Spectroscopic investigations of CdS at high pressure

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The photoluminescence spectrum and absorption spectrum as well as resonant Raman scattering tuned by pressure in heavily doped CdS have been studied. The pressure coefficients of shallow levels (I_2 and I_1) and deep levels (G_5 and R) are measured. A new optical-absorption method under pressure was developed and the shift of band gap with pressure of CdS in the direct-band-gap wurtzite phase and indirect-band-gap rock-salt phase was measured. From the experimental results of resonant Raman scattering tuned by pressure we conclude that at about 27 kbar CdS undergoes a complete phase transition from the wurtzite phase to the rock-salt phase. After the phase transition there is no two-phase mixture, and the material still has semiconductor characteristics.

I. INTRODUCTION

Useful information about the electronic band structure, localized states, and vibrational properties as well as structural phase transitions of semiconductors can be obtained by measuring the dependence of the electronic and phonon spectrum under high hydrostatic pressure. Application of uniform pressure preserves crystal symmetries while altering all semiconducting properties through changes in the interatomic distance.

Cadmium sulfide (CdS) is an important material for investigating electronic and phonon properties by using high pressure. Grusche[1] first investigated the effect of pressure on the band gap of CdS and found that the direct band gap increases at the rate of 4.4 meV/kbar with pressure. Later, Edwards and Drickamer[2] measured the shift of the optical-absorption edge of CdS under pressure and found an abrupt red shift of the absorption edge at about 27 kbar pressure, which they attributed to a first-order phase transition from a direct-band-gap wurtzite to an indirect-band-gap rock-salt structure. Subsequently, the observation of large diamagnetism and low resistivity in pressure-quenched chlorine-doped CdS has indicated the possibility of superconductivity above 77 K.[3] Recently, Batlogg et al.[4] carried out resistivity measurements of undoped and Cu-doped CdS and concluded that the lower electrical resistivity in the high-pressure phase of CdS was due to imperfections and defects generated during the first-order phase transition from wurtzite to the rock-salt structure. In 1963 Owen et al.[5] finished a high-pressure x-ray diffraction study and found that cadmium sulfide underwent a phase transition from wurtzite to rock-salt structure as the pressure was increased beyond 27 kbar. Recently, Venkateswaran et al.[6] observed that the E_1–LO-phonon spectra still persists beyond the phase transition up to 42 kbar, which provides evidence for a mixed wurtzite–rock-salt structure at least up to 42 kbar.

We think that the unusual properties of the pressure-quenched CdS mentioned above can be explained by the combined effects of the band structure and behavior of defects as CdS undergoes a phase transition from a direct-band-gap wurtzite to an indirect-band-gap rock-salt structure under high pressure. In order to understand the change of band structure and defect states in CdS under pressure, we have carried out an investigation of optical properties including photoluminescence, Raman scattering, and the optical-absorption spectrum at high pressures.

We present the experimental details in Sec. II with emphasis on a new optical-absorption method used under pressure. The essential features of the photoluminescence spectra, such as I_2 (excitons bound to neutral donors), I_1 (the exciton bound to the neutral acceptor), G_5 (the exciton bound to the deep acceptor), and R (designating the deep-level states), are described in Sec. III A. The shift of the band gap with pressure before and after the phase transition is measured by a newly developed high-pressure optical-absorption method at 77 K and this is described in Sec. III B. In Sec. III C, the pressure-tuned resonance Raman scattering technique is employed to investigate the details of the CdS phase transition.

II. EXPERIMENTAL TECHNIQUES

The cadmium sulfide used in our experiments was prepared by a vapor-phase transport method. The sample was not intentionally doped during the growing process, although there was still a considerable amount of impurities such as carbon and chlorine in the sample. In addition, some of the heavily doped cadmium sulfide samples were obtained from the U.S. Army Missile Command, Huntsville, AL.

Photoluminescence, Raman scattering, and optical-absorption measurements under high pressure were performed in a gasket diamond-anvil cell at 77 K using a 4:1 methanol-ethanol mixture as the pressure-transmitting medium. The above mixture can retain fluidity up to 145 kbar. Pressures of up to 100 kbar were measured from the shift in ruby emission using 14 422 cm^{-1} as the atmospheric pressure reference and -0.76 cm^{-1}/kbar as

the pressure derivative for the R_1-line emission (ruby line) at 77 K.

For photoluminescence and Raman scattering a backscattering geometry was employed. The sample was mechanically polished down to about 30 μm in thickness and the c axis was in the plane of the crystal. Resulting platelets were cleaved into squares with dimensions of about 50 μm on a side and loaded into the diamond-anvil cell. The 4579-Å line from an argon-ion laser was chosen as the exciting radiation for the photoluminescence measurements. The exciting light radiation was focused through a microscope optical system to a spot about 15 μm in diameter on the sample. The laser power focused on the sample was about 50 mW for Raman scattering and 20 meV for photoluminescence measurements.

