

Effects of hydrostatic pressure on the low-temperature photoluminescence spectrum of heavily doped CdS

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The photoluminescence spectrum of heavily doped CdS is studied under pressure at 300 and 6 K in a diamond anvil cell. The pressure-induced shift of the broad green luminescence peak at 300 K is found to depend on the impurity content of the sample. At 6 K, the I_2 (donor-bound), I_1 (acceptor-bound), G_5 (bound-to-bound) excitons and the 1LO and 2LO replicas of G_5 are observed in addition to a red luminescence due to the Cd interstitials. The pressure coefficients of the excitons and the LO replicas are slightly lower than that of the band edge. The red luminescence, on the other hand, shifts at a rate of 7.28 ± 0.45 meV/kbar which is about 75% larger. These experiments did not indicate any pressure ionization of the donor impurities. No luminescence could be observed beyond the transition into an indirect-band-gap, rocksalt phase.

I. INTRODUCTION

Brown *et al.*¹ reported dc flux exclusion approaching the Meissner value at 77 K in freshly pressure-quenched cadmium sulfide (CdS) containing chlorine impurities. This indicated the possibility of superconductivity at liquid-nitrogen temperatures. The anomalous magnetic behavior was shown to depend sensitively on the chlorine content of the sample and the pressurization parameters. A theoretical model² proposed that high-temperature superconductivity is possible via an impurity-based mechanism. The diamagnetic anomaly was attributed to the combined effect of the band structure and the behavior of donor impurities under stress. As CdS undergoes a phase transition at ~ 27 kbar, from a direct-band-gap wurtzite to an indirect-band-gap rocksalt structure, it was supposed that the indirect band gap contributes to a high density of electronic states. Also, if the impurities ionize under pressure, the large number of electrons available can take part in an excitonic superconducting mechanism. Since both the experiment and theory predict an important role for the impurities, it is of interest to investigate the behavior of impurities under pressure.

A study of the photoluminescence and Raman LO-phonon spectra in pure and chlorine-doped CdS under hydrostatic pressure up to 42 kbar at room temperature was reported earlier.³ The broad green edge emission observed is due to a thermal average of various free and impurity-bound excitons. The excitons are resolved at 6 K and their pressure dependence in undoped CdS was also studied.⁴ Our room-temperature measurements showed that in pure and lightly chlorine-doped CdS, the pressure-induced shift of the luminescence energy is linear and in agreement with the shift of the optical-absorption edge.⁵ In heavily chlorine-doped CdS, however, the shift was $\sim 20\%$ higher, indicating a possible ionization of impurities at high pressures. In our low-temperature study on undoped CdS, we found that both the A (free exciton associated with the top valence band) and I_2 (donor bound exciton) excitons follow the band edge. The LO replicas

of these excitons shifted at a rate that combines the shifts of both the band edge and the LO-phonon energies. The 1-bar spectrum at 6 K showed that the phonon-assisted bands of I_2 exciton also has a kinetic energy broadening similar to those of the A exciton.

We present here a study of the photoluminescence (PL) spectra of heavily chlorine-doped CdS under pressure at 300 and 6 K in the wurtzite phase of CdS. The experimental details are given in Sec. II. The essential features of the PL spectra and their behavior under pressure are described in Sec. III. The pressure coefficients of all the features observed in heavily doped CdS are discussed in comparison to those of undoped CdS. The absence of pressure ionization of the impurities is also discussed. Section IV is a summary.

II. EXPERIMENTAL

The 4579-Å line of an argon-ion laser was used for excitation in a backscattering geometry. The room-temperature spectra were excited with ~ 50 mW of power. At 6 K, ~ 0.1 mW of power was used in the green luminescence region and ~ 10 mW for the red luminescence band. A Spex 0.85 m double monochromator and a cooled RCA photomultiplier tube with photon-counting electronics were used for recording the spectra. The resolution of the instrument was set at ~ 1.3 cm⁻¹ (100- μ m slit width).

The high-pressure measurements were done in a gasketed diamond anvil cell. The room-temperature measurements were carried out in a commercial cell⁶ of the U. S. National Bureau of Standards (Ref. 7) design, with a 4:1 methanol-ethanol mixture as the pressure medium. For the low-temperature study, a Merrill-Bassett type⁸ diamond anvil cell attached to a continuous flow helium cryostat was used. Solid argon, loaded by the indium dam technique,⁹ served as the pressure transmitting medium at 6 K. Pressure was applied at room temperature and the cell was cooled. The pressure at 6 K was found to be ~ 5 – 7 kbar lower than that at 300 K. The position and

