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Low-temperature studies of the photoluminescence in CdS under hydrostatic pressure

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We report the first study of the effect of pressure on the photoluminescence and Raman spectra of CdS at 6 K using a diamond-anvil cell. The shifts of the free and bound excitons and their phonon replicas are followed up to ~25 kbar when CdS undergoes a phase transition from a direct-gap wurtzite to an indirect-gap rocksalt structure. In the latter structure, the luminescence is not present. The Raman spectra of the LO phonon and its overtones are also studied under pressure. Accurate low-temperature values of the pressure coefficients of the excitons, their LO replicas, and the Raman LO phonon are deduced.

INTRODUCTION

The observation of large diamagnetism and low resistivity in pressure-quenched chlorine-doped cadmium sulfide (CdS) has indicated the possibility of superconductivity above 77 K in these samples.[1] A theoretical model[2] suggests that this anomalous diamagnetism could be due to an excitonic mechanism involving a large number of donor impurities in the high-pressure rocksalt phase of CdS. Little is known about the behavior of impurities under pressure. It is, therefore, of interest to study them both from a fundamental point of view, as well as in the light of excitonic superconductivity.

We report the first study of the free and impurity-bound excitons and their LO replicas in CdS at 6 to 8 K under hydrostatic pressure. It is of interest to do the experiment at low temperatures so that the signature of each impurity via its bound exciton can be tracked separately, rather than the broadened thermal average that we have previously studied[3] at 300 K. While the optical properties of many semiconductors have been studied under pressure,[4] relatively few studies have been undertaken at low temperature because of the difficulties of working with a diamond-anvil pressure cell at liquid-helium temperatures.[5] This work thus represents one of the few contributions in the field.

We observe the energies of the excitons and their LO replicas to increase linearly with pressure, up to about 25 kbar. While the excitons follow the band edge, the LO replica energies change at a rate that combines the shifts of both the band edge and the LO phonon energies. Around 25-kbar CdS undergoes a phase transition from a direct-gap wurtzite to the indirect-gap rocksalt structure. The luminescence is effectively quenched around the phase transition, as observed by a sharp decrease in the intensity, and the exciton lines are broadened considerably. We could not observe any luminescence that could be attributed to the rocksalt phase, presumably a result of the nonradiative paths provided by the large number of defects formed.

The Raman LO phonon and its overtones are also observed, and they increase in frequency at about the same rate as at room temperature. We correlate this shift to that of the LO replicas observed in the luminescence spectra and obtain reasonable agreement.

EXPERIMENTAL DETAILS

A Merrill-Bassett–type[6] diamond-anvil cell was used. It was attached to a continuous flow helium cryostat, and temperatures of 6 to 8 K were achieved routinely. Solid argon loaded using the In dam technique[7] was used as the pressure transmitting medium. Fluorescence from the ruby R lines was used to calibrate the pressure using the accepted value[8] of $d\nu_{R_1}/dP = -0.762$ cm^{-1}/kbar. The pressure was found to be hydrostatic to ±1 kbar at the highest pressure, as observed via the linewidth of the ruby lines.

The 4579-Å line from an Ar$^+$ laser was used to excite the photoluminescence and Raman spectra. The intense bound exciton lines were excited with about 0.1 mW of power, while the weaker LO replicas and the Raman LO phonons were excited with 10 mW. A Spex 0.85 m double monochromator with holographic gratings and photon counting electronics was used to record the spectrum. A resolution of 0.4 cm^{-1} was used in the free and bound exciton region and 1.3 cm^{-1} in the other regions.

RESULTS AND DISCUSSION

The sample used was a nominally pure (not intentionally doped) platelet of CdS containing residual Cl impurities. In the photoluminescence spectrum, we observe the free exciton associated with the top valence band (A), excitons bound to neutral (I_2 and I_5), and ionized donors (I_3). LO replicas up to A-4LO and I_2-3LO are observed (Fig. 1, top panel). The peaks were identified from their energies at atmospheric pressure.[9,10] The 1-bar spectrum in Fig. 1 was taken outside the pressure cell with the incident light polarized mainly along the $\hat{c}$ axis. Polarization information is lost inside the pressure cell since there are two or three crystals randomly oriented with respect to each other. Therefore, the relative intensities of (say) the A-1LO and I_2-1LO inside and outside the pressure cell are different.

According to semiclassical theory, the peak energies and shapes of the LO replicas depend on the kinetic energies of the excitons.[11,12] The asymmetric shape represents a Maxwellian distribution of kinetic energies, and this can be observed clearly in the 1-bar spectrum of Fig. 1. The peak

