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Resonant-Raman-scattering and photoluminescence studies in glass-composite and colloidal CdS

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Pressure-tuned resonant Raman scattering was used to determine the band-gap shift due to quantum size effects of microcrystalline CdS in glass composites and colloids. The wurtzite- to rocksalt-phase-transition behavior in the microcrystallite CdS systems was also studied and is quite different from that in bulk CdS. This different behavior is attributed to the large number of defects in microcrystallite CdS systems. We systematically investigated these defect properties in terms of the pressure coefficients of the photoluminescence peaks. This work demonstrates that the main defects in the CdS-glass composites are cadmium vacancies, V_{Cd}; whereas in the CdS colloids the defects consist of cadmium vacancies, V_{Cd}; sulfur vacancies, V_{S}; interstitial sulfur, I_{S}; and cadmium atoms adsorbed on the surface, S_{Cd}.

I. INTRODUCTION

In recent years semiconductor microcrystallites with diameters of 20–200 Å have been actively investigated to understand the size dependence of their electronic and phonon structure when the microcrystallite particle diameter is comparable to or smaller than the bulk free excition diameter.[1-3] The quantum size effects should transform the continuous bands of the bulk crystal into a series of discrete states. The simplest model used to predict the optical properties of microcrystallites in colloids and composites employs the standard effective mass Hamiltonian used in semiconductor physics.[1-3] More sophisticated models including Coulomb and polarization terms can be used to interpret the size dependence of the band gap for both large and small particles.[3,4]

The determination of the ionization energies of defects and impurities is one of the basic problems in semiconductor physics. The way in which shallow and deep traps are affected by quantum size effects with respect to the lowest exciton state tells us about the nature of the defects. The shallow hydrogenic traps have only a long-range Coulomb potential. Therefore the wave function of the shallow traps will have a greater spatial delocalization than that of the deep traps. According to the effective mass theory, the shallow impurity states should move with the band edge of the small semiconductor clusters similar to the excitions. But the bonding energy will increase only slightly due to the wave-function confinement and the increase of the effective mass of the carriers. On the other hand, the deep traps have a short-range potential and a very localized wave function. Therefore the quantum size effects on deep traps will be smaller. Generally the donor-type deep traps, the wave function of which consists mainly of a superposition of the conduction-band wave functions, will shift slightly up on comparison with the energy levels in the bulk material. So the binding energy of deep traps in small clusters will increase, with the same behavior for acceptor-type traps.

In recent years extensive work has been reported on size-dependent electronic absorption spectra, which are extremely sensitive to the spatial extent and thus in agreement with the above description. In order to further investigate the electronic and phonon properties of these small clusters in colloids and composite materials, we focus now on resonant-Raman-scattering and photoluminescence studies of these materials under pressure.

The CdS particles in colloids and composites in our study were prepared by the method of nucleation during the chemical reaction, so it is difficult to control the stoichiometry and impurity content in these small particles. In fact these small particles contain a large number of defects and impurities although the doping is not intentional. These impurities, lying below the exciton states, naturally obscure the absorption edge of the small particles. However, resonance Raman scattering can be employed to find the band edge in terms of the resonant intermediate states—i.e., the lowest (1*s*) Wannier exciton. The object of the present work is firstly to use resonant Raman scattering tuned by pressure to find the band edge for the CdS microcrystallites in glass composites and colloids. Secondly, we will investigate the wurtzite- to rocksalt-phase-transition behaviors of CdS particles in glass composites and colloids and compare the pressure behavior of the phase transition of these small particles with the bulk material. Finally we will investigate the optical properties of the defects in CdS microcrystallites in glass composites and colloids in terms of the pressure behavior of the photoluminescence peaks.

II. EXPERIMENTAL

The pressure dependence of the photoluminescence and the LO and 2LO Raman intensities was measured for CdS microcrystallites in glass composites and colloids up to 90 kbar. In order to improve the signal-to-noise ratio for the weak Raman and photoluminescence spectra of CdS particles in a diamond-anvil pressure cell (DAPC) we used a 45° incident light micro-Raman system instead of the normal 180° backscattering geometry used in high-pressure Raman scattering. In the case of 45° illumination, the laser light is reflected by a surface mirror and then focused by an objective lens onto a thin sample at 45°. The resulting photoluminescence and Raman scattering with a 135° scattering angle is collected by a microscopic objective at right angles to the sample surface, and then enters a 0.85-m Spex double monochromator without passing through a semitransparent beam splitter which is required for the 180° micro-Raman scattering system. Compared to the backscattering system, the present system has higher collection efficiency and higher spatial resolution as well as a higher signal-to-noise ratio, which has very important advantages for Raman and photoluminescence experiments in a DAPC. In order to further improve the signal-to-noise ratio, we chose a low luminescence diamond pair for the DAPC. Within the entire frequency region for photoluminescence and Raman scattering, the background due to the diamond was found to be smaller than 50 counts per second.

The samples were polished plates (~ 30 μm thick) of CdS-glass composite with 80 ± 20 Å diameter CdS crystallites, which were loaded into a gasketed diamond-anvil cell along with pure water as a pressure transmitting medium. This was done because the commonly used medium, a 4:1 methanol-ethanol mixture, reacted with the CdS-glass composites and colloids. The pressure was determined by the standard ruby fluorescence method. Up to 90 kbar the relative shift between the R_1 and the R_2 lines is no larger than one wave number, indicating that true hydrostatic pressure was well maintained in the diamond-anvil cell. The colloidal microcrystallite CdS used in our experiment was prepared by injection of a 20-ml $9.3\times10^{-3}M$ $CdSO_4$ aqueous solution into 100 ml of rapidly stirred $5\times10^{-3}M$ Na_2S aqueous solution at room temperature. The particle diameter measured by (transmission electron microscopy) (TEM) is 60 ± 20 Å. For colloidal CdS we directly injected the fresh CdS colloid in a water solution into the sample chamber of the diamond-anvil cell.

