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Resonance Raman scattering and optical absorption studies of CdSe microclusters at high pressure

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The pressure dependence of the HOMO–LUMO transition energy and the frequency of the longest wavelength longitudinal optical vibration of 45 Å diameter CdSe clusters in methanol–ethanol solution have been measured up to 50 kbar. The LO mode shifts to higher frequency at a rate of 0.43 cm⁻¹/kbar, which corresponds to a Grüneisen parameter of 1.1. The HOMO–LUMO transition shifts to higher energy at 4.5 meV/kbar, yielding a deformation potential of 2.3 eV. The pressure dependence of these properties closely resemble those of the corresponding bulk solid, confirming the point of view that the lattice properties of these clusters resemble those of the bulk, even though the optical properties are quite distinct.

INTRODUCTION

Experimental advances in preparing semiconductor clusters of 20–200 Å diameter, and the realization that their electronic structure differs significantly from that of the corresponding bulk solids, has sparked intense interest in these materials.¹ It is well established that the electronic energy levels in these microclusters are shifted to higher energy due to quantum confinement. Other properties of the electronic excited states of semiconductor clusters have been considered in detail within the context of simple models, which predict many interesting phenomena.^{2,3} A major assumption throughout this work is that the lattice properties of the clusters are the same as those of the bulk material.

From the standpoint of lattice dynamics, the cluster size of 20–200 Å is an interesting regime, because it approaches the limit of boundary conditions set by the theory. Within this range, the surface to volume ratio is changing enormously, and the effects of surface reconstruction and surface tension will eventually manifest themselves even in the “bulk” properties of the cluster. Several experiments on platinum and gold particles in this size regime demonstrate that surface tension results in a contraction of the lattice constant in clusters.⁴ 45 Å clusters consist of about 1800 atoms, are eight unit cells across, and half the atoms are in the surface layer. In platinum and gold, the lattice parameter for this size cluster is reduced by almost 4%. In contrast to these metals, semiconductors exhibit very directional, covalent bonding, with open tetrahedral structures, so that the effect may not be similar in these systems. Nonetheless, a 4% lattice contraction in CdSe would cause a +0.09 eV blueshift of the band gap, compared to the +0.71 eV shift due to quantum confinement, and the –0.18 eV energy of the Coulomb attraction between the electron and hole. Thus, the lattice properties of these clusters are of interest from many different points of view.

X-ray or electron diffraction techniques can provide direct information on bond length contractions, but the resolu-

tion is ultimately limited by the finite size of the cluster. For a 45 Å cluster, the resolution is limited to about 1%–2%. Measurement of the vibrational and electronic properties of clusters under high pressure is another very sensitive method for determining the lattice properties. In particular, two important quantities, the mode Grüneisen parameters, and the deformation potential can be measured. The Grüneisen parameters provide a measure of the anharmonicities of the vibrations, and are determined by the overlap of the ground state atomic wave functions in adjacent sites. The deformation potential gives information about the effect of increased overlap in adjacent sites on the excited electronic states.

We present here high pressure resonance Raman and optical absorption data on CdSe clusters in the 35–55 Å diameter range, consisting of approximately 1800 atoms. The surface Se atoms are bonded to phenyl groups in order to passivate the surface and prevent aggregation. These clusters are crystalline, with the zincblende structure, the lattice constant has been determined by x-ray diffraction to be 6.05 ± 0.6 Å, in close agreement with the bulk value of 6.052 Å.⁵ These are the smallest clusters which have been studied under high pressure to date. A previous study of the effect of pressure on the LO vibration of much larger CdS clusters, 300 Å in diameter, containing 550 000 atoms, has appeared recently.⁶ In addition, pressure induced phase transitions in large metallic tin clusters have been studied.⁷ The pressure dependence of the LO phonon frequency and the band gap of bulk wurtzite CdSe have also been studied previously.^{8–10}

EXPERIMENTAL AND RESULTS

The preparation and characterization of the CdSe cluster samples used in these experiments has been presented in detail elsewhere.⁵ These clusters were annealed by refluxing in 4-methyl pyridine at 150 °C. The cluster samples have been characterized using transmission electron microscopy, x-ray powder diffraction,⁵ small angle x-ray scattering, and high pressure liquid chromatography,⁵ as well as by resonance Raman, infrared absorption, and transient hole burning.^{11–13}

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The CdSe clusters dissolved in pyridine were dispersed in a 4:1 methanol-ethanol solution which served as the pressure transmitting medium in most of the high pressure work. If the amount of pyridine was too high, the pyridine would crystallize out at moderate pressures,¹⁴ and hence an optimal concentration of pyridine had to be determined by trial and error. A typical solution contained 4 methanol:1 ethanol:0.5 pyridine, and contained 0.1% by weight CdSe clusters. A satisfactory dispersion in methanol-ethanol had an orange color and the solution was clear, and remained so even up to the highest pressures in the experiment. Some Raman experiments were performed on clusters homogeneously dispersed in polystyrene, also at approximately 0.1% by weight.

