

Luminescence Spectra and Raman Excitation Profiles in Small CdS Particles

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The "edge"-luminescence spectra and the Raman excitation profiles of small CdS particles chemically deposited on transparent substrates show size effects. The peaks are shifted to higher frequencies as the size of particles decreases. Aggregated samples show maxima at lower frequencies than those of the bulk material and behave as amorphous films. After the samples are warmed, a new peak appears in the luminescence spectra whose position depends on the size and aggregation of the particles. An explanation of the shifts based on the size-quantization of the band width or of the localized electronic levels is given.

1. Introduction

The Raman and luminescence spectra of CdS have been studied by a number of investigators. Recent results have been reported by Korneichuk *et al.* (1), Koteles and Winterling (2), Schrey *et al.* (3), Yu (4), Senoner *et al.* (5), and Yoshida *et al.* (6), while earlier results have been summarized in excellent review articles by Cardona *et al.* (7), Richter (8), and Cho *et al.* (9). The position and the intensity of Raman lines and of luminescence bands depend on the temperature (10)-(14), the pressure (15), the film thickness (16), etc. Scott and Damen (17) observed surface effects in the Raman spectra of thin CdS deposits. Berry (18), Stasenko (19), Skomyakov *et al.* (20), and Hayashi *et al.* (21) reported size effects in the absorption spectra of small CdS particles.

This work deals with the investigation of luminescence spectra and Raman excita-

tion profiles of small CdS particles. We describe the manner in which the spectra of CdS change on varying the size and the aggregation of particles.

2. Experimental Procedure

The samples were prepared from the following commercial products: (1) Cadmium sulfate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) cryst. suprapur (Merck 2028) and thioacetamide GR (Merck 8170); (2) Cadmium sulfide suprapur powder (Merck 2020) consisting of large particles ($\sim 2000 \text{ \AA}$ in diameter). (3) Cadmium sulfide high-purity single crystals (obtained from Semi-Elements, Inc., Saxonburg, Penn.) Thin films were prepared by chemical deposition on fused quartz plates or on CaF_2 single-crystal plates (Merck). From the above compounds the following samples were prepared and studied:

Sample A. This is a thin yellow CdS deposit prepared by keeping a 0.2% CdSO_4

aqueous solution with a 0.1% thioacetamide solution over a clean quartz (or CaF_2) plate for 24 hr at room temperature. The deposits were washed with water and acetone and dried in air or by firing for 1 hr at 800°C in a stream of purified H_2S . Electron micrographs showed that the deposit consists of spherical particles of 100 \AA in diameter with a $200\text{-}\text{\AA}$ particle separation.

Sample B. This is a brownish-yellow pellet of CdS prepared by pressing 0.2 g of commercial powder at 10 kbar.

Sample C. This is a reddish-yellow pellet of CdS prepared by grinding a single crystal or a small amount of commercial powder of CdS in an agate mortar and pressing at 10 kbar. The sample consists of particles smaller than 1000 \AA in diameter. The degree of aggregation in this sample is ca 1.

Sample D. This is a thin deposit of CdS prepared as in Sample A but using more concentrated solutions and increasing the time of deposition. The films obtained have a degree of aggregation from 0.2 to 0.6 and the particles are of diameter from 100 to 1500 \AA . This method of preparation gives more homogeneous films than that used by Skomyakov *et al.* (20).

Sample F. By mixing a concentrated solution of CdSO_4 with a concentrated solution of thioacetamide and warming at ca 90°C a fine powder has been obtained. The powder was dried by firing for 1 hr at 800°C in a stream of H_2S . This extremely pure powder (22) of grain size ca 2500 \AA was compressed in a pellet.

The Raman and luminescence spectra were recorded on a Jobin-Yvon Ramanor HG-2S model spectrometer. Exciting radiation was provided by a Spectra Physics 125 model He-Ne laser, a Spectra Physics 165-03 model Argon laser, and a Spectra Physics 375 model dye laser employing rhodamine dyes. The laser beam was incident at approximately 60° from the normal to the sample surface. The secondary radiation (Raman and luminescence) emerging per-

pendicular to the sample surface was collected into the monochromator without polarization. The intensity of luminescence bands was not corrected to the efficiency of gratings. The intensity of the scattering radiation was normalized against the intensity of 435 cm^{-1} line of $\text{C}_2\text{H}_5\text{OH}$ or 315 cm^{-1} line of quartz. The reference compound ($\text{C}_2\text{H}_5\text{OH}$ or quartz) was on the front of the monochromator. A block diagram is shown (inset) in Fig. 3. The luminescence spectra were also recorded using a commercial spectrophotometer (of Aminco-Browman Co) employing a Xenon lamp. The Raman lines were not observed with this instrument because of its low resolution. All measurements were performed at room temperature.