Emission and light-scattering photon-counting data were collected using a back scattering geometry, analyzed with a 0.85-m double-grating spectrometer and a RCA 31034A photomultiplier, and stored in a computer. The spectral resolution was at least 0.2 meV.

For optical-absorption measurements we developed a new gasket structure which can exactly measure optical absorption under high pressure, and this is shown in Fig. 1. There are two layers in the composite gasket structure. The thicknesses of these stainless-steel layers are 0.25 and 0.02 mm. Holes of 0.4 and 0.15 mm are drilled in the thick and thin layers, respectively. Then the two gaskets are polished using fine sandpaper and Al_2O_3 powder. Finally these two gasket components are joined with holes remaining concentric using an Epoxy adhesive. The larger hole in the thicker layer acts as a high-pressure chamber while the smaller hole in the thin layer acts as an optical aperture stop. We have not observed a marked change in the size of the small hole under increased pressure because the force acting on the side of the large hole is much greater than that for the small one.

Before the small hole is covered by the sample the light of a tungsten lamp is focused on a 0.4-mm-diameter spot

FIG. 1. The gasket structure for optical-absorption measurements in a diamond-anvil cell.

centered on the small hole and the spot position is fixed. The intensity of the transmitted light with no sample is then measured, giving the initial light intensity I_0. Then we place a thin sample (typically 10 μm) along with small pieces of ruby chips in the larger hole covering the smaller one. The light transmitted through the sample and fluid mixture is measured using the above-mentioned spectral system. Up to 100 kbar the size of the small hole does not change and the 10-μm-thick sample is not damaged. The pressures therefore exerted on the sample is hydrostatic, and no uniaxial stresses are applied to the sample.

III. RESULTS AND DISCUSSION

A. Photoluminescence spectrum at 77 K

Measuring the photoluminescence spectrum under high pressure is an important method for investigating impurity states in semiconductors. According to effective-mass theory, a shallow impurity state has a long-range Coulomb potential. Its wave function consists mainly of Bloch states of the band edge near the energy of the impurity state. If we neglect the change of the effective mass of the band edge under pressure, the shift of the photoluminescence spectrum due to a shallow impurity state should be the same as the band edge. If the effective mass increases with pressure or the curvature of the band edge decreases, then the binding energy of a shallow impurity state will increase with pressure. As a result the shift of the photoluminescence spectrum coming from a shallow state becomes less than the band-edge shift. Likewise, if the binding energy of the shallow state decreases with pressure the shift of the spectrum is greater than the band edge. Generally speaking, the change of the effective mass with pressure is small especially for the conduction-band edge.[7,8] The case for the deep-level states is quite different. Because deep levels have a localized potential, relatively small wave functions, and large lattice relaxation, the binding energy of a deep level can be simply written as

$$E = \sum_{(n,k)} A_{nk} A_{nk}^* E_{nk}$$

$$+ \sum_{(n,k),(n,'k')} A_{nk} A_{n'k'}^* \langle \phi_{nk} | V | \phi_{n'k'} \rangle , \qquad (1)$$

where ϕ_{nk} and E_{nk} are the wave function and energy for a perfect crystal, respectively. V is the effective impurity potential.

The first term on the right-hand side represents the effect of the band structure on the binding energy of the deep level. It is well known that the band structure of a semiconductor changes drastically with pressure.[7,8] Therefore the changes of band structure and density of states under pressure will play an important part in determining the binding energy of a deep level. The second term in Eq. (1) represents the effect of coupling between the band states on the binding energy of the deep level. Because the potential of a deep level is very localized, the coupling matrix element will contribute to the binding energy of the level. However, for shallow impurity states
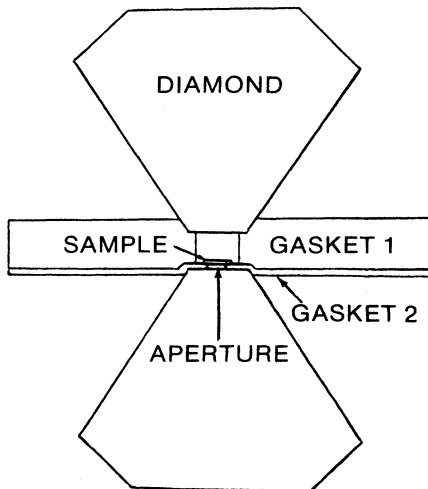
the contribution of the second term is very small. Therefore the luminescence spectra due to a deep level will not move with the band edge, but depends greatly on the competition between the two terms mentioned above. So we can easily distinguish between shallow and deep impurity levels according to their pressure coefficients obtained from the luminescence spectra.