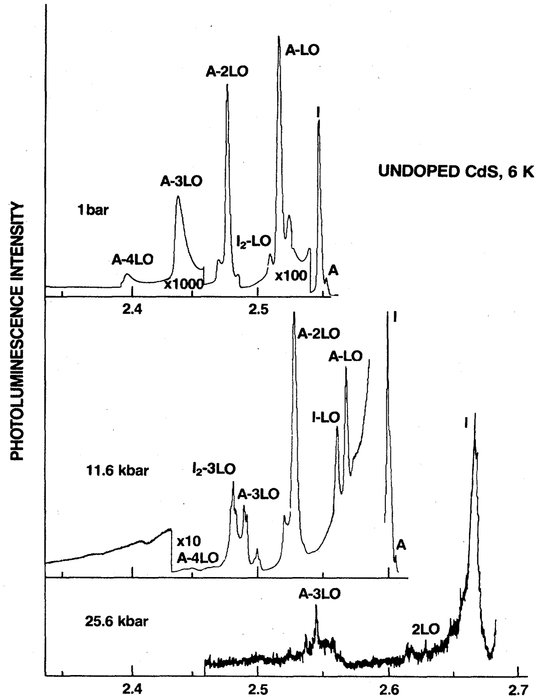

FIG. 1. The luminescence spectrum of nominally pure (undoped) CdS at 6 K for three pressures. The intensity scale for the 25.6-kbar spectrum is a factor of 40000 times less than the 11.6-kbar spectrum. The 1-bar spectrum was taken outside the pressure cell.

energy of the mth order phonon assisted band is given by

$$E_{\text{ex-}m\text{LO}} = E_{\text{ex}} - mE_{\text{LO}} + ukT \ , \qquad (1)$$

where E_{ex} is the energy of the A (or I_2) exciton, E_{LO} the energy of the 1-LO phonon, and $u=1$ when $m=0$, $u=\frac{3}{2}$ when $m=1$, and $u=\frac{1}{2}$ when $m=2$. Since the zero-phonon peak, which is seen in the spectrum, is shifted to lower energies from the free exciton energy by about kT, the energy separation between the exciton peak and its 1-LO replica should be $E_{\text{LO}}-2.5kT$, while that between the 1- and 2-LO replicas should be $E_{\text{LO}}+kT$. At 8 (± 2) K, these separations should be 36.1 (± 0.4) and 38.5 (± 0.2) meV, respectively, in good agreement with our experimental values of 36.2 ± 0.3 and 38.8 ± 0.3 meV (at 1 bar). These separations

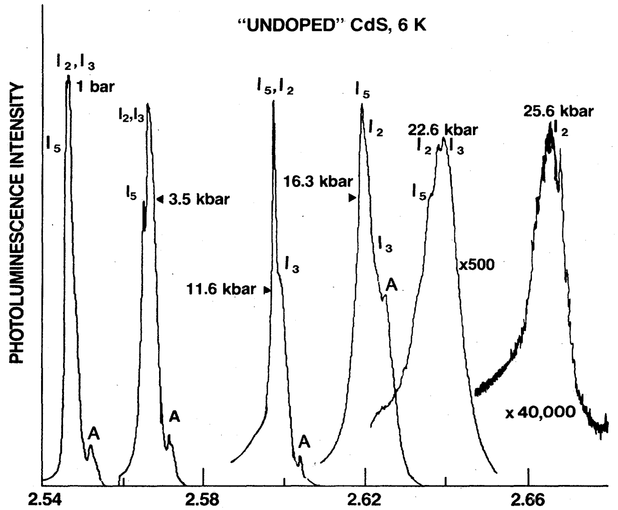

FIG. 2. The luminescence spectrum of CdS at 6 K in the free and bound exciton region for several pressures. Note the quenching of the luminescence in the region of the phase transition (~25 kbar).

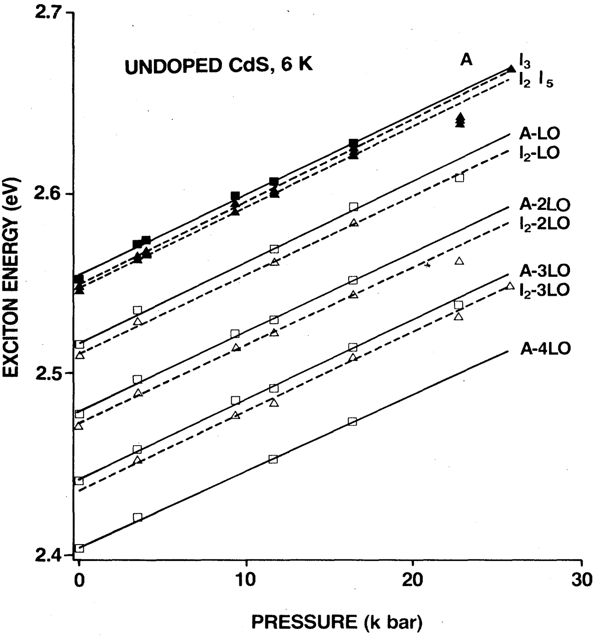

FIG. 3. The energies of the free and bound excitons [solid square (A) and triangles (I_3, I_2, and I_5 in decreasing order of energy)] and their LO replicas (open squares and triangles) as a function of pressure. The lines correspond to straight line fits by the method of least squares.