3. Results and discussion

Figure 1 shows the Raman lines (sharp peaks) and the luminescence bands (broad backgrounds) of Samples A, B, C obtained with a 488-nm excitation line ($\omega_L = 20,492 \text{ cm}^{-1}$). The spectra of Sample B (Fig. 1b) are similar to those of a single crystal [see also Ref. (23)] but the spectra of A and C are different. One can see an inversion of Raman peak intensities in comparison to those of B and a shift of luminescence band to higher (Fig. 1a) or lower (Fig. 1c) frequencies. The Raman lines of small CdS spheres (Samples A and C) are not shifted in comparison to those of bulk material (single crystal or Sample B). However, the Raman lines of small oriented cylinders are shifted to lower frequencies (17). The explanation is given elsewhere (24-26). The Raman lines at $305, 607, \dots \text{ cm}^{-1}$ are due to the LO phonon mode and its overtones. The luminescence band is due to (Wannier) excitons, exciton-phonon interactions, etc. (12, 27, 28) and occurs near the absorption edge. We call this the "edge"-luminescence band (ELB).

The position of luminescence bands can

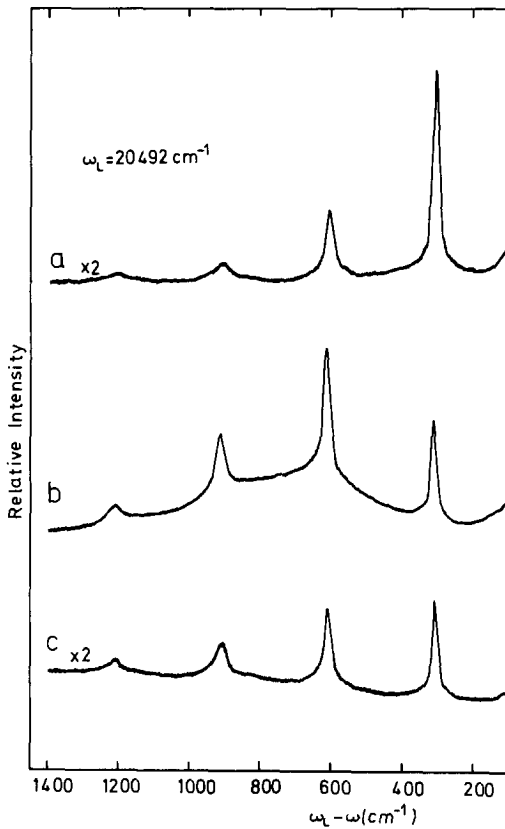


FIG. 1. Raman spectra (sharp peaks) and luminescence spectra (broad backgrounds) a, b, c of Samples A, B, C respectively, for laser incident from the CdS side. Excitation line of 488 nm.

be seen easily by using an excitation line of short wavelength. Figure 2 shows the Raman and luminescence spectra of Samples A, B, C obtained with a 454.5-nm ($\omega_L = 22,000 \text{ cm}^{-1}$) excitation line. The ELBs of samples A, B, and C occur at 468, 505, and 509 nm, respectively. We have not found any difference in ELBs of Sample A either dried in air or in a stream of H_2S . Samples of the type D give ELBs which occur in the region from 470 to 495 nm. The shift from 468 to 505 nm, which was observed in the ELBs is due to the increased size of particles. ELBs of Sample F have the same features as those of Sample B. Powder of CdS scraped from substrates of Sample A and pressed into a pellet shows a luminescence band at 530 nm. This shift to