Figure 2 shows the shift of the luminescence spectrum of CdS with pressure at 77 K. According to Thomas and Hopfield[9] and Reynolds et al.,[10] we can identify the luminescence peak I_2 as coming from the transition of a bound exciton of a neutral donor and I_1 as coming from the transition of an exciton bound to a neutral acceptor. The peak G_5 is attributed to the exciton bound to the deep center,[10] the G_5-LO peak is a phonon replica of process G_5, and the wide R peak is produced by the transition of free electrons in the conduction band to cadmium vacancies and interstitial cadmium levels (see Fig. 2). Table I shows the energy of the luminescence peaks at atmospheric pressure and their pressure coefficients at 77 K.

Figure 3 shows a linear least-squares fit to the data as a function of pressure. All the luminescence peaks have increasing energy with increasing pressure below 30 kbar. The I_2 peak is due to the transition of excitons bound to neutral donors (a shallow state in CdS). Therefore the pressure coefficient (4.50 meV/kbar) of the I_2 peak represents the shift of the direct band gap of CdS below the phase transition. The pressure coefficient is in good agreement with the rate of 4.40 meV/kbar obtained by Venkateswaran, Chandrasekhar, and Chandrasekhar.[6] The energy difference between the G_5 and G_5-LO peaks is 36 meV. The value for the phonon energy obtained by Raman scattering (given in Sec. III B) is 37.7 meV at room temperature. The pressure coefficients of the G_5 peak and its phonon replica G_5-LO are the same (4.8±0.12 meV/kbar) within experimental error and are

TABLE I. Results of photoluminescence measurements in heavily doped CdS at 77 K.

Description	dE/dp (meV/kbar)	Binding energy (eV)	E_0 (eV)
I_2	4.50±0.02	0.0066[a]	2.536±0.001
I_1	4.50±0.05	0.0177[a]	2.528±0.003
G_5	4.80±0.12	0.140	2.401±0.003
G_5-LO	4.83±0.09		2.365±0.002
R	6.1 ±0.20	0.470	2.076±0.007

[a]D.G. Thomas and J. J. Hopfield (Ref. 9).

slightly higher than the I_2-peak shift with pressure. This larger pressure coefficient and its strong electron-phonon coupling ($S = 1.0$ at 1 atm) is evidence that the G_2 peak is due to a transition involving a deep level 0.14 eV below the band edge. Whether this deep level is associated with an acceptor-type or donor-type deep level is not clear from the available literature.[10] According to Hjalmarson's theory of deep levels,[11] if this deep level is a deep donor type close to the conduction band, then its wave function should be composed mostly of Bloch states in the conductions bands. This is due to the small difference in energy between band states and the deep level in the denominator of the Green's function. Based on the above analysis, it is impossible that the pressure coefficient of a deep level close to the conduction-band edge is larger than that of a standard shallow donor in a direct-band-gap semiconductor. Therefore the G_5 peak must be produced by a transition of an exciton bound to a acceptor-type deep level (140 meV from the top of the valence band Γ_q). The 0.3-meV/kbar difference in the pressure coefficients means that the deep level moves closer to the valence band at the rate 0.3 meV/kbar.

It can be seen from Fig. 2 that the strength of the electron-phonon coupling for the G_5 deep level decreases
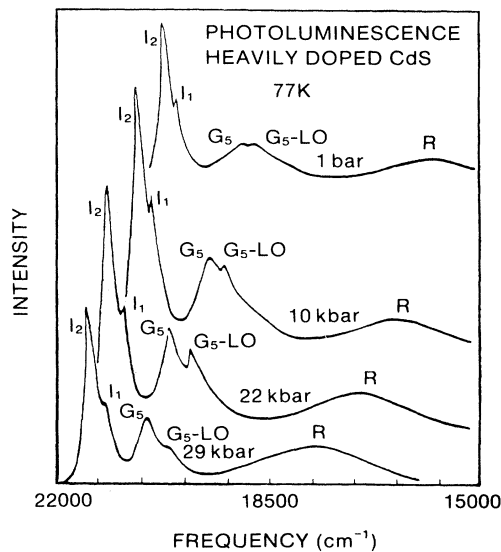

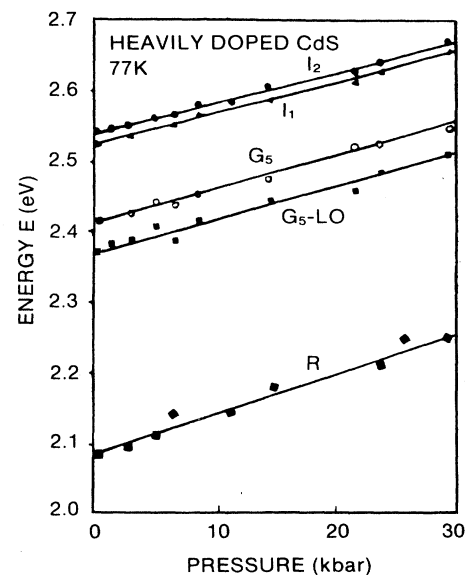FIG. 2. Photoluminescence spectra of doped CdS at 77 K for several pressures.