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

Description	dE/dP (meV/kbar)	$\left(\frac{dE}{dP}\right)_{A\text{-1LO}} - (m-1)\left(\frac{dE}{dP}\right)_{\text{1LO}}$ (meV/kbar)
A	4.36 ± 0.13	. . .
A-1LO	4.42 ± 0.15	. . .
A-2LO	4.33 ± 0.14	4.35 ± 0.15
A-3LO	4.33 ± 0.13	4.28 ± 0.15
A-4LO	4.15 ± 0.12	4.21 ± 0.15
	dE/dP (meV/kbar)	$(dE/dP)_{I_2} - m\left(\frac{dE}{dP}\right)_{\text{1LO}}$
I_3	4.51 ± 0.07	. . .
I_2	4.40 ± 0.15	. . .
I_5	4.42 ± 0.11	. . .
I_2-1LO	4.30 ± 0.14	4.33 ± 0.15
I_2-2LO	4.25 ± 0.12	4.26 ± 0.15
I_2-3LO	4.31 ± 0.13	4.19 ± 0.15

TABLE II. Analysis of LO phonon data in CdS.

	$d\nu/dP$ (cm^{-1}/kbar)				
	1-LO	2-LO	3-LO	Pressure range	Temperature
Present work	0.56 ± 0.04	0.95 ± 0.07	1.55	< 26 kbar	6 K
Previous work	0.56 ± 0.03[a]	1.12 ± 0.04[a]	· · ·	< 25 kbar	300 K
	0.42 ± 0.05[a]	0.80 ± 0.06[a]	· · ·	> 27 kbar	
	0.45[b]	0.86[b]		< 10 kbar	300 K
	0.41[c]			< 4 kbar uniaxial stress	4.2 K

[a] Reference 3. [b] Reference 15. [c] Reference 14.

do not change much with pressure.

A new feature we observe is that the LO replicas of the I_2 bound exciton also show similar behavior due to the kinetic energies of the excitons. The 1-LO is 36.6 ± 0.3 meV below the I_2 peak energy while the 2-LO replica is 39.1 ± 0.3 meV below that of the 1-LO replica energy, again in good agreement with the calculation.

As pressure is applied, the spectrum shifts to higher energies, roughly following the band gap (Fig. 1). Around the phase transition (22 to 26 kbar) the luminescence intensity drops until, in the exciton region, it is about 40 000 times weaker at 25.6 kbar than at 3.5 kbar (Fig. 2). The quenching of the luminescence occurs since the sample shrinks in volume by about 20% when it goes into the rocksalt phase, and a large number of defects are formed, providing nonradiative paths for deexcitation. In addition, the gap in the rocksalt phase is indirect, which typically has a lower luminescence.

The energies of the excitons and their LO replicas are plotted as a function of pressure in Fig. 3. The lines correspond to straight line fits. The pressure coefficients obtained are listed in Table I. The coefficients of the A, I_2, and I_5 excitons are all close to that of the band edge,[13] and our 300-K measurements.[3] The ionized donor I_3 seems to shift a little faster, which also contributes to the broadening of the lines at higher pressure.

The energies of the LO replicas also increase linearly with pressure (Table I), with coefficients that reflect both the increase in the band gap, as well as the increase in the LO phonon frequency. Following Eq. (1), the pressure coefficient of the m-LO replica of the A (or I_2) exciton (the slope in Fig. 3) should be

$$\left(\frac{dE}{dP}\right)_{\text{ex-}m\text{LO}} = \left(\frac{dE}{dP}\right)_{\text{ex}} - m\left(\frac{dE}{dP}\right)_{1\text{LO}} , \tag{2}$$

since the term ukT is a constant in Eq. (1). Here $(dE/dP)_{\text{ex}}$ is the pressure coefficient of the A (or I_2) exciton, and $(dE/dP)_{1\text{LO}}$ is that of the 1-LO phonon. From the Raman spectrum of the LO phonon and its overtones, we obtain $(dE/dP)_{1\text{LO}} = 0.068$ meV/kbar (Table II). The coefficients for the 2- and 3-LO Raman phonons are twice and thrice as much, respectively (this has been previously established by both uniaxial[14] and hydrostatic[3] pressure measurements at 300 K). Equation (2) can, therefore, be used to calculate the slopes of the LO replicas knowing the slope of the exciton A (or I_2) and that of the Raman LO phonon. These calculated values are listed in the third column of Table I, and they compare well with the slopes measured using the luminescence data (second column of Table I). For the replicas of the A exciton, comparing the slopes of the A-1LO with the A-mLO gives better agreement than when compared with the A exciton. Within the uncertainty of the fits, it is not possible to make a definite statement on this point.

The Raman spectrum of the 1-, 2-, and 3-LO phonons was also studied at 6 K. The pressure coefficients obtained are in good agreement with both our 300-K work[3] and previous measurements[14,15] (Table II).

CONCLUSION

We have studied the photoluminescence and Raman spectrum of CdS at 6 K under hydrostatic pressure. The pressure coefficients of the free and bound excitons agree well with that of the room-temperature luminescence in the same sample,[3] as well as that of the absorption edge.[13] We have studied for the first time the LO replicas of the free and bound excitons under pressure. Their pressure coefficients are found to be in good agreement with those calculated from differences between the coefficients of the appropriate exciton and the Raman LO phonons.

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