In order to find the band edge of the small CdS particles using pressure-tuned resonant Raman scattering the 4579-Å (2.708-eV) line from an argon-ion laser was chosen as the excitation radiation wavelength. Both Raman and photoluminescence measurements of CdS-glass composites and colloids were performed at this excitation wavelength. The laser power focused on the sample at a 45° angle was about 100 mW for Raman scattering and 80 mW for photoluminescence measurements.

III. RESULTS AND DISCUSSIONS

A. Pressure-tuned resonant Raman scattering

Resonant Raman scattering induced by pressure is extremely useful for determining the band gap and the properties of intermediate states as well as structural phase transitions. Using this technique, electron-phonon coupling mechanisms, and the properties of the phonon scattering matrix elements, intermediate states can be determined based on the analysis of Raman scattering intensity and linewidths. In II-IV semiconductors with a polar unit cell like CdS, the main electron-phonon coupling mechanism is the Fröhlich interaction.[5] Long-wavelength longitudinal-optical phonons are accompanied by a strong macroscopic electric field inside a solid, which can in turn couple to the electrons and holes. So generally in II-VI semiconductors such as crystalline CdS strong first-order LO phonon Raman scattering and its overtones have been observed.[6]

X-ray experiments show that bulk CdS crystals and microcrystallites in glass composites and colloids have the wurtzite structure with a polar unit cell.[7] Therefore CdS has strong first-order LO phonons and LO phonon overtones in Raman scattering. Under pressure the wurtzite phase of CdS undergoes a first-order phase transition from the wurtzite phase to the rocksalt phase. According to a group-theoretical analysis, first-order Raman scattering is forbidden in the rocksalt phase of CdS, which has an inversion symmetry center. Therefore we can use the pressure dependence of the Raman scattering intensity to study the phase-transition behavior of the bulk and microcrystallite CdS.

1. Bulk CdS

The bulk CdS used in our experiment was prepared by a vapor phase transport method and not intentionally doped and a second sample of bulk CdS doped with Cu was obtained from the U.S. Army Missile Command, Huntsville, AL. Both of the bulk samples have strong I_2 luminescence coming from the emission of an exciton bound to a neutral donor at low temperature (77 K). At room temperature and atmospheric pressure the photoluminescence peak due to the bound exciton occurs at 2.452 eV. This peak shifts upward in energy at the rate of 5 meV/kbar as pressure is increased.[8] The 4765-Å (2.602-eV) line of the Ar^+ laser was used for Raman scattering and typical Raman spectra of bulk CdS are shown in Fig. 1 for several pressures. At atmospheric pressure the Raman shift for the LO phonon line of the two bulk CdS samples is 304 cm^{-1}. The phonon frequency, fitted as a linear function of pressure, shifts at the rate of 0.50 ± 0.03 cm^{-1}/kbar (see Fig. 2). When the pressure approaches 27 kbar, the band gap has increased from 2.452 to 2.582 eV, which is close to the exciting photon energy of 2.602 eV. At a pressure of 27 kbar the Raman intensity has increased dramatically due to the resonance effect. When the pressure is slightly above 27 kbar both the LO phonon Raman scattering and photoluminescence suddenly disappear, the color of the sample changes from yellow to dark orange, and a 20% decrease in crystal volume is simultaneously observed. If the phase transition were not complete, that is, if there is a mixed wurtzite-rocksalt phase in the sample as Venkateswaran, Chandrasekhar, and Chandrasekhar[9] observed in pure and heavily doped CdS samples, then we would expect to observe a LO phonon Raman peak whose intensity would be proportional to the wurtzite phase volume

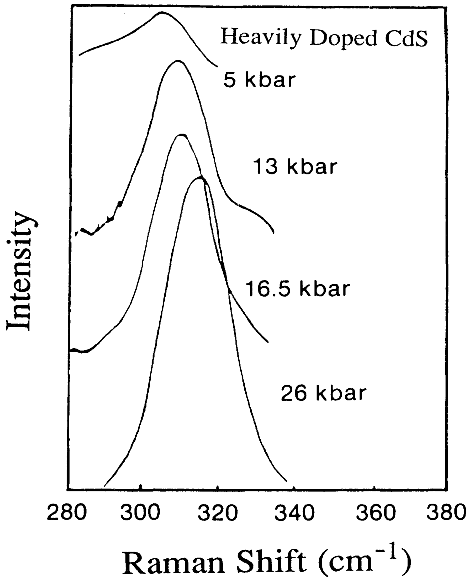

FIG. 1. Resonant-Raman-scattering spectra for several pressures in the wurtzite phase after the phase transition.

fraction. This sudden disappearance of the LO phonon Raman scattering means that the bulk CdS sample undergoes a complete first-order phase transition from the direct band-gap wurtzite phase to the indirect band-gap rocksalt phase.

Upon returning to atmospheric pressure after reaching 50 kbar, the sample shows no photoluminescence, probably due to a large number of nonradiative defect centers induced by the phase transition, and the free exciton becomes very weak due to scattering by induced defects. The Raman scattering intensity of the LO phonon is almost the same as that measured before the onset of the phase transition. When the pressure is increased beyond 27 kbar the LO phonon Raman peak disappears again. This is consistent with our expectation that the I_2 bound exciton states are important intermediate states for resonant Raman scattering in heavily doped CdS. It also shows that CdS returns to its original wurtzite structure with the same band gap as before the phase transition.[8] The intensities of the LO phonon Raman scattering depend on the electron-phonon coupling strength of the intermediate states. Hopfield[5] used a Fröhlich Hamiltonian to derive the coupling strength of a bound exciton to a long-wavelength LO phonon,