FIG. 3. Energies of shallow levels I_2 and I_1 and deep levels G_5 and R in doped CdS as a function of pressure.

with increasing pressure. According to the Huang-Rhys[12] theory of electron-phonon coupling

$$I_n = I_0 S^n / n! , \qquad (2)$$

where I_n is the intensity of the nth phonon-replica luminescence, I_0 is the intensity of the zeroth phonon line and S_{LO} is the Huang-Rhys electron-phonon factor. Figure 4 shows the change with pressure of the first-order coupling strength S_{LO} of the G_5 deep level. The coupling strength steadily decreases from a value of 1 at atmospheric pressure to 0.62 at 29 kbar. This is not surprising since before the phase transition CdS has a wurtzite structure which has a crystal symmetry lower than that of the zinc-blende structure due to the long bond along the c axis. A splitting of the valence bands A and B (see Fig. 5) results from the large polarization crystal field in CdS. Initially, the pressure decreases the length of the weak bond along the c axis. This leads to a decrease in the crystal field and, consequently, to a decrease of the electron-phonon coupling strength. On the other hand, an increase in pressure will reduce the lattice constants and reduce the displacement δ of the lattice atoms around the defect. The coupling strength S is proportional to δ^2.[12] Therefore the electron-phonon coupling strength decreases with increasing pressure.

The R peak has a wide energy range due to the excitation of electrons in the conduction band to Cd vacancies and interstitial levels. The presure coefficient of the R peak is 6.1 ± 0.20 meV/kbar, which is larger than that for the other peaks. As mentioned above, this wide peak is an acceptor-type deep level depending on the valence band. The relative intensity of the peak increases with pressure and, concurrently, the half-width at half maximum of the peaks I_2 and I_1 (excitons bound to a neutral donor and acceptor, respectively) increase while their intensity decreases. These results show that very many CdS vacancies and interstitials, as well as dislocations, will be brought about by the increased pressure. Under increasing pressure the sample dimensions show a gradual reduction in size up to the phase transition and with $\delta v / v \approx 20\%$ as measured by the experiment.[13] Beyond
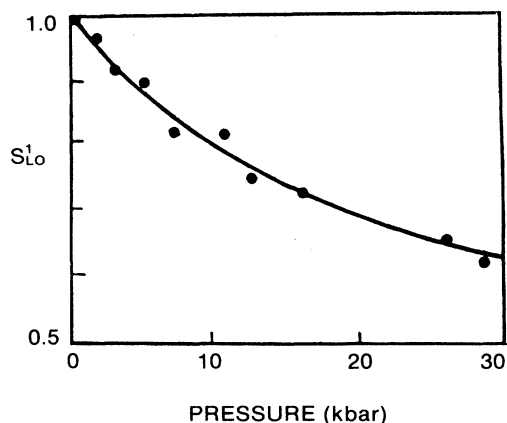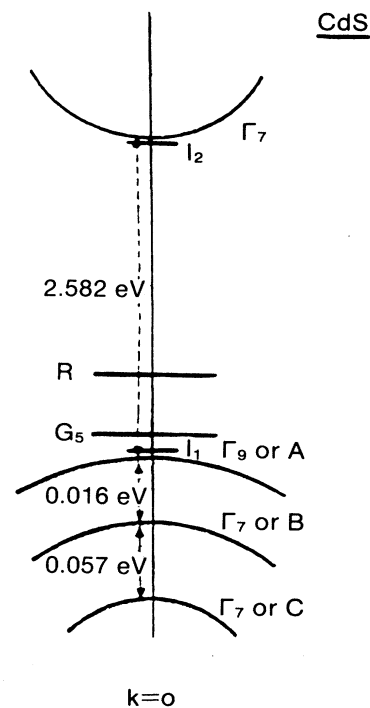

FIG. 5. Energy-level diagram in heavily doped CdS; the binding energies are given in Table I.

the phase transition all luminescence disappears due to the nonradiative-recombination centers and the indirect band gap of CdS in the rock-salt phase. After releasing the pressure the sample returns to a wurtzite structure from the rock-salt structure (Sec. III C), but still no luminescence is observed and the absorption edge does not recover to its original value (Sec. III B). The nonradiative recombination centers induced by pressure still remain in the sample. This fact implies that if there exists a strong deformation stress around a defect that will destroy the lattice stability around the defect due to the Jahn-Teller effect, then the defect will not recover to its equilibrium position.

