Structural transformations and metastability in semiconductor nanocrystals

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STRUCTURAL TRANSFORMATIONS AND METASTABILITY IN SEMICONDUCTOR NANOCRYSTALS


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Pressure-induced structural phase transitions have been studied in CdSe, CdS, InP and Si semiconductor nanocrystals. Nanocrystals transform via single nucleation of the phase transition with a kinetic barrier that increases in increasing cluster size. The structural transition path causes a shape change in the nanocrystals, which dictates the surface energy and thus the kinetic and thermodynamic stability of the transformed nanocrystal. These finite size effects can be used to tune the metastability of the nanocrystals versus pressure. Enhanced metastability allows structural and optical measurements in a regime inaccessible to the bulk solid, as well as possible recovery of the dense high pressure phase to atmospheric pressure.

Keywords: Metastability; Nanocrystal; Phase transition; High pressure; Kinetics

1. INTRODUCTION

Solid–solid phase transitions often involve multiple steps, such as nucleation followed by growth, and the rate-limiting step can vary with the material and the conditions (Hanneman et al., 1964). Details of the dynamics of the various processes are often obscured by other steps or dominated by impurities or defects (Turnbull, 1956). In addition, the kinetics can dominate observations of the phase transition and conceal experimental information about the relative thermodynamic energies of

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the various phases (Besson et al., 1991; Xiaoyuan and Jeanloz, 1987). The pressure behavior of several bulk semiconductors has been well-studied, however, results can vary depending on the experimental conditions. For example, pressure gradients can cause inhomogeneous strain and lower the phase transition pressure in single crystals (Besson et al., 1991).

For these reasons it is desirable to study phase transitions in systems with a finite number of atoms. As the size of the material is reduced, the kinetics of the phase transition are simplified and are dominated by nucleation. This has been observed in liquid to solid phase transitions in small metal droplets (Turnbull, 1950; 1952). In addition, if defects can be easily removed from the system, homogeneous nucleation will be observed. In a finite, perfect system, kinetics of phase transitions from one crystal structure to another will directly reflect the actual motion of the atoms along the transition path and all atoms, including those on the surface, will contribute to the total energy of a given crystalline phase. It may then be possible to observe the mechanistic details of the phase transition.

The phase diagram and kinetic stability of a crystalline phase depend on size. Therefore, size can be used as a synthetic tool. An obvious example of this effect is the appearance of carbon in the form of C\text{60} and its derivatives which are not present in bulk carbon (Kroto et al., 1985). Also well-known is the melting point depression in small metal (Buffat and Borel, 1976; Peppiatt and Sambles, 1975) and semiconductor (Goldstein et al., 1992) clusters. The lower melting point allows the formation of thin films of solids by heating an array of clusters at lower temperatures than feasible for conventional thin film preparations of the same material (Pehnt et al., 1995).

Pressure can also be combined with size to alter the structural stability. Semiconductor nanocrystals remain stable well above the pressure at which the extended semiconductor changes phase (Tolbert and Alivisatos, 1995a). Once the nanocrystals transform to the high pressure phase, increased metastability is also observed in the reverse direction with decreasing pressure. Similar results have been observed for semiconductor thin films (Cui et al., 1992). High pressure structures of many semiconductors are metallic, thus it is of interest to be able to recover the high pressure phase at ambient conditions. In addition, the wider range of stability under pressure for nanocrystals results in the
ability to study various bond-length dependent properties such as compressibility and electronic features in a wider pressure regime than available for conventional bulk materials.

Semiconductor nanocrystals are an ideal sample for phase transition studies due to the high quality of samples that can be achieved. The optical absorption of a semiconductor cluster shifts with size, and this "quantum size" effect has driven nanocrystal research and caused the continuous refinement of nanocrystal synthesis (Alivisatos, 1996). Semiconductor nanocrystals can currently be synthesized in the 15–500 Å range, containing $10^2$–$10^7$ atoms. They can be made with narrow size distributions (approximately 5% deviation in diameter for the prototypical sample, CdSe) and are highly crystalline. Defects can easily be annealed out at modest temperatures since, in addition to the reduced melting temperature, a defect need only travel a distance on the order of a nanometer to reach the surface.

As synthesized, the surfaces of semiconductor nanocrystals are capped with organic ligands that serve to passivate the surface bonds, prevent agglomeration, and allow the clusters to be dissolved in a variety of solvents depending on the nature of the ligands. This allows the surface energy to be adjusted to observe the effect on the phase transition. In addition, in a sample of nanocrystals prepared for pressure-induced phase transition studies, the nanocrystals are dissolved in an organic pressure medium and each nanocrystal remains separated. Therefore, the effect of any defect is localized to a single nanocrystal and transformation in any one nanocrystal will not affect the others. This is opposite to what commonly occurs in a bulk solid, where nucleation typically occurs at defects and the phase transition can then propagate throughout large neighboring areas of the solid.

