

## Phase transitions of CdS microcrystals under high pressure

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The experiment under high pressure using a diamond anvil cell (DAC) requires the utilization of synchrotron radiation. High-pressure experiments were performed using a DAC on CdS microcrystals, both in the far-IR and in the X-ray regions, in order to study the lattice dynamics and lattice stability concerned with the phase transitions. From these experiments, experimental evidence is presented indicating that a CdS microcrystal of smaller diameter shows a higher transition pressure for lattice transformation under pressure. The origin of such an increase in the transition pressure in the microcrystals is discussed in relation to the surface tension.

**Keywords:** phase transitions; CdS microcrystal; high-pressure experiments; far-IR transmission; X-ray powder diffraction.

### 1. Introduction

The intrinsic physical properties of microcrystals are different to those of bulk crystals, because of the increase in the proportion of atoms at the surface of the inner atoms. For example, the surface phonon mode occurs instead of the bulk phonon mode in bulk crystals. The purpose of the present study is to address, among others, the following questions: (1) What is the lattice stability concerned with the lattice transformation under pressure? (2) What is the phonon spectrum before and after the lattice transformation? (3) Is there any change in the structure from that in the bulk crystal? The simplest way to answer these questions is to carry out both far-IR spectroscopy and X-ray diffraction on microcrystals under high pressure. An X-ray diffraction study along similar lines to the present study has been reported recently on CdSe nanocrystals by Tolbert & Alivisatos (1994) and Si nanocrystals by Tolbert *et al.* (1996).

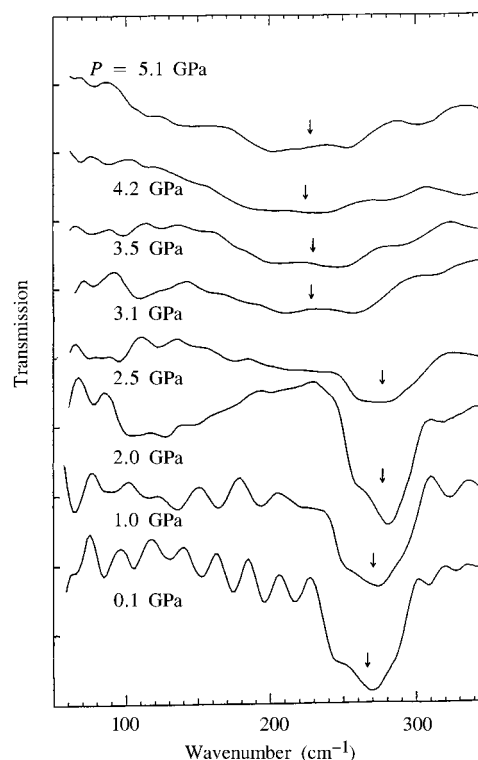
### 2. Experimental

CdS microcrystals were prepared using a conventional gas evaporation technique developed by Kimoto *et al.* (1963). The particle size distribution was measured by transmission electron microscopy. The microcrystals obtained showed a definite size distribution and in the present paper the average diameter is used to represent the physical properties. We prepared microcrystals with different average diameters of 8.0, 14.7, 39, 84,

131, 160 and 400 nm. High-pressure experiments were performed using a DAC technique. The diameter of the pinhole of the steel gasket which forms the pressure cell with a pair of diamond windows was almost 0.5 mm for the far-IR transmission measurements and 0.2 mm for the X-ray diffraction measurements. Microcrystals were immersed in the pressure cell together with Apiezon grease, which is almost transparent in the far-IR region and works as a pressure-transmitting material. For the X-ray diffraction measurement, a mixture of methanol and ethanol was used as the pressure-transmitting material. The generated pressure in the pressure cell was monitored by measuring the wavelength shifts of the fluorescence spectra of ruby chips in the pressure cell. The transmission spectra of CdS in the far-IR region were obtained at beamline BL6A1 of UVSOR at the Institute for Molecular Science in Okazaki (Japan) and also partially at beamline U4-IR of the NLSL VUV ring at Brookhaven National Laboratory (USA). Far-IR transmission measurements at the highest pressures, up to 21 GPa, were carried out at UVSOR owing to the benefit of the high brilliance of synchrotron radiation.

The power spectrum was obtained by a Fourier transformation of the recorded interferogram using a Martin–Pupplet-type interferometer at UVSOR and by a Michelson-type at the NLSL.