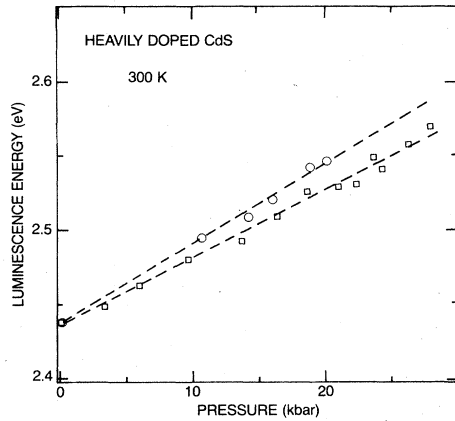


FIG. 1. Energy of the luminescence peak as a function of pressure in heavily doped CdS at 300 K. Circles (Ref. 3) and squares refer to measurements on two different samples.

width of ruby R_1 fluorescence were used to determine the pressure and its uniformity. The inhomogeneity in pressure was less than 1 kbar.

The heavily doped CdS used in this investigation was grown with 0.1 wt. % LiCl included in the melt for producing a high level of doping. Spectra reported are all unpolarized for it is difficult to know the orientation of the sample inside the pressure cell.

III. RESULTS AND DISCUSSION

There is a linear blue shift (increase in energy) of all the luminescence peaks (both at 300 and 6 K) with increasing pressure, up to about 25 kbar. The luminescence is quenched close to the phase transition, as observed by a sharp decrease in intensity both at 300 and 6 K. We could not observe any luminescence in the indirect-band-gap rocksalt phase. The luminescence does not recover at atmospheric pressure once the sample has undergone the phase transition. This can be attributed to the large number of defects formed during the lattice reordering. The sample looks yellow at atmospheric pressure and turns deep red beyond 27 kbar. The volume reduction associated with the phase change can also be observed when viewed under a microscope. Releasing the pressure after

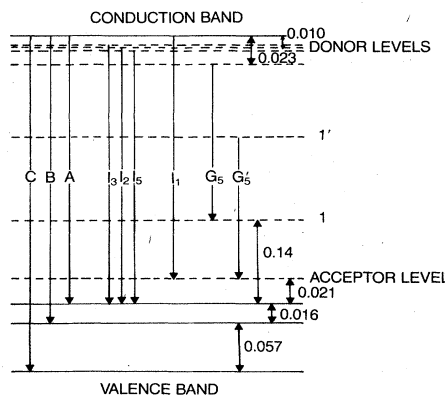


FIG. 2. Energy-level diagram in a doped CdS crystal. The numbers indicate energies in eV.

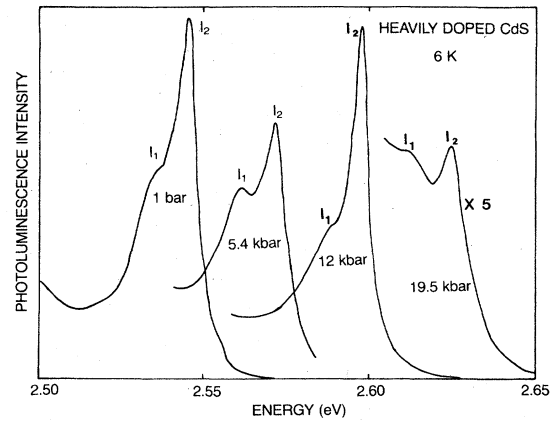


FIG. 3. Luminescence spectra of heavily doped CdS at 6 K in the bound exciton region for several pressures.

27 kbar does not recover the yellow color to the sample, in accordance with the optical-absorption measurements of Edwards and Drickamer.¹⁰ The orange appearance of the sample is presumably due to the cubic zinc-blende intrusions.

A. Room-temperature measurements

The shift of the luminescence energy with pressure is found to vary in the range of 4.54 to 5.35 meV/kbar for different samples, i.e., close to the band-edge shift as for undoped CdS or $\sim 20\%$ higher as in Ref. 3. Figure 1 shows two sets of measurements. It is clear from this figure that the experimental points cannot be combined to a single set of data within the errors of measurement. The heavily doped sample is known to be spatially inhomogeneous and the exact spatial profile of the impurity concentration is not available. The different shifts of the luminescence energy may, therefore, arise from the different impurity concentrations in the small pieces chosen for investigation under pressure. We believe that the $\sim 20\%$ higher shift of the luminescence energy (circles in Fig. 1) arises when the chlorine (donor) content is large

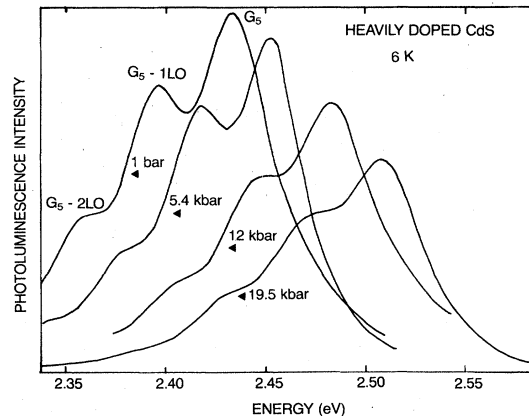


FIG. 4. Luminescence spectrum of heavily doped CdS at 6 K in the bound-to-bound exciton region for several pressures. The exciton and its 1LO and 2LO replicas can be seen.