In addition to the fine synthetic control, nanocrystals of semiconductors are a good choice for pressure-induced phase transition studies due to the general high pressure properties of semiconductors. Semiconductors have open, directional bonding, and thus typically undergo transformations to denser phases in the range of 1–20 GPa, pressures that can be easily reached with a diamond anvil cell. These first order phase transitions are accompanied by a discontinuous change in volume, often as large as 15–20%, and an increase in coordination number, both of which can cause strain and local disorder in transformed bulk solids (Venkateswaran et al., 1992).
Current synthetic methods allow for the study of phase transitions in nanocrystals ranging from the more ionic CdS and CdSe to the more covalent InP and Si. Tetrahedrally-bonded semiconductors typically occur in either the cubic zincblende or hexagonal wurtzite structures. Both zincblende and wurtzite are four-coordinate structures, but one of the second nearest neighbor distances is shorter in wurtzite. Therefore, wurtzite is favored by the more ionic binary semiconductors (Lawaetz, 1972) such as CdS and CdSe, although the zincblende forms are very close in energy.

Semiconductors commonly transform under pressure from a four-coordinate to a six-coordinate or distorted six-coordinate structure. In general, as the ionicity decreases, the first high pressure phase tends towards a metallic, lower symmetry structure. Experimental results for CdS and CdSe show structural phase transitions from the wurtzite phase to the six-coordinate rock salt phase at about 3.0 GPa (Edwards and Drickamer, 1961; Onodera, 1969; Yu and Gielisse, 1971), and zincblende CdS transforms to rock salt at approximately the same pressure (Corll, 1964). InP naturally occurs in the zincblende phase and also transforms to rock salt, but at a higher pressure of 10.8 GPa (Jamieson, 1963a; Menoni and Spain, 1987; Minomura and Drickamer, 1962). Si has a very rich phase diagram. Of interest to this paper is the conversion of Si from the diamond structure (zincblende with identical atoms) to the pseudo-six-coordinate beta-Sn structure at approximately 11 GPa (Jamieson, 1963b; Weinstein and Piermarini, 1975), followed by two other higher-coordinate phases and then the primitive hexagonal phase at approximately 16 GPa (Hu and Spain, 1984; McMahon et al., 1994; Olijnyk et al., 1984). Rock salt CdS and CdSe are semiconductors (Yu and Gielisse, 1971), whereas rock salt InP (Jamieson, 1963a; Menoni and Spain, 1987) and all of the high pressure phases of Si are metals (Jamieson, 1963b).

This paper reviews studies of pressure-induced phase transitions in semiconductor nanocrystals including CdS (Chen et al., 1997), CdSe (Tolbert and Alivisatos, 1995b), InP (Herhold et al., 1996), and Si (Tolbert et al., 1996) clusters. Section 2 covers details that are important to these experiments. The effect of size on the phase transition kinetics is examined in Section 3, including some recent high temperature work by Chen et al. Section 4 looks at the effects of the transition path on cluster shape. In Section 5, the effect of the surface on the phase transition
behavior is examined. Finally, Section 6 discusses the implications of high pressure metastability induced by finite size for both the discovery of new materials and the study of properties in a new pressure regime.

2. EXPERIMENTAL DETAILS

CdSe (Katari et al., 1994; Murray et al., 1993) and InP (Guzelian et al., 1996; Micic et al., 1994) nanocrystals were synthesized from organometallic precursors in coordinating solvents at high temperatures. Si nanocrystals were synthesized by gas pyrolysis of Si$_2$H$_6$ and O$_2$ (Littau et al., 1993). Cd$_{32}$S$_{14}$(SC$_6$H$_5$)$_{36}$DMF$_4$ clusters were synthesized according to the literature preparation (Herron et al., 1993). These clusters were monodisperse with a Cd$_{32}$S$_{50}$ zincblende core of 15 Å diameter.

The pressure range of 1–30 GPa necessary for these experiments can be easily accessed with diamond anvil cells (Jayaraman, 1986). For the experiments described here, a combination of piston-cylinder and Merrill-Bassett style diamond anvil cells was used. The Merrill-Bassett cell, although limited to a lower pressure range (10–15 GPa for the cells used here), is physically smaller, and is therefore easier to heat the sample by heating the entire cell. Temperature gradients in the sample are then negligible since the entire cell is heated. To reach temperatures up to 600 K, the cell was resistively heated inside a small ceramic oven. The main body of the cell, including bolts and washers, was built out of Inconel 718 to reduce thermal expansion effects on cell pressures. Temperatures were measured using a K-type thermocouple attached to the steel gasket. In all experiments, pressures were measured with standard ruby fluorescence techniques (Barnett et al., 1973).