B. Optical absorption at 77 K

In our photoluminescence experiment we observe that the phase-transition pressure varies from sample to sample depending on the concentration of impurities in the sample. In general, when the pressure reaches 30 kbar at 77 K, it is observed that the CdS sample suddenly changes in color from yellow to dark orange. After this change, regardless of the exciting laser power, we do not observe any luminescence.

In order to investigate the change of band structure from wurtzite to rock-salt phase, we developed a new method which measures the optical absorption on the diamond-anvil cell as mentioned in Sec. II. Figure 6 shows the shift of the absorption edge with pressure, in the low-pressure wurtzite phase, and the high-pressure NaCl phase. The changes of optical-absorption coefficient with photon energy with the sample in the wurtzite phase before the pressure-induced transition to the

FIG. 4. Electron-phonon coupling factor S of deep level G_5 in heavily doped CdS as a function of pressure.
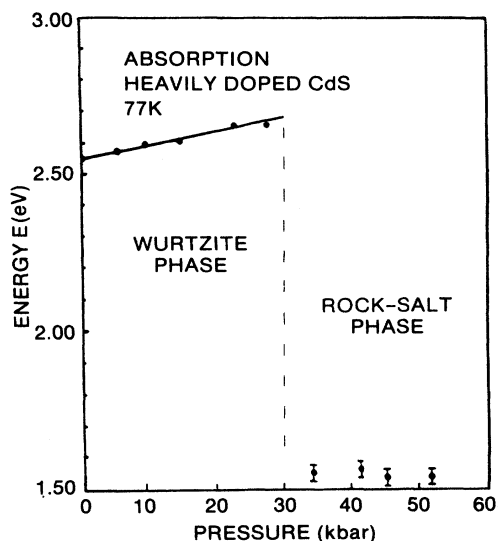
FIG. 6. Shift of absorption edge with pressure in wurtzite-phase and rock-salt-phase CdS.

rock-salt phase, the rock-salt phase at 53 kbar, and the case for the return to atmospheric pressure once the sample has been through the phase transition are shown in Fig. 7. Before the phase transition the absorption edge in direct-band-gap wurtzite is very sharp due to the excitons bound to neutral donors. For a given pressure both the photoluminescence and absorption spectra are measured, and it is found that the absorption edge and photoluminescence I_2 peak energies fit exactly. We measured the pressure coefficient of the band gap in the wurtzite phase of CdS as 4.5 ± 0.05 meV/kbar. The same result was obtained for the photoluminescence measurements.

Unfortunately, we were unable to observe the absorption peak due to the exciton bound to the deep acceptor center G_5 in the direct-band-gap wurtzite phase of CdS. This reflects the fact that the G_5 peak in the photo-
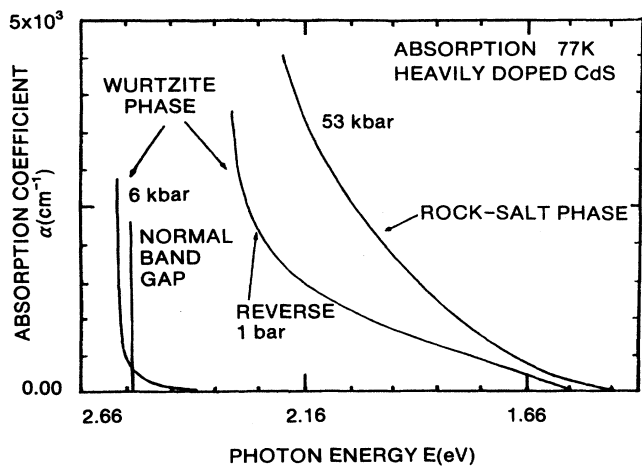

FIG. 7. The absorption coefficients of heavily doped CdS in the wurtzite phase; the rock-salt phase and the absorption coefficients upon reversing to atmospheric pressure after the phase transition, as a function of photon energy.

luminescence spectra is due to the deep acceptor level, which has only a small component in its wave function of the Γ valley states in the conduction band, and it has a small photoionization cross section.