Raman and optical absorption measurements on the cluster solution were performed in a gasketed diamond anvil cell.¹⁵ Pressure was measured by the ruby fluorescence technique.¹⁶ In a typical experiment the 100 μm thick 301 tempered stainless steel gasket had a hole 200 μm in diameter. In some experiments, particularly for optical absorption, a 200 μm diameter hole was drilled in an unindented gasket blank, giving a 250 μm pathlength.

In the resonance Raman experiments the incident 530 nm light was from a cw dye laser pumped by the 477 nm line of an argon ion laser. The dye laser linewidth was 0.3 cm^{-1} . The Raman scattered light was isolated using a SPEX Triplemate, and the spectrum was collected using a Photometrics CCD camera. The resonance Raman of the CdSe clusters at atmospheric pressure has been described in detail elsewhere.¹² Briefly, when the incident radiation is resonant with the cluster HOMO-LUMO transition, a single Raman peak is observed at 205 cm^{-1} . This mode has been assigned as the longest wavelength totally symmetric longitudinal optical vibration supported by the cluster.

The resonance Raman spectra of the clusters at three pressures are shown in Fig. 1, and Fig. 2 shows the shift of the frequency of this peak as a function of pressure. The filled circles are data points taken on clusters in methanol-ethanol, and the open squares are data points taken on clusters in polystyrene. The straight line through the data represents a least-squares fit from which we obtain $d\omega/dP = 0.43 \text{ cm}^{-1}/\text{kbar}$. At pressures above 50 kbar, the Raman peak was no longer observable. The laser frequency was not tuned as the pressure was increased, so that the loss of intensity is at least in part due to off resonance conditions as a result of the pressure shift of the electronic level. However, the frequency of the mode which is observed has been shown not to depend on the laser frequency over a broad range.¹² No evidence of hysteresis in the vibrational frequency was observed.

Optical absorption measurements were performed with a micro-optic setup that has been described previously.¹⁷ An Oriel 200 Watt tungsten lamp contained in a suitable housing was used as the source. The focusing optics and aperture on the housing gave a spot larger than the diameter of the hole in the gasket. Finer focusing was unnecessary, since the sample filled the entire volume of the cell in this case. White light passed through the cell was collected through the microscope, into a fiber optic, and was dispersed using a Jarrell-Ash 0.5 m monochromator. The transmitted light in-

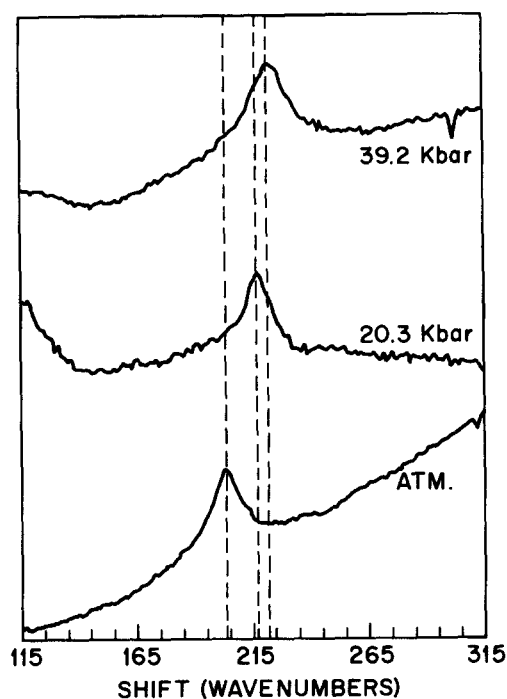


FIG. 1. The resonance Raman spectra at three different pressures of 45 Å diameter CdSe clusters in methanol-ethanol solution.

tensity at each wavelength was measured using an RCA C31034 Phototube and an electrometer interfaced to a PC. Scans obtained with the sample in the cell were ratioed to scans in which a methanol-ethanol blank was in the cell, and the logarithm of this ratio, or the sample OD, is shown in Fig. 3 for three pressures (other pressures have been omitted for the sake of clarity).