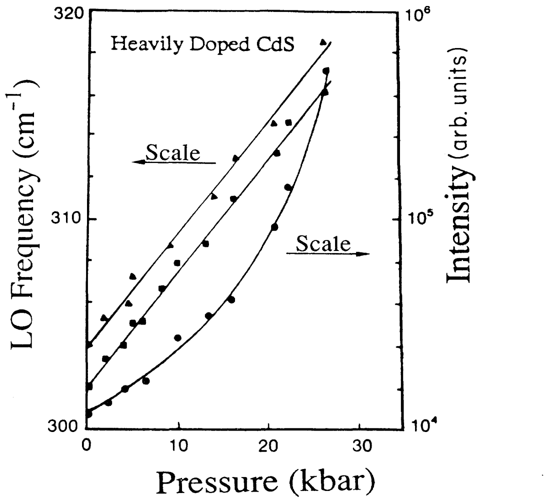

FIG. 2. Energy of the LO phonon and its corresponding Raman intensity as a function of pressure. The symbols ▲ and ■ represent the Raman shift with pressure before the phase transition and its reversal to the wurtzite phase after the phase transition, respectively. ● represents the change of the Raman intensity with pressure.

$$S_{\mathrm{LO}}=\frac{\kappa e^2}{a_{\mathrm{eff}}}\left[\frac{1}{\epsilon(\infty)}-\frac{1}{\epsilon(0)}\right]\left[\frac{1}{\hbar\omega_{\mathrm{LO}}}\right], \qquad (1)$$

where a_{eff} is the effective orbital radius of the bound exciton. $\epsilon(\infty)$ and $\epsilon(0)$ are the electronic and ionic polarizabilities, respectively, of the semiconductors. ω_{LO} is the LO phonon frequency and $\kappa=1/2\pi$. The bound exciton has a smaller effective orbital radius than the free exciton (30 Å), so the bound exciton intermediate state will increase the phonon scattering matrix element thus increasing the Raman scattering intensities. On the other hand, Damen and Shah[6] have proved that phonons with wave vector $\sim 1/a_{\mathrm{eff}}$ can participate in the LO phonon Raman scattering. This effect will further increase the Raman intensity and the half-width of the Raman spectra due to phonon dispersion. This would explain the strong Raman scattering and wide half-width (22 cm^{-1}) of the Raman spectra in doped bulk CdS.

2. CdS-glass composites

The CdS particle diameter in our glass composite is about 80±20 Å (as determined by x-ray diffraction). Typical resonance Raman spectra for the CdS-glass composite at several pressures are shown in Fig. 3. Figure 4

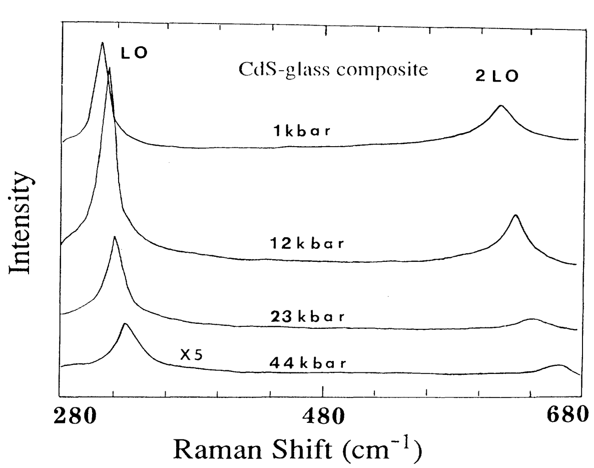

FIG. 3. LO and 2LO phonon Raman scattering spectra at several pressures in a CdS-glass composite.

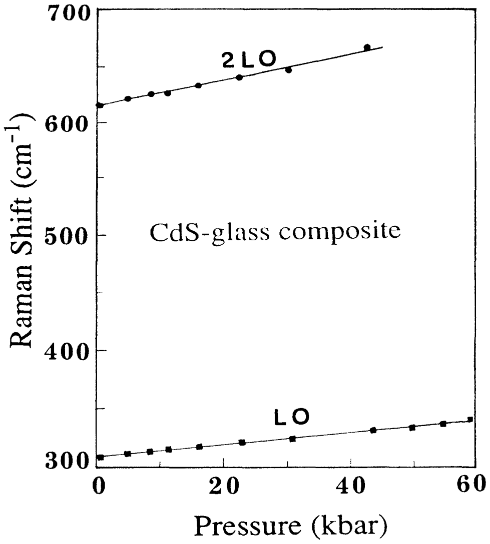

FIG. 4. The dependence of the LO and 2LO Raman peak with pressure for a CdS-glass composite.

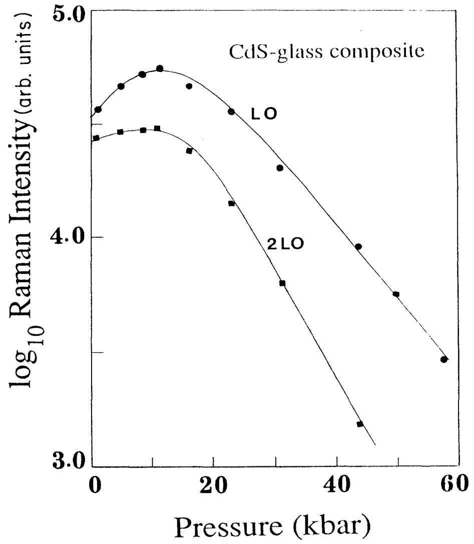

FIG. 5. The dependence of the LO and 2LO Raman intensity on pressure in CdS-glass composite.

shows the frequency shifts of the LO phonon and 2LO phonon Raman scattering with pressure. At atmospheric pressure the Raman shifts of the LO phonon and 2LO phonon are 308 and 617 cm^{-1}, respectively. The LO and 2LO phonon frequencies increase linearly with pressure at the rate of 0.47$\pm$0.01 and 0.98$\pm$0.02 cm^{-1}/kbar, respectively. The pressure coefficients of the LO and 2LO phonon Raman scattering in CdS-glass composites are similar to those of bulk CdS. The Raman shifts of the LO and 2LO phonons in CdS-glass composites at atmospheric pressure are 4 and 9 cm^{-1} higher, respectively, than those of bulk CdS. A possible explanation for the slightly higher Raman shift of the LO phonon is due to heavy doping in the small particles during the preparation of CdS-glass composites. Some experimental results have shown that the Raman shift of bulk CdS increases with increased doping.[9] The half-width of the LO phonon Raman spectrum is about 14 cm^{-1}, which is smaller than that of bulk CdS (22 cm^{-1}). In the photoluminescence spectra of the CdS-glass composites we have not observed the peak I_2, which comes from the transition of the exciton bound to a shallow donor. The intermediate states for Raman scattering in CdS-glass composites should include the 1*s* free exciton.