When the pressure is raised beyond 30 kbar at 77 K, the 1-μm CdS sample suddenly changes color from yellow to dark orange and has numerous finely textured dark streaks in it. As shown in Fig. 7, at 53 kbar the slope of the absorption edge for the rock-salt phase is strikingly different from that of the direct-band-gap wurtzite phase and is clearly attributed to indirect transition and band-tail processes. Liu and Rabii[14] have calculated the energy-band structure of CdS in the rock-salt phase for a lattice constant of 5.32 Å and indicated that the CdS rock-salt phase is an indirect-band-gap semiconductor with a band gap of 1.5 eV. In heavily doped indirect-band-gap semiconductors it is possible to conserve momentum by impurity scattering without phonon assistance. The absorption coefficient can be written as

$$\alpha(h\nu) = A (h\nu - E_g)^2 , \tag{3}$$

so that the energy-gap value can be obtained from a straight-line plot of $\alpha^{1/2}$ against $h\nu - E_g$ by extrapolating to $\alpha = 0$. In this way we measure the band gap of the CdS rock-salt phase to be 1.55 ± 0.02 eV with no significant change with pressure from 30 to 53 kbar as shown in Fig. 6. Batlogg et al.[4] obtained a 1.7-eV band-gap value of CdS at pressures from 30 to 60 kbar at 300 K and, assuming no significant change in the pressure coefficient, attributed the indirect-band-gap transition in rock-salt CdS to a Σ_v-X_c transition (from the Σ valley of the valence band to the X valley of the conduction band). Our measurements of the rock-salt phase are in good agreement with the indirect-band-gap value obtained in the above calculation. However, it is very difficult to exactly determine the indirect band gap of CdS because, during the phase transition from tetrahedral to octahedral coordination, the large number of defects and dislocations induced by pressure will form band-tail states. It is possible that the constant pressure coefficient of CdS in the rock-salt phase at 53 kbar is due to transition between band tails.

After the phase transition, we released the pressure to atmospheric pressure and measured the absorption edge as shown in Fig. 7. The absorption coefficient changes slowly with photon energy. This reflects the fact that the huge defects induced by pressure remain in the sample and lead to band-tail absorption. When the photon energy is close to the band edge, the slope of the absorption edge becomes sharp. We extrapolate the straight-line part to $\alpha = 0$ to obtain a 2.31-eV band gap. The band gap does not revert to its original value of 2.542 eV at 77 K. According to the pressure-induced resonance Raman scattering investigation (given in Sec. III C), we believe that after releasing the pressure the sample completely reverts to the wurtzite phase. The 0.232-eV shift in the band gap is not due to the hysteresis of the first-order phase transition, but comes from the shrinkage of the band gap due to the defects induced by pressure in the sample.

C. Resonance Raman scattering induced by pressure

Brafman and Mitra[15] and Briggs and Ramdas[16] have studied the pressure dependence of LO-phonon spectra in CdS and found that, up to the phase transition, LO-phonon Raman scattering can be observed, and beyond the phase transition all Raman spectra disappear. According to a group-theoretical analysis, first-order Raman scattering is forbidden in the rock-salt phase of CdS, which has an inversion-symmetry center. This explains the disappearance of the first-order Raman scattering after the phase transition, but recently Venkateswaran et al.[6] have observed that the intensity of the LO-phonon Raman scattering spectra changes very little soon after the phase transition, and steadily decreases to $\frac{1}{3}$ of that value at 42 kbar both in the heavily doped and pure samples. This provides evidence for a mixed wurtzite–rock-salt phase at least up to 42 kbar.

In order to determine if there remains a wurtzite phase after the photoluminescence disappears, we designed a pressure-induced resonant Raman scattering experiment. The Raman cross section for one-phonon Stokes scattering can be written as

$$\sigma(\omega_S) \propto |R^{\alpha\beta}\epsilon_i^\alpha\epsilon_S^\beta|^2 , \qquad (4a)$$

with

$$R^{\alpha\beta} = \sum_{i,j} \frac{P_{0j}^\alpha M_{ji} P_{i0}^\beta}{(E_j - \hbar\omega_i + \hbar\omega_0)(E_i - \hbar\omega_i)} , \qquad (4b)$$

where i and j denote excited electronic states of energy E_i and E_j, P_{0i} and P_{0j} are the momentum matrix element with the ground state 0, M_{ji} is the phonon scattering matrix element, ω_i is the frequency of incident light, ω_0 is the phonon frequency, and ϵ_α and ϵ_β are the incident and scattered photon polarizations, respectively. Damen and Shah[17] have proved that for heavily doped CdS the enhancement in the LO-phonon scattering cross section for the I_2 bound exciton is larger than for the free exciton because the I_2 bound exciton has a smaller effective radius than that of the free exciton that leads to a strong exciton–LO-phonon interaction matrix element M_{ij}. At room temperature and atmospheric pressure the absorption edge due to I_2 is 2.452 eV and the pressure coefficient is 5 meV/kbar for heavily doped CdS. We chose the 4765-Å line of our Ar$^+$ laser as the incident light which has a photon energy of 2.602 eV. The band gap of CdS at 30 kbar should be 2.602 eV. Thus we can use resonance Raman scattering to study the phase transition induced by pressure.