The spectra in Fig. 3 show features which are typical of II-VI cluster samples smaller than the bulk exciton. The

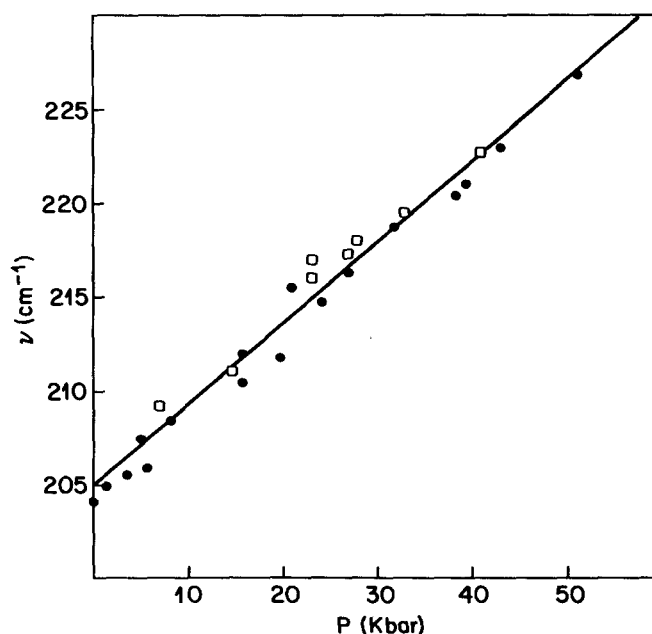


FIG. 2. The dependence of the resonance Raman peak on pressure. Dark circles are for points obtained with the clusters in a solution consisting of four parts methanol to one part ethanol. Open squares are for clusters embedded in polystyrene.

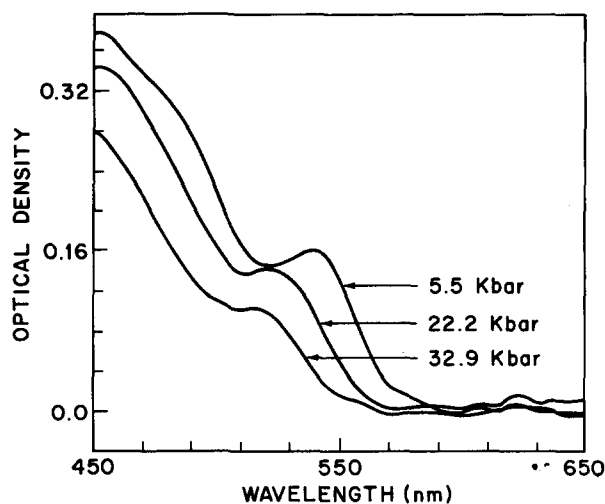


FIG. 3. The electronic absorption spectrum of 45 Å diameter CdSe clusters in methanol-ethanol solution at three different pressures.

characteristic features are a broad shoulder at the absorption onset, with a continuously rising absorption on the high energy side. The shoulder is due to the HOMO-LUMO transition in the clusters, and its width is determined by the inhomogeneous distribution of cluster sizes in the sample (estimated at 10% variation in diameter). The HOMO-LUMO transition in these samples at atmospheric pressure occurs at 2.2 eV, shifted from 1.84 eV for the bulk band gap. The HOMO-LUMO absorption edge shifts to higher energy with increasing pressure. The shape of the spectrum does not appear to change, but the overall optical density of the sample does decrease with increasing pressure. The OD does not recover when the sample is returned to lower pressure, but the energy of the absorption also showed no hysteresis.

In another set of experiments the optical density of the sample was deliberately set very high, so that the transmission went from 100% to 0% within 20 nm of the onset of absorption. This experiment gave a set of shifted absorption curves which remained coparallel up to 50 kbar (see Fig. 4). From these two experiments we have determined that the shift of the HOMO-LUMO transition energy with pressure

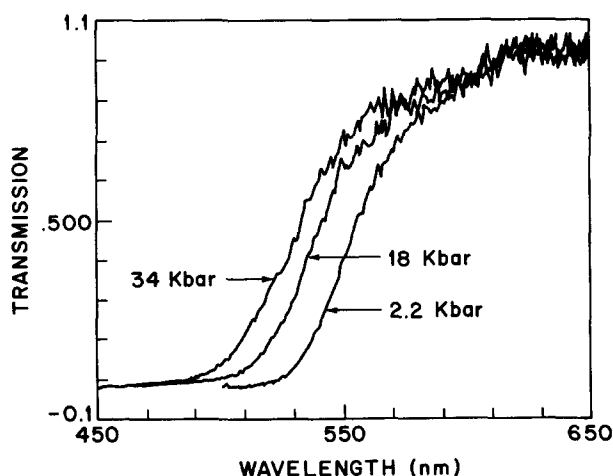


FIG. 4. Transmission curves at high optical density for three different pressures.

is 4.5 ± 0.2 meV/kbar. The spectra in Fig. 3 show that the absorption higher in energy than the HOMO-LUMO transition blue shifts in the same manner.