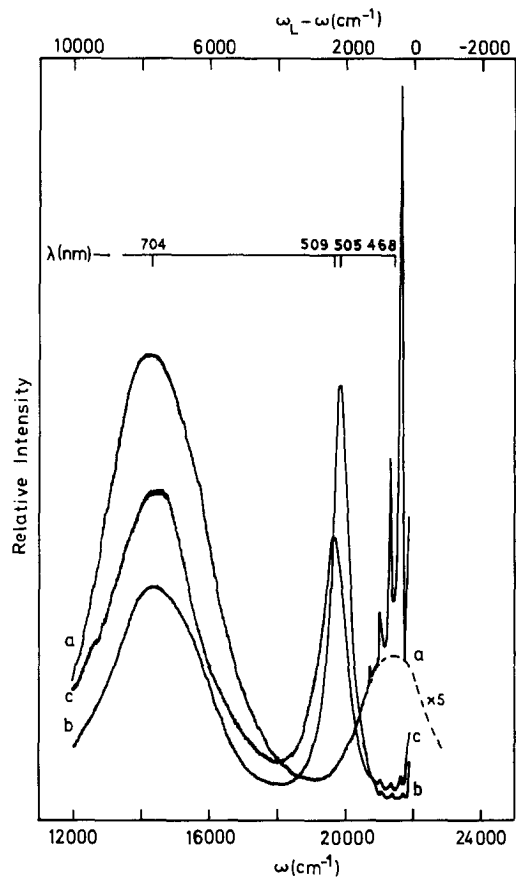


FIG. 2. Raman spectra (sharp peaks) and luminescence spectra (broad peaks) a, b, c, of Samples A, B, C respectively, for laser incident from the CdS side. Excitation line of 454.5 nm. The dashed part of curve a has been drawn by taking into account a similar spectrum obtained by a uv excitation (i.e., 351.1 + 363.8 nm of Ar laser).

longer wavelengths, observed also in the spectra of Sample C, is due to the aggregation of the particles and is analogous to that observed in the absorption spectra of small metal particles [see, for example, (26)]. The luminescence band at 704 nm, which does not show considerable differences from one sample to another, is due to anion vacancies (27). Figures 1 and 2 show that strong Raman bands can be obtained by using an excitation wavelength close to ELB. The Raman excitation profiles (REP) of Fig. 3 show that the highest Raman intensities can be obtained with excitation lines of 478,

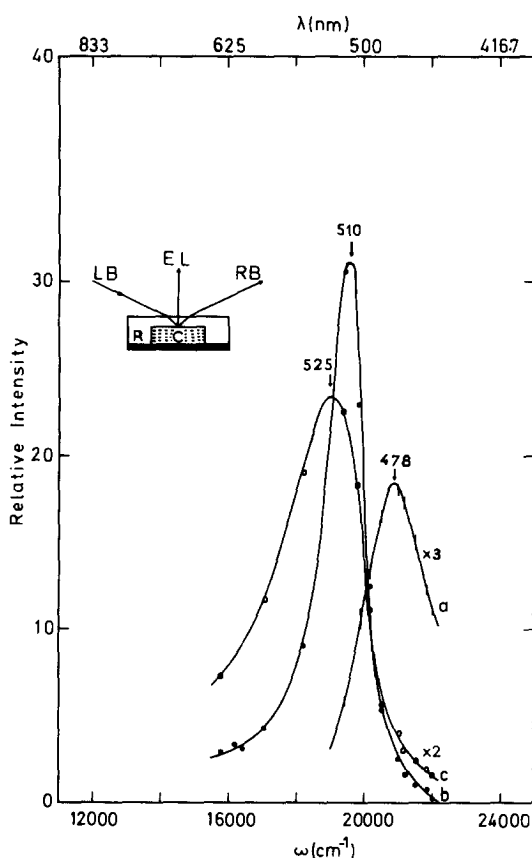


FIG. 3. Excitation Raman profiles a, b, c of Samples A, B, C respectively. LB = laser beam RB = reflectance beam, EL = entrance lens, R = reference (liquid), C = compound (CdS).

510, and 525 nm for the samples A, B, and C respectively. From Figs. 2 and 3 one can see that the peak positions of ELBs occur at shorter wavelengths than those of REPs. This is due to the fact that the mechanism in the two processes (luminescence and scattering) is different. However, both ELBs and REPs are shifted to shorter wavelengths (higher frequencies) as the particles become smaller and the particle separation is large. Conversely, the bands of aggregated samples (of type C) occur at longer wavelengths than those of the bulk material. Aggregated samples behave as amorphous films [see, for example, (29)]. After Samples A, B, C are warmed at 350°C for

10 min, the intensity of ELBs decreases and another peak appears in the region from 16,000 to 18,000 cm^{-1} . Figure 4 shows that the position of this new peak depends on the sample structure. One can see that the ELBs disappear (Fig. 4a) or become weaker (Fig. 4b,c) after warming and a new peak appears at 565 and 581 nm for the Samples A and B respectively, and a weak shoulder at 588 nm for the Sample C. A new structure appeared also in the absorption spectra of CdS films after warming (30).

Samples of type D give luminescence spectra and REPs whose the maxima occur in an intermediate position between those labeled with (a) and (b).

It is known that the average exciton sizes in the bulk CdS are a few hundreds of angstroms [see (31)], that is, of the same order as the particle sizes of Sample A (or D).