X-ray powder diffraction experiments on CdS microcrystals were carried out at the undulator line BL18C of the Photon Factory (KEK-PF). Focused monochromatic 20 keV X-rays were collimated to a beam of 60  $\mu\text{m}$  diameter. The diffraction pattern on the CdS microcrystal in the DAC was obtained by angle integration of the raw pattern of a Debye–Scherrer ring, which was recorded on a Fuji imaging plate.



**Figure 1** Development of far-IR transmission spectra of CdS microcrystals with an average diameter of 400 nm with pressure. Spectra were taken at 4  $\text{cm}^{-1}$  resolution.

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**3. Far-IR spectra under high pressure**

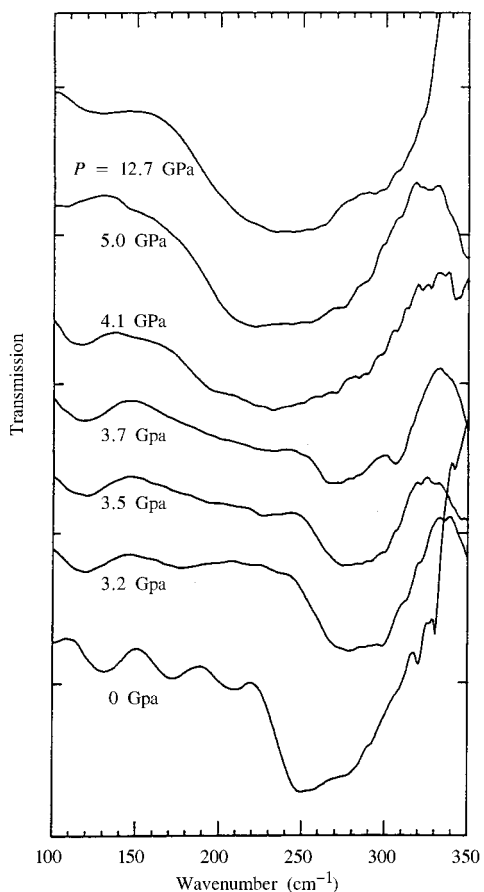
The optically observable phonon in a microcrystal is a so-called surface phonon. According to the continuum mode developed by Genzel & Martin (1972), which describes a surface phonon in a spherical microcrystal for the lowest mode of polarization, the surface phonon energy ( $\omega_s$ ) is given by the following equation:

$$\varepsilon(\omega_s) = -2\varepsilon_m.$$

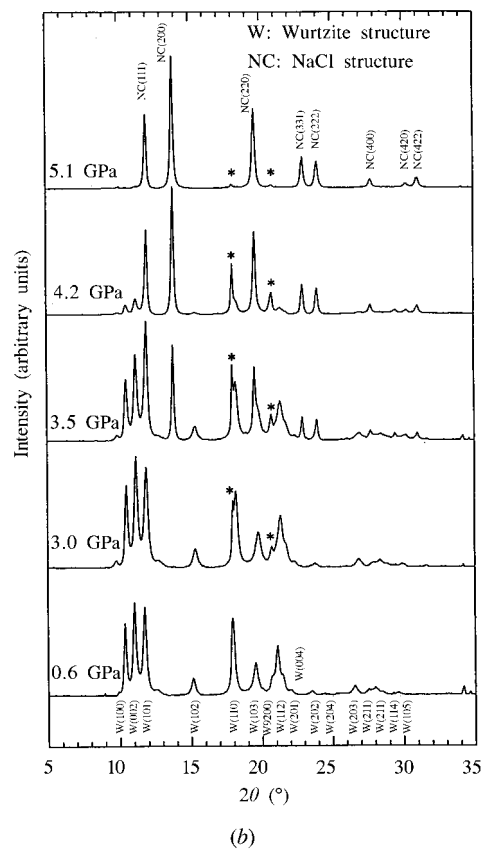
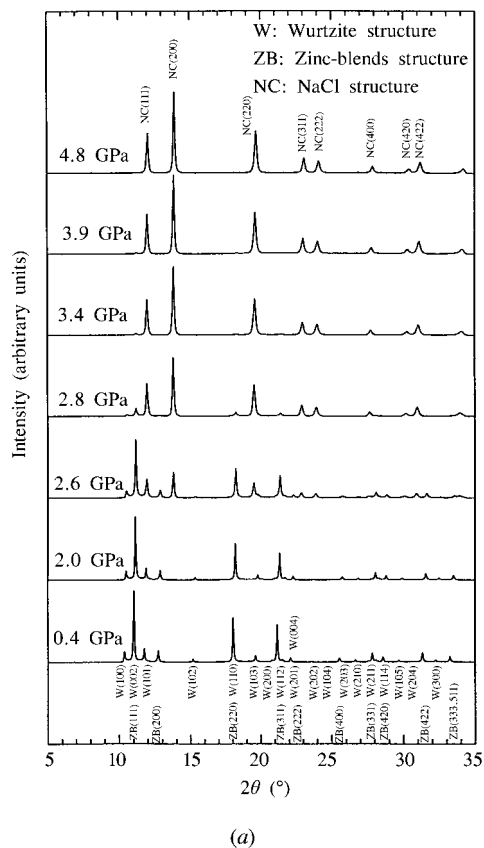
Here,  $\varepsilon(\omega)$  is the real part of the dielectric function of the bulk CdS;  $\varepsilon_m$  is the dielectric constant (Apiezon-N grease) surrounding the sphere and was determined to be 2.25 by Nanba *et al.* (1994).