Figure 5 shows the LO and 2LO phonon Raman intensities as a function of pressure. The excitation photon energy is 2.708 eV (4579-Å line). Initially the intensities of the LO and 2LO phonon Raman lines increase with increasing pressure. At about 12 kbar the intensities reach a resonant maximum. Then the intensities decrease with increasing pressure until at 60 kbar the LO phonon Raman intensity has decreased to 8% of the intensity at 1 bar.

The resonant behavior of the Raman intensity in the CdS-glass composite does not have a sharp cutoff as observed for bulk CdS. When pressure drives the band gap close to the excitation photon energy, the LO phonon Raman intensities experience an increase of more than an order in magnitude for the bulk CdS but for CdS-glass composites the LO phonon Raman intensities have only doubled in magnitude. This reflects the fact that the energy levels of the free excitons in the CdS-glass composites are distributed over a large energy region due to the nonuniform size of the microcrystallite CdS particles in glass. Fortunately there are two remarkable characteristics which allow us to identify the resonant pressure region. Firstly, the LO phonon Raman intensities have a dramatic increase in the resonant pressure region. Secondly, the background of the LO Raman scattering spectra becomes very strong due to the resonant excitation of free excitons. The maximum of the Raman intensity with pressure occurs at 12 kbar. From the photoluminescence measurements (see Sec. III B 1) the band-gap shift with pressure in CdS-glass composites is found to be 5.1 meV/kbar. Therefore the band gap of 80$\pm$20 Å CdS particles in glass is about 2.647 eV at room temperature compared with heavily doped bulk CdS band gap of 2.452 eV.

The band-gap shift to high energy relative to the bulk material is about 0.197 eV in our 80$\pm$20 Å size CdS particles. The particle size is larger than a free exciton (Bohr radius $a_0 = 30$ Å). Nevertheless there remains a 0.197-eV energy shift. Nair, Sinha, and Rustagi[10] used a variational calculation to model the lowest electron-hole state in the semiconductor spheres many times larger than the size of the bulk free exciton and find that there is still a significant energy shift above the bulk free exciton level, perhaps due to the remaining confinement effect on the total electron-hole wave function. The above-measured energy shift is in agreement with the predictions of Nair, Sinha, and Rustagi. On the other hand, the energy gap (2.647 eV) determined from the resonant-Raman-scattering measurements is 37 meV higher in energy than peak 1 of the photoluminescence spectra (see Sec. III B 1).

This energy difference is close to the one LO phonon (38 meV). Therefore peak 1 in the photoluminescence spectra may be due to the one LO phonon replica of the 1*s* free exciton. Potter and Simmons[11] have observed that the absorption peak is about 40 meV higher in energy than the photoluminescence peak 1. In the small-particle CdS the electron-phonon coupling mechanics clearly plays an important role in determining the spectral features. Recently calculations by Schmitt-Rink, Miller, and Chemla[12] have shown that the coupling between the electron and LO phonon in small semiconductor particles becomes weaker than in the bulk.

3. *Colloids*

Figures 6 and 7 show the LO and 2LO phonon Raman spectra and the Raman intensities and Raman frequencies, respectively, for our 60±20 Å CdS colloids at several pressures. The Raman shifts and half-widths are almost the same as that in CdS-glass composites. The pressure coefficients of the LO and 2LO phonon Raman scattering are 0.49 and 0.98 cm^{-1}/kbar, respectively. The maxima of the LO and 2LO phonon Raman intensities occur around 20 kbar. There are no band-edge or shallow state processes in the photoluminescence spectra of CdS colloids. If we assume that the band-gap shift with pressure in our CdS colloids is the same as that of the CdS-glass composite, then the band gap in the colloids is about 2.606 eV. Compared to the band gap of the heavily doped bulk CdS, the band-gap shift in the colloids is about 0.154 eV. Peak 1 of the photoluminescence spectra in CdS colloids given in Fig. 9, which has been identified as a free exciton transition process (2.44 eV) by some authors,[13] actually comes from donor-type deep levels with a binding energy of 0.152 eV (see Sec. III B 2). The Raman intensities of CdS particles in colloids begin to decrease when the pressure is higher than 25 kbar. When the pressure is higher than 45 kbar, peak 1 from the photoluminescence spectra resonates with the exciting photon energy. But the Raman intensities of the LO and 2LO phonons continue to decrease with increasing pressure except for the strong background of Raman scattering. This fact is additional evidence that peak 1 does not come from the band-edge processes but from deep levels. Because Raman scattering is an instantaneous process a deep level which has a larger lattice relaxation and longer lifetime cannot be used as an intermediate state for Raman scattering.

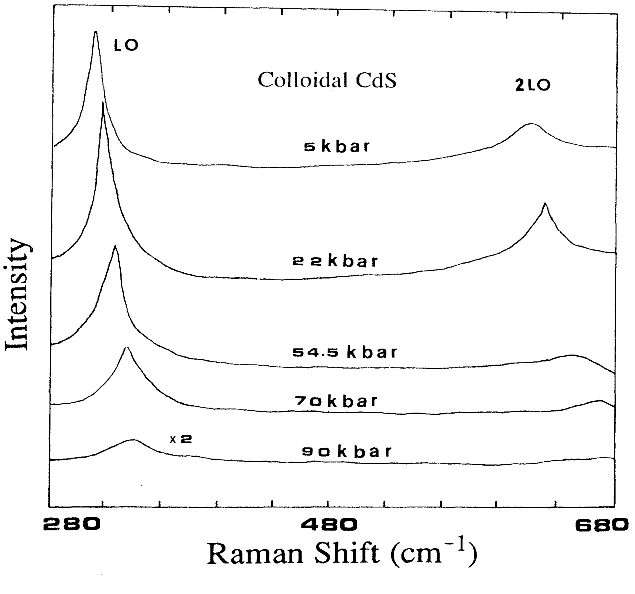

FIG. 6. The LO and 2LO phonon Raman scattering spectra for several pressures in CdS colloids.

