thus it is a much better approximation to replace the bare-exciton frequency  $\omega_{ex}^0$  in the propagators by the experimental exciton frequency  $\omega_{ex}$  plus a large imaginary part  $i\Gamma(\omega, T)$ . This will give the type of broad resonance we need to explain our data, including temperature dependences of the type shown in Fig. 2.

It is necessary to assume no additional strong frequency dependences beyond those already accounted for. This might tend to favor the processes in Fig. 3(c) of Ref. 1 over those of Fig. 3(b), but this will require further study. Due to the exciton's kinetic energy, the integrals over the  $k$  vectors of the intermediate states of processes such as that of Fig. 3(b) of Ref. 1 should provide additional smoothing of the  $\omega_L$  dependence beyond the substantial amount already provided by large exciton linewidths represented by  $\text{Im}\Sigma$ .

In a more complete paper to be submitted shortly we shall discuss many more experimental details and hope to say more about the theory of this effect including how the above arguments relate to a more detailed treatment of the exciton-photon interaction.<sup>9</sup>

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<sup>1</sup>R. C. C. Leite and S. P. S. Porto, Phys. Rev. Letters **17**, 10 (1966).

<sup>2</sup>B. Tell, T. C. Damen, and S. P. S. Porto, Phys. Rev. **144**, 771 (1966).

<sup>3</sup>See the contributions by E. Gutsche and J. Voigt, in Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, R. I., 1967, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1968), p. 337; C. E. Bleil and J. G. Gay, ibid., p. 360.

<sup>4</sup>R. Loudon, Advan. Phys. **13**, 423 (1964).

<sup>5</sup>D. A. Kleinman, private communication.

<sup>6</sup>J. L. Birman and A. K. Ganguly, Phys. Rev. Letters **17**, 647 (1966); A. K. Ganguly and J. L. Birman, Phys. Rev. **162**, 806 (1967).

<sup>7</sup>B. Segall and G. D. Mahan, Phys. Rev. **171**, 935 (1968).

<sup>8</sup>If the LO branch has noticeable dispersion, then the multiple-phonon lines due to processes (b) and (c) in Ref. 1 will be much broader than the single-phonon line because the multiple phonons have a distribution of  $k$  values. In process (a) only  $k \approx 0$  phonons are emitted. Our data show no broadening of the multiple-phonon lines beyond that due to phonon lifetimes, but this does not favor process (a), since there is apparently little dispersion in the LO branch of CdS: Reference 2 gives the frequency of the 2-LO-phonon line as very close to twice that of the one-phonon line.

<sup>9</sup>E. Burstein, D. L. Mills, A. Pinczuk, and S. Ushioda, Phys. Rev. Letters **22**, 348 (1969).

## EVIDENCE FOR THE EMISSION OF SLOW POSITRONS FROM POLYETHYLENE\*

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A measurable flux of slow positrons was found to be emitted from the surface of a polyethylene absorber.

In 1950, Madansky and Rasetti<sup>1</sup> reported on an attempt to detect thermal positrons which should have, according to their estimates, stood a reasonable chance of being emitted if they started out within a diffusion length of the surface of an absorber. Using positrons from a Cu<sup>64</sup> source, both metallic and dielectric absorbers were used, but no evidence of slow positron emission was found within the limits of sensitivity of their

experiment. However, Cherry,<sup>2</sup> in the course of an experimental determination of the secondary-emission coefficient of positrons, did observe the emission of positrons with energies below 10 eV that had been transmitted through a mica window whose exit side had been coated with a thin film of chromium.

In the case of the dielectric absorbers, it seems likely that the difference in results re-