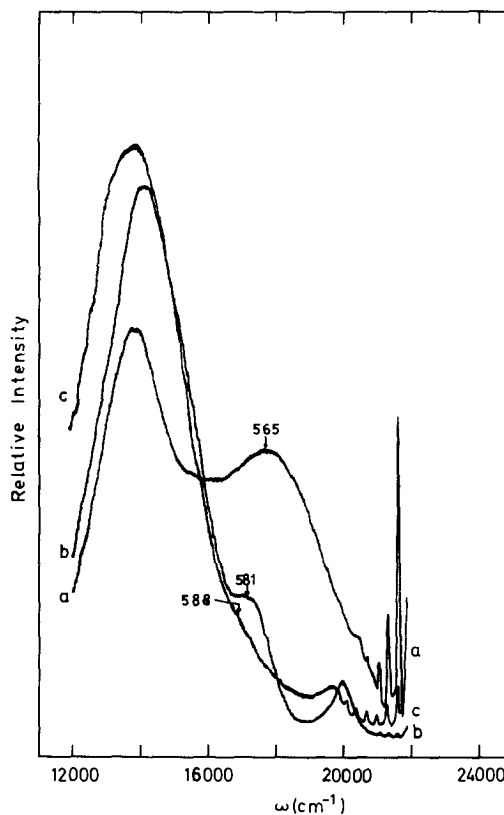


FIG. 4. Same as Fig. 2 but after warming at 350°C for 10 min.

However, it has been predicted theoretically that when the dimensions of a semi-conducting crystal are decreased to the size of the order of the excitonic size (32–37) or of the gap width [see (19) and references therein], the structure of the excitons or of the gap width itself will be strongly affected by the finite geometry. The size effect in ELBs and REPs described above (Figs. 1–3) is a consequence of quantum size effect of the gap width or of the excitonic levels of the semiconductor CdS. Figure 2 shows that the peak intensity decreases and the peak position is shifted to higher frequencies as the particle size decreases. These effects are in accordance with the fact that the gap frequency of a semiconducting crystal increases as the thickness of the crystal decreases (19), while the longitudinal excitonic peaks disappear for crystal thickness smaller than the dead layer (~ 70 Å for CdS) of semiconductors [see (31) and references therein]. However, the transverse excitonic peaks in the reflectance spectra became more intense as the crystal thickness decreases (31). The size effects can not be observed (at room temperature) as a peak shift in the absorption spectra—because of the small value of the absorption index of CdS in this spectral region (38, 39), nor in the specular reflectance spectra—because of the strong scattering of the particles. However, the uv absorption spectra of Sample A observed with a Unicam SP700 A spectrophotometer show a peak at 236 nm and a shoulder at 212 nm. The spectra of large particles or thick films show peaks at longer wavelengths [see (40) and (41)]. This shift is due to the size quantization of the E_1 transition of CdS. Similar shifts have been observed in the absorption spectra of thin InSb films (42). The uv spectra of Sample A show that it consists of small crystallites with hexagonal structure (41, 43). But the gap energy of cubic CdS is nearly the same as that of hexagonal CdS (41) and consequently the shifts, which

have been observed, are not due to a change in the crystal structure.

The ELBs and REPs of Sample C (Figs. 1c, 2c, 3c) occur at lower frequencies than those of the bulk material. The explanation is that crushing the CdS powder produces a large amount of strain and dislocations in the crystallites. This introduces localized states in the gap. This is the reason that aggregated samples (C) behave like amorphous films.

The impurity centers (and other centers) created by thermal treatment lead to similar size effects. The peaks in the absorption spectra occur at lower frequencies than those of the pure material (41, 44–46). The impurities introduced in CdS crystals after warming are metallic in nature, namely, Cd atoms (30). The impurity-electron sizes in CdS crystals are ca. 100 Å [see (47) and references therein], namely, of the same order as the particle sizes in Sample A. Bendow (48) predicted theoretically that when the dimensions of a semiconductor are decreased to the size of the order of the bulk impurity-electron size the impurity absorption edge shifts to higher energies. The peak shift shown in Fig. 4 is attributed to the size quantization of the impurity-electron levels in CdS.

The effects described in this paper are only in qualitative agreement with the theories because of the thermal and the size distribution broadening and mixing of excitonic lines at room temperature. At low temperature one can avoid the thermal broadening of lines. But at the moment we are not able to perform low-temperature measurements in our laboratory. We are now continuing our experiments at room temperature on the Raman and luminescence spectra of other inorganic powders, such as ZnS, PbI₂, AgI.

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