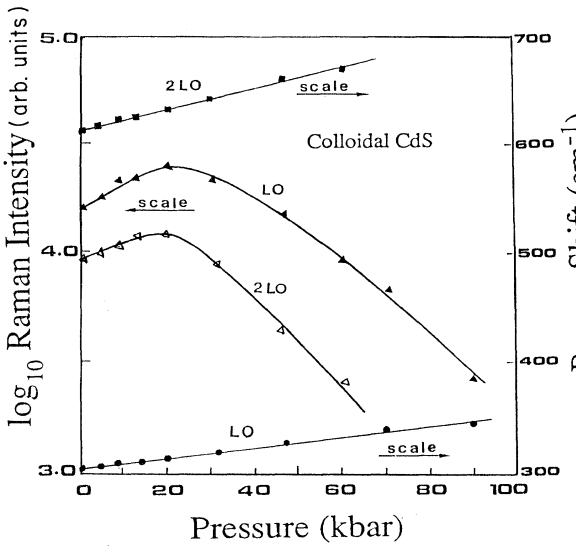

FIG. 7. Raman shift and Raman intensity for LO and 2LO Raman scattering as a function of pressure in CdS colloids.

The complete phase transition in bulk CdS occurs suddenly at 27 kbar at room temperature. When the pressure goes beyond 27 kbar, the Raman intensity of the LO phonon suddenly disappears from the maximum close to resonance and at the same time the color of the sample changes from yellow to dark orange and a 20% decrease in the crystal volume is observed.[8] But the Raman intensities of the LO phonon in glass composites and colloids monotonically decrease from the maximum (at 12 kbar for the composites and 20 kbar for the colloids) to 8% of the 1-bar intensity. Over this pressure region the color of the sample gradually changes from yellow to dark orange. Therefore the pressure-induced phase transition for the CdS small particles in the glass composites and colloids is quite different from that occurring in bulk CdS crystals. From the change of the LO phonon Raman intensity and the color of the sample we can conclude that the phase transition from the wurtzite to the rocksalt phase in the small CdS particle system occurs over a large pressure region. But recent high-pressure studies of microcrystalline CdS with 300-Å-diam particles in colloids suggest that a complete phase transition from wurtzite to rocksaltlike bulk material occurs below 40 kbar.[14] If we assume that the LO phonon Raman intensity is roughly symmetric around the resonant pressure, then in our case the evidence for a phase transition from a wurtzite to rocksalt phase at a pressure below 40 kbar is very weak.

The difference in phase-transition behavior between the bulk and small-CdS-particle system may be due to a number of effects. First we compare the photoluminescence spectra of the heavily doped bulk CdS and CdS small-particle systems. The system of small particles has a very strong luminescence spectra due to defects especially in CdS colloids. In the colloids all the photoluminescence is caused by defects such as V_S, V_{Cd}, I_S, and Cd surface states.

Around a defect, especially a vacancy, the lattice reconstruction will change the symmetry of the original lattice, which causes a degenerate level to split (the Jahn-Teller effect). If we assume that the Jahn-Teller energies can be created by the alignment of the defects produced by a uniaxial stress, then we can roughly estimate the stress around the defect. The magnitude of the Jahn-Teller energy per electron is unknown for CdS. The value for silicon is about 0.2 eV.[15] If we assume that the uniaxial stress coefficient is 2 meV/kbar, then there exists about a 100-kbar stress around a vacancy which will shift the local phase transition to a much higher pressure. This result may overestimate the stress around a vacancy, but nevertheless one can envision at least several tens of kbar around the vacancy due to the Jahn-Teller effect.

The large number of defects induces a large strain in the small particles and thereby can bring about a large change in the phase-transition pressure. For example, the two small-CdS-particle systems have similar particle size and band-gap values. In CdS colloids it requires a pressure of 90 kbar to decrease the LO phonon Raman intensity to 8% of that at 1 bar, but in CdS-glass composites the requisite pressure is only 60 kbar to decrease the intensity to the same value.

A second contribution to the phase transition is due to the large surface effects of the small particles. Several experiments on platinum and gold particles demonstrate that surface tension and reconstruction energy result in a contraction of the lattice constants in small particles.[16] But there is no clear evidence on how the surface tension and reconstruction in small semiconductor particles affect the phase-transition pressure. Comparing the photoluminescence spectra of these systems, one observes a strong photoluminescence coming from the surface states for CdS colloids, which is in contrast to the composite material where there is no remarkable luminescence due to these surface states. The large number of surface states will further increase the lattice relaxation and reconstruction energy in several surface layers. This would increase the phase-transition pressure in CdS colloids relative to that in the composite material.

B. Photoluminescence measurements

In Sec. III A we have used resonant Raman scattering induced by pressure to determine the band edge of small CdS particles in glass composites and colloids. In this section we will discuss the defects in CdS-glass composites and colloids as they manifest themselves in photoluminescence measurements under pressure. It is well known that the band structure of semiconductors changes drastically with pressure. Generally, hydrostatic pressure will drive antibonding conduction bands and bonding valence bands up and down, respectively.