DISCUSSION

A. Determination of the Grüneisen parameter

From the pressure dependence of the LO vibrational mode, the mode Grüneisen parameter defined by

$$\gamma_i = \frac{B_0}{\omega_{LO}} \left(\frac{d\omega_i}{dP} \right)$$

can be obtained where ω_i is the mode frequency and B_0 is the bulk modulus. Neither the bulk modulus nor γ_i have been measured for the zincblende phase of CdSe. B_0 was therefore obtained using the Andersen-Nefe plot, which exhibits a linear relationship when $\ln B$ is plotted against $\ln V_0$, where V_0 is the specific volume for the related structures. We obtain 530 ± 10 kbar for the bulk modulus of cubic CdSe from such a plot, which included the Zn chalcogenides and CdTe. Using this value for the bulk modulus and our measured pressure dependence we get $\gamma_i = 1.1$. This value is in good agreement with the Grüneisen parameters for the LO mode of bulk II-VI semiconductors generally.^{18,19}

CdSe has been shown to transform to the NaCl structure in the interval 25–29 kbar pressure.^{9,20} At such a structural transition the Raman peak should disappear, because first order Raman scattering is symmetry forbidden for the NaCl lattice. It is well known, however, that the zincblende-rocksalt phase transition is not sharp, and the two phases coexist over a large pressure range.²¹ In high pressure Raman studies on bulk CdS,²² as well as in very large CdS clusters,⁶ the intensity of the LO mode is observed to decrease only gradually above the phase transition pressure. In our experiments we continue to observe the Raman peak up to 50 kbar, with decreasing intensity above 30 kbar. The decrease in intensity may not be meaningful because pressure is tuning the laser off resonance. Because of the difficulties associated with calibrating the intensity of the Raman line as increasing pressure changes the sample OD, and because no peaks are associated with the high pressure phase, resonance Raman scattering is not a good technique for studying the phase transition in II-VI clusters.

Determination of the deformation potential

The optical absorption of the Cd chalcogenides under pressure was first investigated by Edwards and Drickamer.⁸ For CdSe they report a blue shift of the band gap of 3.7 meV/kbar. More recently, Mei and Lemos have reported a blue shift of 5.8 meV/kbar for wurtzite CdSe, from high pressure photoluminescence measurements.⁹ Our measurements on 45 Å diameter zincblende clusters show a shift of the absorption onset to higher energy with increasing pressure of 4.5 meV/kbar, in good agreement with the bulk measurements. This shift yields a value of 2.3 eV for the deformation potential of the HOMO-LUMO transition in the clusters, which is consistent with a recently calculated value of 2.1 eV for the bulk deformation potential for zincblende CdSe.²³

SUMMARY AND CONCLUSIONS

The focus in this work has been on the pressure dependence of those properties which are most important in the theory of quantum confinement in semiconductor clusters, the bulk properties of the cluster. Specifically, the deformation potential for the HOMO–LUMO transition and the Grüneisen parameter of the longest wavelength longitudinal optical vibration in 45 Å CdSe clusters have been determined to be 2.3 eV and 1.1, respectively. These measurements support the conclusion that the lattice properties of 45 Å diameter CdSe clusters closely resemble those of the corresponding bulk solid, even though the electronic excited states of these particles differ considerably from the bulk. This is consistent with the fact that the lattice properties are determined by local, nearest neighbor forces, whereas the characteristic length scales which are important for the optical electronic properties are much longer. In contrast with the situation in noble metals, there is no observable effect of surface reconstruction or surface tension on the lattice properties of the interior of the cluster, despite the fact that half of the atoms are in the surface layer. It is not clear how general this result is. It could change with different types of surface passivation processes on CdSe, and it could be different for clusters of other semiconductors. The properties we have measured relate to the electron and hole in the $1S$ state, and the wave function for this state has a node on the surface, so that these measurements are weighted strongly towards the interior of the cluster. Other properties of the clusters will depend on the detailed configuration of the surface, including fluorescence emission, and vibrational modes of the clusters which could be observed in Raman scattering off resonance, and the pressure dependence of these is of great interest.

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