Figure 8 shows the Raman scattering spectra shift with pressure before the phase transition. At atmospheric pressure the Raman shift of the LO phonon is 304 cm^{-1}. The phonon frequency, fitted as a linear function of pressure, shifts at the rate of 0.5 ± 0.03 cm^{-1}/kbar. It can be seen from Fig. 8 that the Raman scattering intensity of the LO phonon increases with increasing pressure. There is a strong background for the Raman scattering spectra of the LO phonon due to luminescences of the polaritons and high-energy electrons, especially at high pressure. This effect makes it difficult to correctly measure the
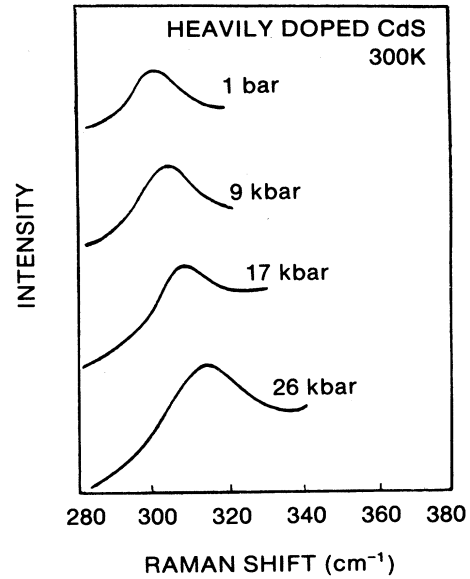

FIG. 8. Resonant Raman scattering spectra for several pressures before the phase transition.

change of Raman scattering intensity with pressure. When the pressure is close to 27 kbar, the band gap increases from 2.452 to 2.582 eV, thus getting close to the exciting photon energy of 2.602 eV. At this pressure the Raman intensity reaches a maximum due to a resonance effect. When the pressure is just beyond 27 kbar, both the photoluminescence and Raman spectra suddenly disappear and the color of the sample changes from yellow to dark orange. Upon increasing the pressure to exactly 30 kbar, if the phase transition has not completely changed the structure from wurtzite to rock salt—that is, if there is a mixed wurtzite–rock-salt phase in the sample—then we should observe a weak Raman peak of the 1-LO phonon or some new peak of the zinc-blende structure due completely to the resonance effect. But we have not observed any Raman spectra up to 50 kbar.

The interesting thing is that after we increase the pressure to 50 kbar, and then release it to atmospheric pressure, huge defects are induced by pressure in the sample which act as nonradiative centers. No luminescence can be observed, but the Raman spectra become very sharp as shown in Fig. 9. Then we increase the pressure to 26 kbar step by step and measure the frequency and intensity of the LO phonon with pressure as shown in Fig. 9. The shift of the LO-phonon frequency with pressure occurs at the rate of 0.5 ± 0.01 cm^{-1}/kbar and this is the same rate as that found before the phase transition. The Raman shift of the LO phonon as we return to atmospheric pressure is 302.0 cm^{-1}, which is 2.0 cm^{-1} smaller than before the phase transition probably arising from the high-energy tail of the luminescence (see Fig. 7). The change of the Raman scattering intensity of the LO phonon is similar to that obtained by Damen[17] using a continuously tuned dye laser. The free exciton becomes very weak due to scattering by defects induced by pressure, but the Raman scattering intensity of the LO phonon is almost the same as that measured befor the phase transi-
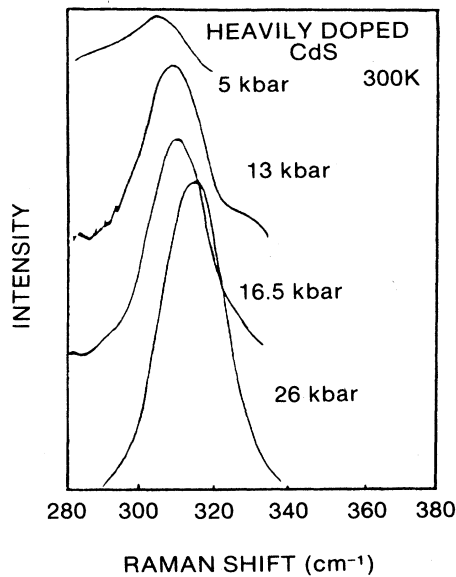
FIG. 9. Resonant Raman scattering spectra for several pressures in the wurtzite phase after phase transition.