The change of the band structure under pressure must affect the defect states. According to the effective mass theory, a shallow impurity state has a long-range Coulomb potential. Its wave function is primarily a product of an envelope function and Bloch states of the band edge near the energy of the impurity state. Therefore the shallow states are localized in k space but delocalized in real space. If we neglect the change of the effective mass of the band edge with pressure, the shallow state level should follow the band edge when the edge moves as a result of applied pressure. But deep levels have a very localized potential and relatively small wave function so the deep level is delocalized in k space and localized in real space. The coupling matrix elements from all bands will contribute to the binding energy of deep levels. Therefore the deep level does not in general follow the band edge under pressure and the pressure derivatives for the deep levels are considerably smaller than the corresponding derivative of the direct band gap.[17,18] Recently Ren, Dow, and Wolford have theoretically calculated the pressure dependence of deep levels in GaAs.[19] They gave the following equation for the pressure derivative of deep levels in GaAs:

$$\frac{dE}{dP}=\frac{\int dE'(E-E')^{-1}[dD_{1,b}(E')/dP]}{\int dE'(E-E')^{-2}D_{1,b}(E')}\ , \qquad (2)$$

where E and E' are the deep level energy and band energy, respectively, $D_{1,b}$ is the local spectral density, l represents the substitutional deep point defect at the cation or anion, and b is the irreducible representation of the point group associated with the deep level. In CdS, b is the A_1 representation (s symmetry) and the E representation (p symmetry), respectively. According to this theoretical calculation, the deep levels closer to the conduction band are dominated by the conduction bands and exhibit positive values of dE/dP. But levels near the valence band are not affected by the conduction band so strongly and can yield energy with $dE/dP<0$, characteristic of valence-band dominance.

1. Photoluminescence in CdS-glass composites

Figure 8 shows the photoluminescence spectra of the 80±20 Å size CdS particles in glass composite at several pressures. The band gap is about 2.647 eV as determined from the measurement of the resonant Raman scattering induced by pressure. Peak 1 is below the band gap in energy (2.609 eV) by about one LO phonon (38 meV) and its pressure coefficient (5.1 meV/kbar) is in good agreement with the pressure coefficient of the band gap in bulk CdS. Therefore peak 1 can be attributed to the one LO phonon replica of the free exciton.

The broad, relatively intense low-energy luminescence peak 2 also observed in other experiments[13] is about 2.17 eV in energy at 1 bar. Its pressure coefficient, 6.2

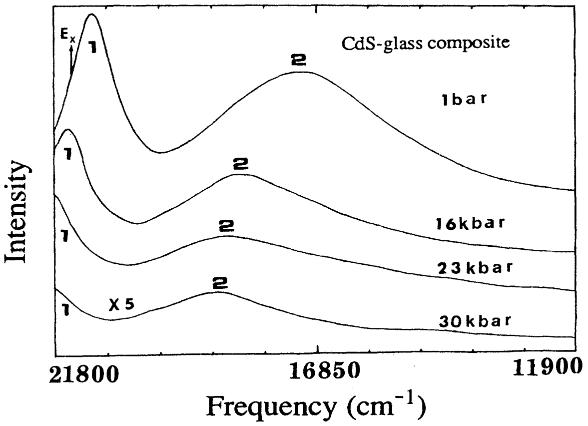

FIG. 8. Photoluminescence spectra of CdS-glass composite at room temperature for several pressures. E_x represents the band edge of free exciton.

meV/kbar, is larger than that of the band edge (see Fig. 10). This luminescence peak therefore is due to the recombination between free excitons and an acceptor-type deep level which has a -1.1 meV/kbar pressure coefficient relative to the maximum of the valence band and its binding energy is 0.48 eV. In fact, the present authors[8] and Venkateswaran, Chandrasekhar, and Chandrasekhar[20] both observed the so-called R acceptor-type deep levels in heavily doped vapor-phase transport grown bulk CdS which has the same binding energy and pressure coefficient as that observed in CdS-glass composites. From its pressure behavior it is possible to attribute peak 2 to the recombination of a free exciton and an A_1 (s) symmetry Cd vacancy V_{Cd}. A neutral cadmium vacancy has six electrons coming from the sp^3 orbitals of the nearest four sulfur atoms. Therefore there are two holes at the A_1 symmetry cadmium vacancy state making it a double acceptor-type deep level. The wave function of a cadmium vacancy mainly consists of sp^3 orbitals of sulfur atoms, that is, the wave function of a cadmium vacancy mainly comes from Bloch states of the valence bands. Under pressure the cadmium vacancy level will move with the valence band to a lower energy. An A_1 symmetry cadmium vacancy state can couple strongly to the lowest s symmetry valence resulting in a quicker decrease in energy relative to the valence-band maximum which was p symmetry. Therefore the cadmium vacancy deep level has a negative pressure coefficient. Recently Kobayashi, Sankey, and Dow[21] have calculated the binding energy of a cadmium vacancy in bulk CdS. This result demonstrates that the cadmium vacancy state is an acceptor-type deep level with about 0.52 eV binding energy. This result is in good agreement with our observations in CdS-glass composite and bulk material. During the heat treatment of the CdS-glass composite (with a peak temperature in the range of 575 °C–750 °C) sulfur has a greater tendency than cadmium to leave the glass may be form crystallites.[22] Therefore the CdS crystallites in glass may be deficient in cadmium, which leads to a greater number of V_{Cd} in CdS particles.[22] But previous work attributed peak 2 to a recombination at surface states and sulfur vacancies.[22,23] First, a neutral sulfur vacancy has two electrons from the sp^3 orbitals which form a donor-type deep level close to the conduction band. It is impossible for a donor deep level to have a larger pressure coefficient than the band edge. If peak 2 is due to the dangling bonds of surface states then peak 2 will not have such a sensitive response to pressure. The pressure behavior of surface states will be discussed in the section on CdS colloids.