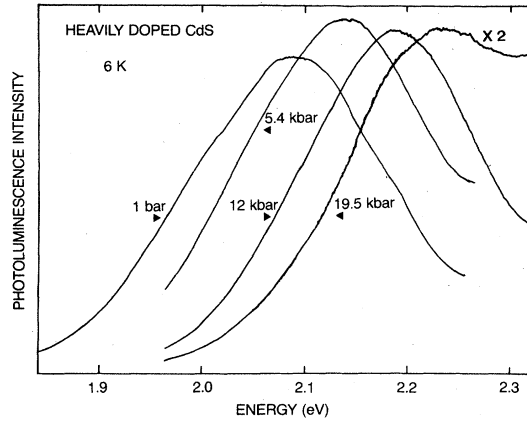


FIG. 5. Red-luminescence spectrum in heavily doped CdS at 6 K for various pressures.

and the lower shift (squares in Fig. 1) is seen when the chlorine content is small.

It is known that CdS becomes a degenerate semiconductor for a donor concentration $N_d \geq 10^{18} \text{ cm}^{-3}$. In the degenerate case, the luminescence energy would follow the Fermi level rather than the band edge. A pressure-induced reduction in the effective mass (m^*) or an increase in N_d would yield a larger shift for the Fermi energy (E_F) than the band edge. An increase in N_d can come from the ionization of donor impurities under pressure, which can be checked by low-temperature luminescence studies.

B. Low-temperature measurements

The heavily doped CdS contains a large number of cadmium and sulfur vacancies and interstitials besides lithium (acceptor) and chlorine (donor) impurities. Figure 2 shows a schematic energy-level diagram in a doped CdS crystal. The various transitions are indicated by downward arrows. In the green luminescence region (2.3–2.5 eV), we observe both the I_1 (recombination of the free electrons in the conduction band with the holes bound to neutral acceptors) and I_2 (recombination of the electrons bound to neutral donors with the free holes in the top valence band) excitons (see Fig. 3). In addition, the recombination of the bound electrons with the bound holes (designated G_5 , following Ref. 11) is also seen (see Fig. 4). One of the impurity levels involved in this transi-

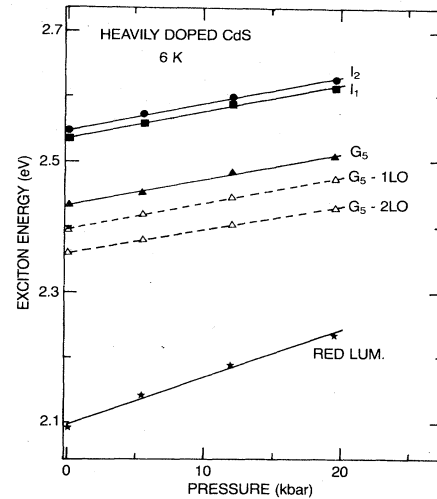


FIG. 6. Energies of the excitons (solid symbols) and the LO replicas of the G_5 exciton (open triangles) as a function of pressure. The lines represent linear least-squares fit to the data.

tion is a deep level lying at ~ 0.14 eV from the band edge. Whether this deep level is associated with an acceptor or donor is not clear from the available literature. Since our experiment cannot distinguish between the two possibilities, we denote them by G_5 and G'_5 , respectively, in Fig. 2. The G_5 exciton couples strongly with the LO phonon. Two emission peaks separated from G_5 by 1-LO- and 2-LO-phonon energy can be seen in Fig. 4. All the exciton peaks and their LO replicas are broadened considerably as compared to undoped CdS, due to the high level of doping. Free excitons are not observed in this sample. The red luminescence, associated with Cd interstitials, shifts only slightly with temperature and appears at 2.09 eV (2.07 eV at 300 K) in the 1-bar spectrum of Fig. 5. The green luminescence in CdS:Cl is weaker and broader, as compared to that in undoped CdS, owing to the defects produced on doping. The broad red luminescence is enhanced a little at low temperatures and is seen with moderate intensity. The luminescence intensity decreased by a factor of 5 at 19.5 kbar as compared to that at 5.4 kbar (Figs. 3–5). This is indicative of the phase transition, that has already begun at room temperature when the pressure was a little higher (24.2 kbar). The luminescence vanishes completely on increasing the pressure further.

