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Luminescence of CdS Generated By High Intensity Excitation
Below the Bandgap

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ABSTRACT

High excitation photoluminescence of CdS at low temperatures excited by photons below the bandgap show the same general features as those obtained by one-photon band to band absorption. The excitation spectrum of the M-line shows no structure corresponding to a giant two-photon absorption expected for the direct creation of excitonic molecules.

Die Photolumineszenz von CdS bei tiefen Temperaturen, angeregt durch intensives Laserlicht unterhalb der Bandkante, zeigt qualitativ dieselben Züge wie die, die durch direkte Band-Bandanregung zustande kommt. Das Anregungsspektrum der M-Linie weist keine Strukturen auf, die einer Zweiphotonenriesenabsorption, verursacht durch Direktanregung von Exzitonmolekülen, entsprechen würden.

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In recent years, photoluminescence under high-intensity excitation has been investigated in a large number of semiconductors. In particular, the case of CdS has been studied by several research groups using laser excitation with photon energies larger than the band gap.¹⁻⁶ Several new features in the luminescence spectrum were observed. The observed spectra and their intensity dependence are in good qualitative agreement among various groups, although the interpretations vary to a considerable extent. Most people, however, believe that the new features in the spectrum are due to a high exciton concentration and the existence of exciton molecules. It is conceivable that by studying the luminescence with tunable laser excitations around the exciton lines and the band edge, one might obtain some clarifying information about these new features. This paper reports our preliminary attempt along this line.

The experiments were carried out on pure vapor-phase grown CdS single crystal platelets which were immersed in liquid helium below the λ point. The c-axis was in the plane of the platelets. The excitation source used was a 10 pps N_2 -laser-pumped dye laser⁷ tunable between 4750 and 4950 Å. Its output had a linewidth of about 0.1 Å and an energy per pulse of about 60 μ J in 3 nsec. The dye laser beam was normally focused on the sample by a lens with a 25-cm focal length, producing an estimated maximum intensity of 3 MW/cm² on the sample surface. Filters were used to vary the excitation intensity. The luminescence was collected either in the forward or in the backward direction. After passing through a 1-m Jarrel-Ash double monochromator, it was detected by a photomultiplier and recorded by a gated electronic integrator.⁸

At all laser excitation frequencies we studied, either below or above the band gap (2.582 eV), with or without linear absorption, the luminescence spectra under sufficiently high-intensity excitations, showed features reminiscent of results in previous reports, where the excitation frequencies were always larger than the band gap. As an example, we present in Fig. 1 the intensity-dependent luminescence spectra at two excitation frequencies, one at 2.5542 eV close to the peak of the A_L (longitudinal) excitation, and the other at 2.5511 eV where no linear absorption structure was observed. In both cases, at the lowest intensity (Fig. 1a), we obtained the usual low-excitation luminescence spectrum. At higher excitation intensity (Fig. 1b), a broad line (called M) appeared on the low energy side of the bound exciton line I_2 and started to dominate the spectrum. With even higher excitation intensity (Fig. 1c), another broad line (called P) centered around 2.53 eV appeared and grew nonlinearly with the excitation intensity. It eventually outgrew the M line and its peak shifted slightly to lower energy.

The design of our laser did not allow us to monitor the luminescence intensity under constant laser excitation while the laser was continuously tuned over a large frequency range. We could, however, do so over small frequency intervals. As shown in Fig. 2a, with low excitation intensity, ($\leq 1 \mu\text{J}$ per pulse), the excitation spectrum of the I_2 luminescence line shows clear resonant enhancement at the three exciton lines A_L (2.5542 eV), A (2.5534 eV), and A_F (2.5519 eV). But with high excitation intensity, the excitation spectrum of the M line showed no sharp structure but only a general decline towards the low

frequency side.

We did measure the luminescence spectra of CdS at a constant high-excitation level (8.8 μJ per laser pulse) while varying the laser excitation frequency between 2.5300 and 2.5693 eV in steps of 2.2 meV. Figure 3 summarizes the results for the M line for laser polarizations both perpendicular and parallel to the c-axis. The peak intensity of the M line first increases slowly with decreasing excitation frequency, reaches a peak near the A exciton lines, and then drops below the noise level at ~ 2.535 eV. There is no obvious fine structure in these excitation spectra. A similar behavior was observed for the P line, but the data appeared more strongly scattered. This is presumably because at such an excitation level, the P line is more sensitive to fluctuations of the excitation intensity. As a result, we cannot rule out the possibility of fine structure in the excitation spectrum of the P line. The intensity ratio of the P line to the M line decreases with decreasing excitation frequency. We should emphasize that, in our experiments, the M line could be observed, even when the laser excitation frequency was less than that of the M line.