2. *Photoluminescence in CdS colloids*

Figure 9 shows the photoluminescence spectra of CdS crystallites in colloids at several pressures. The atmospheric pressure spectra coincide with the results of Ramsden and Gratzel.[13] The energy shift of the three peaks as a function of pressure is shown in Fig. 10. From pressure-tuned resonant Raman scattering the band gap for 60±20 Å CdS crystallites in the colloids is determined to be about 2.61 eV. The pressure coefficient of the band edge in CdS colloids should be the same as that in CdS-glass composites (5.1 meV/kbar). The energy position of peak 1 at atmospheric pressure is about 2.44 eV, which is nearly the same as the band gap of bulk CdS at room temperature. This peak has been attributed to the recombination of electrons and holes at the band edge of CdS crystallites in colloids.[13] But from the photoluminescence measurements under pressure, the pressure coefficient of peak 1 is about 2.6 meV/kbar, which is far smaller than the band-edge movement with pressure. This demonstrates that peak 1 is due to the recombination of a donor-type deep level with 0.17-eV binding energy to the conduction band. We are not certain of the identity of the defect which produces the peak-1 lumines-

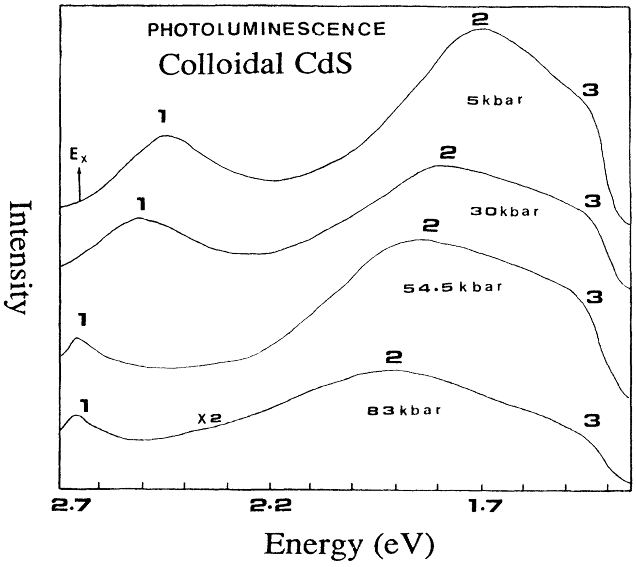

FIG. 9. Photoluminescence spectra of CdS colloids at room temperature for several pressures. E_x represents the free exciton band edge measured from resonant Raman scattering.

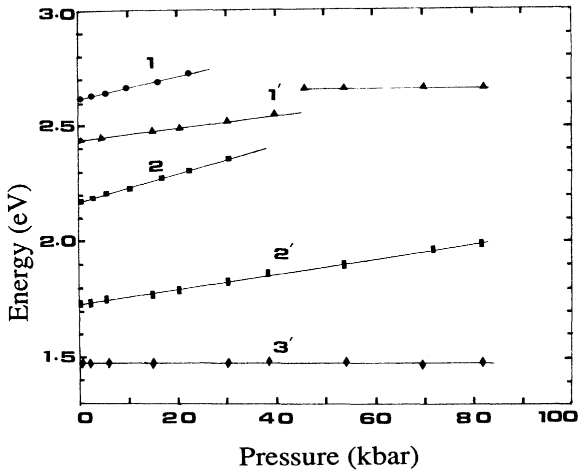

FIG. 10. The energy dependence of photoluminescence peaks on pressure. Curves 1 and 2 represent photoluminescence peaks in CdS-glass composite. Curves 1′, 2′, and 3′ represent photoluminescnece peaks in CdS colloids.

cence, but the chemical techniques for preparing CdS colloids always produce dopants halogen dopants such as F and Cl. These can be substituted for sulfur to produce shallow donors and displace sulfur atoms to interstitial sites producing a donor-type deep level I_S. Pedrotti and Reynolds[24] have demonstrated that an interstitial sulfur forms a level 0.023 eV below the conduction band in bulk CdS. From our photoluminescence results at room temperature, the energy position of peak 1 is about 0.01 eV below the conduction band of bulk CdS.[24] A 0.013-eV difference in energy may be due to the conduction-band gap opening up due to quantum size effects. Nevertheless, from growth techniques and energy positions, it is reasonable to attribute peak 1 to the recombination of electrons on I_S deep donor and holes in the valence band. If interstitial sulfur atoms occupy a position on the c axis in the space of a long weak bond then the wave function of the interstitial sulfur I_S has A_1 symmetry which can couple to the Γ valley of the conduction band, leading to a large positive pressure coefficient (2.6 meV/kbar).

When the pressure is higher than 40 kbar, peak 1 begins to resonate with the exciting photon energy. Then peak 1 becomes the one LO phonon replica of I_S up to 80 kbar. This implies that peak 1 with a 0.3-eV half-width is due to the energy dispersion of I_S, but not to a strong electron-phonon coupling ($S=110$ for a 38 Å size cluster).[25] On the other hand, the large pressure coefficient of peak 1 reflects that a large component of the wave function of I_S is comprised of long-wavelength Bloch states of the Γ valley. In this case it is impossible to generate a very localized wave function and obtain such strong electron-phonon coupling.

Peak 2 in Fig. 9 has a 0.89-eV binding energy with respect to the lowest conduction band and a pressure coefficient of 3.2±0.2 meV/kbar. Previous publications have attributed this peak to the recombination of electrons at a sulfur vacancy and a hole in the valence band. The neutral sulfur vacancy has two electrons from sp^3 orbitals of the nearest four cadmium atoms. Theoretical calculations predict[21] that the energy level of sulfur vacancies should be resonance states in the conduction band. But it is possible that the Jahn-Teller effect splits the twofold degenerate levels and pulls one of them into the band gap. So we accept the point that the main part of peak 2 is due to the recombination of an electron on V_S and hole from the valence band. But the binding energy of V_S is larger than that of I_S. If these two localized states both have A_1 symmetry then the pressure coefficient of V_S cannot be larger than that of I_S, because the component of a given Γ Bloch state in the wave function of a localized state is inverse to the energy denominator of the Green function. Therefore peak 2 with a larger half-width (0.4 eV at 1 bar) is made up of multitransitional processes. The recombination of electrons in the conduction band and holes in V_{Cd} and the recombination of electrons in I_S and holes in V_{Cd} will contribute to the high-energy part of peak 2 and a higher-pressure coefficient. The recombination between the electrons in V_S and holes in V_{Cd} will contribute to the lower-energy part of peak 2 and also have a larger pressure coefficient. Because V_{Cd} has a negative pressure coefficient (see Fig. 10) this result will give peak 2 a larger positive pressure coefficient than that of peak 1 and the half-width of peak 2 will increase with increasing pressure (see Fig. 9). This also demonstrates that peak 2 with a large half-width cannot be attributed to trapped e^--h^+ pair emission which has a weak zero phonon line followed by an intense phonon wing due to strong electron-phonon coupling in the trapped pair ($S=110$).[25] If this is true then the half-width of peak 2 would increase with increasing pressure. Also the electron-phonon coupling should increase with pressure. However, our experimental results in bulk CdS have shown that electron-phonon coupling S decreases with increasing pressure.[8] In addition, if this wide photoluminescence peak comes from one deep center transition and its phonon replica then the half-width of peak 2 should not change with pressure.