Fig. 1 shows the development of the far-IR transmission spectra of commercially purchased CdS powder (400 nm average diameter) with pressure at room temperature. The sharp dip in the spectrum at  $P = 0.1$  GPa appeared at  $268\text{ cm}^{-1}$ . This value is consistent with that expected by continuum theory and is assigned to the absorption due to the surface phonon of the microcrystal. In bulk CdS a  $TO$  phonon mode occurs at  $\sim 240\text{ cm}^{-1}$ . The surface phonon showed a successive blue shift up to  $280\text{ cm}^{-1}$  and 2.5 GPa pressure. At a pressure of 3.1 GPa, a new and very broad band suddenly appeared at  $210\text{--}240\text{ cm}^{-1}$ , rather than a band at  $280\text{ cm}^{-1}$ .

We attributed the sudden decrease in energy to the phase transition with a transition pressure ( $P_t$ ) lying somewhere between 2.5 and 3.1 GPa. It is shown, for example, by Edwards &



**Figure 2** Development of far-IR transmission spectra of CdS microcrystals with an average diameter of 89 nm with pressure. Spectra were taken at  $4\text{ cm}^{-1}$  resolution.



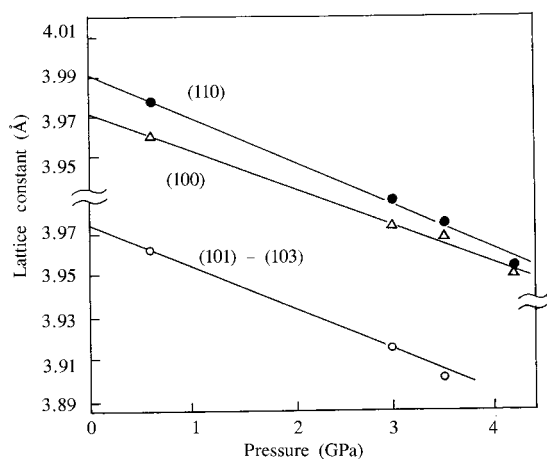
**Figure 3** High-pressure X-ray diffraction data measured on (a) CdS(400 nm) and on (b) CdS(39 nm) at room temperature against pressure.

Drickamer (1961), that bulk CdS undergoes a first-order structural phase transition from a wurtzite (low-pressure phase) to a rock-salt structure (high-pressure phase) around 2.5 GPa. Thus, the  $P_t$  value obtained for the commercially purchased powder with a microcrystal diameter of 400 nm is comparable to that reported for bulk CdS. The fact that the phase transition occurred at a similar pressure to that of bulk CdS indicates that the physical properties of this microcrystal are analogous to those of bulk CdS.

The results of a similar experiment on CdS (84 nm) are shown in Fig. 2. At atmospheric pressure ( $P = 0$  GPa), a sharp peak occurred at  $\sim 265$   $\text{cm}^{-1}$ . With pressure, the peak showed a blue shift up to  $290$   $\text{cm}^{-1}$  at 3.7 GPa. With a further increase in pressure, a broad and strong absorption appeared around  $220$   $\text{cm}^{-1}$  at  $P = 4.1$  GPa. The new band corresponds to the absorption due to the surface phonon in the high-pressure phase after lattice transformation. This result indicates that the lattice transformation in CdS (84 nm) occurred at some pressure between 3.7 and 4.1 GPa. We carried out similar experiments on other CdS microcrystals and found that microcrystals of smaller diameter show a higher transition pressure for lattice transformation.