The above results suggest that the high-excitation luminescence arises from strong two-photon excitations. Our attempt to measure nonlinear absorption as a function of laser frequency and intensity has not been successful because of diffraction from striations on the surface of the sample. The qualitative results, however, did show a strong nonlinearity. Experiments on a better sample are presently in progress.

Shionoya et al.⁴ have designated the M line as arising from the decay of excitonic molecules. Hanamura⁹ has predicted the direct formation

of excitonic molecules via giant two-photon absorption. Gale and Mysyrowicz¹⁰ have observed such a resonant line in the excitation spectrum of exciton-molecular luminescence in CuCl. However, we could not find any resonant enhancement in the excitation spectrum of the M line (see Fig. 3) in the region corresponding to a molecular binding energy given by either Figueira and Mahr,³ or Shionoya *et al.*,⁴ or to any other reasonable binding energy. This suggests that either the M line is not due to decay of excitonic molecules, or that the corresponding molecular state cannot be reached by direct two-photon absorption.

We had suspected that our results might be affected by laser heating of the sample. Shah *et al.*¹¹ determined the sample temperature of the highly excited CdS by analyzing the shape of the acoustic phonon wings of the I_1 bound-exciton emission line. Using their results, we estimate a maximum temperature of $\sim 15^\circ\text{K}$ for the sample under our excitation conditions. Although this temperature is considerably higher than the helium bath temperature, it is not sufficient to account for the continued existence of the M line at 60 cm^{-1} above the excitation frequency.

We therefore suggest that the high-excitation luminescence of CdS in our case came from direct two-photon excitations of carriers via interband transitions. The lack of fine structure in the excitation spectrum might be due to appreciable saturation in the absorption process since otherwise we should have found sharp and strong resonant enhancement around the various exciton lines.

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REFERENCES

1. D. Magde and H. Mahr, Phys. Rev. Letters 24, 890 (1970).
2. D. Magde and H. Mahr, Phys. Rev. B2, 4098 (1970).
3. J. F. Figueira and H. Mahr, Phys. Rev. B7, 4520 (1973).
4. S. Shionoya, H. Saito, E. Hanamura, and O. Akimoto, Solid State Communications 12, 223 (1973).
5. H. Saito, S. Shionoya, and E. Hanamura, Solid State Communications 12, 227 (1973).
6. A. F. Dite, V. I. Revenko, V. B. Timofeev, and P. D. Altukhov, JETP Letters 18, 341 (1973).
7. T. W. Hänsch, Applied Optics, 11, 895 (1972).
8. H. Rosen, P. Robrish, and O. Chamberlain (to be published).
9. E. Hanamura, Solid State Communications 12, 951 (1973).
10. G. M. Gale and A. Mysyrowicz, Phys. Rev. Letters 32, 727 (1974).
11. J. Shah, R. F. Leheny, and W. F. Brinkman, Phys. Rev. B10, 659 (1974).

FIGURE CAPTIONS

Fig. 1. Intensity dependence of the luminescence of CdS for two selected excitation frequencies; $h\nu = 2.5511$ eV(left) and $h\nu = 2.5542$ eV (right). The spectra were taken in the backward geometry. The exciting light is polarized $\parallel$ to the c-axis of the sample. The luminescence is predominantly polarized $\perp$ to c. The excitation laser intensities are:

(a) = 0.01 MW/cm^2 ; (b) 0.1 MW/cm^2 ; (c) = 1 MW/cm^2 . The luminescence spectra are magnified by the amount shown in the figure. The sharp line on the right side of the spectra is due to elastically scattered laser light.

Fig. 2(a). Excitation spectrum of the I_2 emission line (backward geometry). The spectrometer bandpass (1.5 meV) was centered at the peak of the I_2 line and the excitation frequency was scanned over a region near the A ($n = 1$) exciton line with a laser intensity of $\sim .03 \text{ MW/cm}^2$. The input polarization was parallel to c and the output polarization perpendicular to c.

2(b). Excitation spectrum of the M line taken under similar conditions but with a laser intensity of 1 MW/cm^2 . Note that the emission intensity in (b) is much larger than in (a).

Fig. 3. Peak intensity of M line luminescence as a function of excitation photon energy for input polarizations $\vec{\epsilon} \parallel c$ and $\vec{\epsilon} \perp c$. The data were taken in the forward geometry with a laser power of 0.5 MW/cm^2 .

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