Peak 3 in Fig. 9 shows almost no change with pressure. From this pressure behavior of peak 3 we attribute it to the recombination of an electron on a donor-type deep level with binding energy 1.14 eV with respect to the conduction-band edge and a hole in the valence band. In previous room-temperature studies of CdS crystallite colloids, two luminescence effects stand out. (1) The excess Cd^{2+} adsorbed on the surface enhances the luminescence yield and (2) the luminescence is quenched extremely efficiently by hole acceptors (an S^{2-} adatom on sulfur). We identify peak 3 to be due to cadmium atoms adsorbed on the surface of crystallites. An ideal dangling-bond state of cadmium should have the hybrid energy of an sp^3 orbital of the Cd atom below the conduction band. The Jahn-Teller effect distortion will pull the occupied state to lower energy. On the other hand, a dangling-bond state cannot be very sensitive to pressure.

In small CdS particles the lowest free exciton has both electron and hole wave functions confined at the same spatial location, which will lead to a large oscillator strength and a higher radiative rate for free exciton emis-

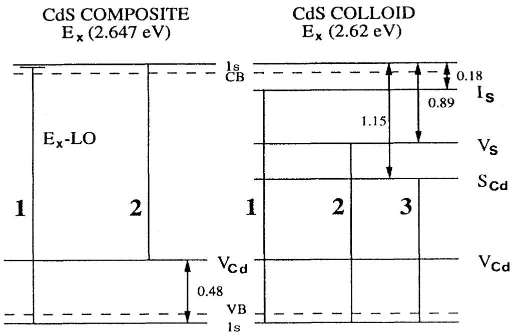

FIG. 11. Energy level diagrams for CdS-glass composite and colloids.

sion. In the CdS-glass composite which has a much better lattice structure than that of CdS particles in colloids, the one LO phonon replica of the free exciton emission has been observed due to the strong Fröhlich electron-phonon coupling in small particles. But we do not observe free exciton emission in CdS colloid because there are a large number of defects such as V_S, V_{Cd}, I_S, and surface states confined in the same space with the free exciton (see Fig. 11). These defects act as strong traps for free excitons.

The intensity of photoluminescence spectra in CdS-glass composites becomes very weak when the pressure exceeds 30 kbar. In this case the conduction-band edge is higher in energy than the exciting photon energy. This fact also demonstrates that the main defects in CdS-glass composites are acceptor-type deep levels. We cannot obtain phase-transition information from the pressure behavior of the photoluminescence but up to 80 kbar we still observe a fairly strong photoluminescence from deep levels in CdS colloids. The experimental results in bulk CdS demonstrate that the phase transition from wurtzite to rocksalt causes the band gap to suddenly drop. The band gap in rocksalt CdS is about 1.52 eV. If this is the case in CdS colloids we should observe a sudden change in the photoluminescence. But from the pressure behavior of photoluminescence spectra we can identify that up to 80 kbar, most of the CdS particles in colloid are still in the wurtzite phase. From the Raman intensity and photoluminescence intensity decrease at high pressure (in excess of 50 kbar) we can say that there is a partial phase transition in small CdS particles that is strongly dependent on the lattice distortion by defects.

The experimental results above have demonstrated that the main defects in the CdS-glass composites are cadmium vacancies, V_{Cd}, but in the CdS colloids the defects consist of V_S, V_{Cd}, I_S, and S_{Cd}. Previous measurements have shown that the bound exciton in the defect states exhibits a strong interaction with the free exciton and causes absorption bleaching, which in turn produces the nonlinear optical properties of the small CdS particle systems. According to our experimental results, the defects, especially the vacancies which may induce nonlinear optical properties, exist inside of our small particles and are not due to surface states.[23] The Jahn-Teller effect will reduce the symmetry of the vacancy states, therefore we can expect that the second-order nonlinear bond susceptiblity χ^2 will become important and the local field factor f will increase around a vacancy.[26]

IV. CONCLUSIONS

We have systematically investigated the phase-transition behavior of small CdS particles in glass composites and colloids as well as bulk CdS by pressure-tuned resonant Raman scattering. We found that the bulk CdS undergoes a sharp phase transition from wurtzite to rocksalt at about 27 kbar. However, the small CdS particles in glass composites and colloids undergo a slow partial phase transition. The pressure at which the microcrystallite material has undergone a complete phase transition is much higher than that for bulk CdS. We attribute this anomalous phase-transition behavior to the strong strains induced by a large number of defects (especially vacancies) in the small particles. On the other hand, the large surface of the small particles also can induce lattice distortion which leads to a shift in the phase-transition pressure.

The free exciton band edge of small CdS particles in glass composites and colloids was determined by means of pressure-tuned resonance Raman scattering measurements. The experimental results show that the high-energy photoluminescence peak in the CdS glass composites is the one LO phonon replica of the free exciton and the high-energy peak in the CdS colloids is produced by the deep donor level I_S. We have systematically analyzed the pressure behavior of each photoluminescence peak in the CdS-glass composites and colloids and have identified the defects causing the corresponding photoluminescence peaks.

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