#### 4. High-pressure X-ray diffraction

In order to discover the change in structure of the microcrystals due to the lattice transformation under pressure, high-pressure X-ray diffraction data were collected at room temperature. Fig. 3 shows the development of the diffraction pattern of (a) CdS(400 nm) and (b) CdS(39 nm) with pressure. In this figure, pressures and indexing of both wurtzite (W) and zinc blende (ZB) structure for the low-pressure phase and those of rock-salt (NC) structure for the high-pressure phase are indicated. In Fig. 3(a) for CdS(400 nm), the high-pressure phase began to appear at 2.6 GPa and finished at 3.4 GPa in the upstroke pressure. On the other hand, the high-pressure phase in CdS(39 nm) appeared at 3.2 GPa and finished at 5 GPa. This result confirms the transition pressure of microcrystals obtained by far-IR transmission measurements under pressure. The precise changes in peak positions of the diffraction lines with pressure were measured for different microcrystals and used to obtain the lattice constant of



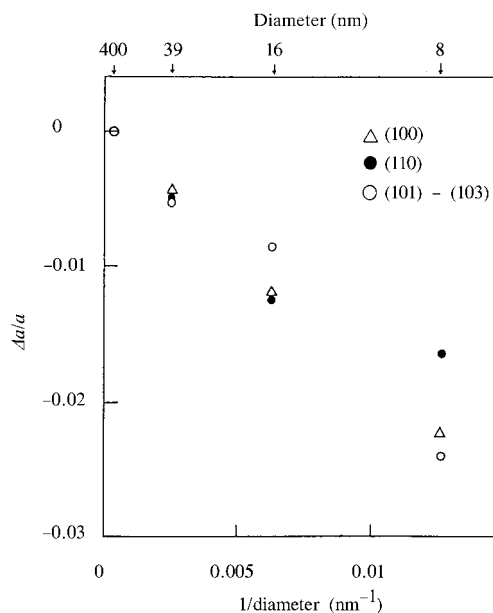
**Figure 4**  
Changes in the lattice constants of CdS(39 nm) with pressure. Note that the curve for (101) - (103) is shifted for clarity.

each CdS microcrystal at atmospheric pressure. A typical example of the changes in the lattice constants of CdS(39 nm) microcrystals against pressure for each index is shown in Fig. 4. These data were used to obtain the lattice constant at atmospheric pressure. Fig. 5 shows plots of the fractional changes in the lattice constants of CdS microcrystals with different diameters at atmospheric pressure as a function of the inverse microcrystal diameter. Data were normalized to that of CdS(400 nm), because CdS(400 nm) shows physical properties similar to those of bulk crystals, and is thus considered to work as a reference sample. Fig. 4 shows that microcrystals with smaller diameter shrink almost proportionally to the inverse diameter.

#### 5. Discussion and conclusions

The fact that the  $P_t$  value of a microcrystal with smaller diameter is enhanced was proved by experiments under high pressure in both the far-IR and the X-ray regions. We consider the following possibilities for such enhancement: (a) the existence of surface tension and (b) an increase in free energy in the microcrystals. Microcrystals with smaller diameter undergo a larger surface tension, because the surface tension exerts a radical pressure on the surface by a factor of  $2\gamma/r$ . Here,  $\gamma$  is the bulk surface energy. The X-ray diffraction data shown in Fig. 5 confirm the existence of such surface tension, which is in proportion to the inverse diameter. Stronger surface tension will give rise to a higher  $P_t$  value, because surface tension produces a hardening of the microcrystal, which gives a similar effect with the reinforcement of bonding. In addition, the role of the lattice imperfections, such as lattice defects and dislocations, and the friction between the grain boundaries in the microcrystals may contribute to the increase in free energy in the microcrystals. The increase in free energy may enhance the transition pressure.

A surface phonon band for the high-pressure phase of CdS microcrystals was found to be very broad compared with that for



**Figure 5**  
Changes in the lattice constants of CdS microcrystals with different diameters at normal pressure against inverse diameter. Points represent data obtained by (100), (110), (101) and (103) diffraction peaks.

the low-pressure phase, as seen in Figs. 1 and 2. The broadening of the surface phonon band for the high-pressure phase originates from the intrinsic properties of the phonon state at high pressures. The large width of the phonon band in the high-pressure phase could be attributed to a shorter lifetime of the phonon state.

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