FIG. 10. Energy of the LO phonon and its Raman scattering intensity as a function of pressure. ▲ and ■ represent Raman shift with pressure before the phase transition and its reverse to wurtzite phase after phase transition, respectively. ● represents the change of the Raman intensity with pressure upon returning to the wurtzite phase after the phase transition.

tion. This fact proves that the I_2 bound-exciton states are important intermediate states for Raman scattering in heavily doped CdS. Impurity states relax Raman selection rules because they break the translational and point-group symmetry. According to Fröhlich's electron-phonon coupling theory, the wave vectors of the LO phonon involved in Raman scattering are on the order of the reciprocal of the bound-exciton radius.[18] It can be seen from Figs. 8 and 9 that the width of the LO-phonon Raman scattering peak has no significant change with pressure and is about 22 cm^{-1}, the same value as that measured by Damen. This implies that the radius of the I_2 bound exciton is not visibly changed by the phase transition. Also, the pressure behavior of LO-phonon frequency and intensity is almost the same before and after reversing through the transition (see Fig. 10). If the sample after pressure release returned to the zinc-blende phase or a combination of zinc-blende and wurtzite phases, we should have observed new Raman modes (certainly TO and LO modes for the zinc-blende structure) with different pressure coefficients. But this was not the case in our Raman scattering measurements. In addition, the resonance Raman scattering data gave a maximum-intensity Raman peak at the same pressure before the onset of the phase transition and upon reversing the pressure after the phase transition. This implied that the band structure recovered completely to the original structure after pressure release. Consequently, the band-gap decrease of 232 meV as measured by absorption is due to the band tail brought about by defects induced by the phase transition. We can conclude therefore that after increasing the pressure through the phase transition, then upon releasing the pressure CdS returns to its original wurtzite band structure. With the aid of a high-power optical microscope, a mixture of yellow and orange microcrystallites can be observed. These must be due to the
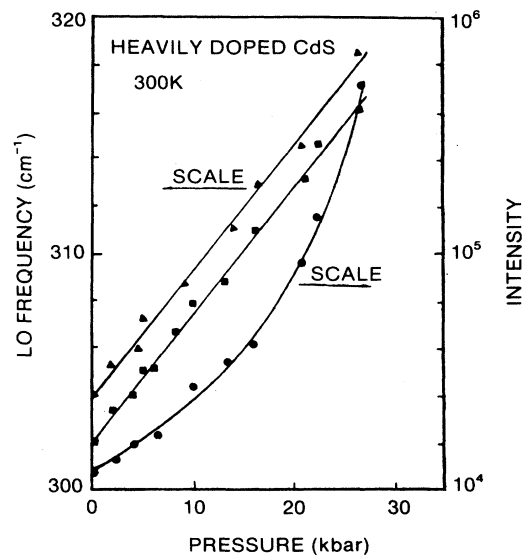
defects induced by pressure. Perhaps most of these defects are Cd atoms on the microcrystallite boundaries. These defects lead to a wide absorption tail and a 0.232-eV band-gap difference between the original band gap and the band gap after the pressure release. It is also suggested that the lower electrical resitivity and the partial diamagnetism in the high-pressure phase could be attributed to these defects.

IV. CONCLUSIONS

From a high-pressure investigation of heavily doped CdS at 77 K we find that the shallow levels (excitons bound to neutral donors, I_2, and excitons bound to neutral acceptors, I_1) have the same pressure coefficient which represents the shift of the band gap with pressure, while peaks of G_5 and R have a larger pressure coefficient than the I_2 peak. Therefore we can attribute the G_5 peak to a transition of an exciton bound to an acceptor-type deep level (0.14 eV above the valence band). Its electron-phonon coupling strength S decreases with pressure due to a decrease of the crystal polarization field. Since the luminescence intensity of the R peak increases with pressure, it is reasonable to attribute this luminescence band to an electron transition from the conduction band to Cd interstitials or vacancies.

By measuring the absorption spectra under pressure, we find that in the wurtzite phase the absorption edge mainly arises from the I_2 bound exciton. In the rock-salt phase from 30 to 53 kbar the absorption edge is not visible with changing pressure. A possible explanation is the absorption processes of the band tails produced by phase transition. A 0.232-eV difference in the band gap be-

tween the material before the phase transition and after reversing to atmospheric pressure from above the phase transition comes from a shrinkage of the band gap due to defects. The bound exciton I_2 is proved to be an important intermediate state for resonant Raman scattering tuned by pressure. We conclude that at room temperature at about 27 kbar CdS undergoes a complete phase transition from a wurtzite phase to a rock-salt phase. In the high-pressure phase we have not observed any Raman scattering spectra, implying that there is not a so-called two-phase mixture.

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