TABLE I. Analysis of exciton data in heavily doped CdS (6 K).

Description	dE/dP (meV/kbar)	$\left. \frac{dE}{dP} \right _{\text{ex}} - m \left. \frac{dE}{dP} \right _{\text{1LO}}$ (meV/kbar)	E_0 (eV)
I_2	4.05 ± 0.17		2.547 ± 0.002
I_1	4.05 ± 0.22		2.535 ± 0.003
G_5	3.89 ± 0.22		2.433 ± 0.003
$G_5 - 1\text{LO}$	3.92 ± 0.06	3.82 ± 0.15	2.3959 ± 0.0007
$G_5 - 2\text{LO}$	3.54 ± 0.03	3.75 ± 0.15	2.359 ± 0.0003
Red luminescence	7.28 ± 0.45		2.096 ± 0.005

TABLE II. Separation between various excitons and their LO replicas at 6 K and 1 bar.

	$E_{\text{ex}} - E_{\text{ex-1LO}}$ (meV)	$E_{\text{ex-1LO}} - E_{\text{ex-2LO}}$ (meV)
Heavily doped CdS		
G_5 exciton	37.6±0.3	36.0±0.3
Undoped CdS ^a		
A exciton	36.2±0.3	38.3±0.3
I_2 exciton	36.6±0.3	39.1±0.3
Calculated ^b	36.5±0.4	38.3±0.2

^aReference 4.^bAccording to the semiclassical theory (Ref. 13).

The energies of the excitons observed in the 6 K spectrum are plotted as a function of pressure in Fig. 6. The solid and dashed lines are obtained from a linear least-squares fit to the data. The pressure coefficients of the I_2 and I_1 excitons (Table I) are smaller than those of the free and donor-bound excitons in undoped CdS (Ref. 4) at 6 K. The shift of the G_5 exciton is even smaller. There is no indication of the pressure ionization of donors (I_2 excitons) in the wurtzite phase as we conjectured from our room-temperature measurement. Pressure ionization of donors, if present, will manifest as a larger slope for the energy of the I_2 exciton as a function of pressure, i.e., the I_2 -exciton line will cross the band-edge line at the ionization pressure (P_i) and the I_2 -exciton peak will not be seen beyond P_i . There is no evidence for this from our measurement. In fact, the pressure coefficients in the doped sample change in a manner opposite to that expected if pressure ionization were to occur. The red luminescence shifts at a rate of 7.28 ± 0.45 meV/kbar which is about 1.6 times the band-edge shift. The different shift is not surprising, since the red luminescence is associated with Cd interstitials.¹² Even though the energy levels of shallow impurities follow the band edge closely, the Cd interstitial level which is deep need not follow the band edge. The difference between the shift of the red luminescence level and the band edge can be attributed to the shift of the Cd interstitial level with respect to the valence band.

The energy difference between the successive LO replicas of the G_5 exciton at 1 bar is given in Table II. For comparison, the values obtained for the A and I_2 excitons in undoped CdS (Ref. 4) are also given. In the case of undoped CdS, the separation between successive LO replicas not being equal to the LO phonon energy was explained on the basis of the kinetic energy of the excitons. However, for the G_5 exciton the values we obtain are in better agreement with the energy of the LO phonon (37.8 meV). This implies that the bound-to-bound exciton has a lower kinetic energy or none at all unlike the free or bound excitons.

IV. SUMMARY AND CONCLUSIONS

From a high-pressure study of the PL spectra at 6 K, we find that in heavily doped CdS, the bound excitons shift at a lower rate than the band edge with pressure. The phonon-assisted bands of the bound-to-bound exciton (G_5) are spaced at LO phonon-energy intervals unlike the free and bound excitons in undoped CdS. This indicates that G_5 excitons are immobile while A and I_2 excitons have a Maxwellian distribution of velocities. The red luminescence shifts at a much higher rate with pressure than the band edge, indicating that the Cd-interstitial level responsible for this luminescence band does not follow the band edge. The large lattice reordering associated with the wurtzite-to-rocksalt-phase transition produces a large number of defects that quench the luminescence entirely beyond 27 kbar. Our room-temperature measurements show that the shift of the green luminescence peak depends on the impurity concentration. There is no evidence for the pressure ionization of I_2 excitons in the wurtzite phase in heavily doped CdS at 6 K and the absence of luminescence in the indirect rocksalt phase makes it impossible to determine whether pressure ionization occurs in that phase.²

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