X-ray diffraction is used to determine the crystal structure before and alter the phase transition. In addition, peakwidths in X-ray diffraction powder patterns are inversely proportional to the crystalline domain size due to Debye-Scherrer broadening (Guinier, 1963), which permits crystallite size to be extracted from the diffraction data. Therefore, it is essential to collect diffraction patterns using angle-dispersive rather than energy-dispersive techniques, since the latter has much lower resolution and information about size from the peakwidths would be difficult to obtain.
X-ray diffraction in the very small sample volume of a diamond anvil cell on samples with broad diffraction peaks requires the focused radiation of a synchrotron source. Powder X-ray diffraction was performed on wiggler beamline 10-2 at the Stanford Synchrotron Radiation Laboratory with a photon energy of 12–20 keV. X-ray powder diffraction patterns were collected in angle-dispersive mode using image plate detection. The resulting powder patterns were then angle-integrated to obtain the diffraction data shown here (for example, see Fig. 2). All nanocrystals studied were small enough that the peakwidths were significantly broader than the instrument resolution.

Bulk rock salt CdSe and CdS are indirect gap semiconductors with phonon-assisted electronic transitions and thus weak, featureless absorption spectra (Edwards and Drickamer, 1961). The band gaps are also red-shifted compared to the low pressure phases. Rock salt nanocrystals were also found to be indirect gap despite their small size (Tolbert et al., 1994b), and therefore the absorption spectrum changes dramatically in the high pressure phase and optical absorption can be used to complement X-ray diffraction data. For absorption experiments, it is essential that the nanocrystals be completely dispersed in the pressure medium to avoid scatter from undissolved sample. Absorption data were collected with a scanning visible–UV Cary Model 118 spectrometer with 2 nm resolution and scan times ranging from 30 min at room temperature to 6–7 min at high temperature. Type II diamonds were used to measure absorption down to 250 nm for the Cd$_{32}$S$_{50}$ clusters.

Important to all high pressure experiments is the choice of surrounding pressure medium. In order to keep the nanocrystals separated from each other, the pressure medium must be chosen so that the nanocrystals are soluble at all conditions of the experiment. Different pressure media can be used if the ligand on the surface of the nanocrystal is changed accordingly. This allows a study of the effect of the ligand/pressure medium interface on the phase transition. CdSe and InP nanocrystals were synthesized with a capping group of tri-n-octyl phosphine oxide (TOPO). For the room temperature work on CdSe and InP nanocrystals, 4-ethyl pyridine was used as the pressure medium, and it also displaced TOPO as the surface ligand. For the work on CdSe kinetics, however, 4-ethyl pyridine could not be used due to its reactivity at high temperatures and pressures. Instead, ethylcyclohexane was used.
as the pressure medium and TOPO remained as the capping group. Si nanocrystals, coated with a layer of silicon oxide, were dispersed in ethylene glycol as a pressure medium. The small CdS clusters were pressurized in two different pressure media: a 3:1 mixture of tetrahydrofuran (THF) and methanol, and a 3:1 mixture of THF and chloroform. All solvents remained hydrostatic under the conditions of these experiments with pressure gradients of no more than 0.5 GPa for pressures up to 10 GPa. Note that each individual nanocrystal does not feel a pressure gradient due to its small size.

3. KINETICS

3.1. Hysteresis

First order pressure-induced phase transitions commonly exhibit a hysteresis between the upstroke and downstroke transformation pressures, as shown for CdSe nanocrystals in Fig. 1. Hysteresis is observed in a wide variety of phase transitions, such as the behavior of magnetic clusters in an applied magnetic field (Jing et al., 1996) and the supercooling of a liquid below its freezing point (Turnbull, 1956). As indicated by the schematic curves at the top of Fig. 1, there is no transformation at the thermodynamic transition pressure where the free energies of the two phases are equal. Instead, the sample must be overpressurized to overcome the kinetic barrier. If the kinetic barrier is the same in both the forward and reverse phase transitions, the hysteresis curve will be symmetric about the thermodynamic transition pressure. There is evidence for this symmetry in the phase transitions of bulk semiconductors (Venkateswaran et al., 1992), although cases of asymmetry do exist in other materials (Rubie and Brearley, 1994).

Also indicated in Fig. 1 are the pressures of the forward and reverse phase transitions for bulk CdSe taken from the literature (Edwards and Drickamer, 1961; Onodera, 1969; Yu and Gielisse, 1971). There are several important things to note about this data. First, the hysteresis in 43 Å CdSe nanocrystals is approximately 3 times that observed in the bulk solid, corresponding to a larger kinetic barrier. Second, the midpoint of the hysteresis curves is shifted to higher pressure. This effect will be discussed in Section 5. The result of these two effects is that
FIGURE 1  Hysteresis curves for the four- to six-coordinate transformation in 43 Å CdSe nanocrystals at 383 (open circles) and 433 K (solids circles). Data were obtained from optical absorption and X-ray diffraction measurements. Thin arrows indicate directions of increasing and decreasing pressure. Volumes were derived from integrating the optical absorption features to obtain the fraction of wurtzite and rock salt present and calculating the volume from the data in Tolbert and Alivisatos (1995b). Solid arrows give the approximate positions of the bulk CdSe upstroke and downstroke phase transition pressures. The schematic representation directly above the hysteresis curves depicts changes in the potential energy curves of the two structures with pressure. On the top is the proposed transition pathway (Tolbert and Alivisatos, 1995b).

the forward phase transition in CdSe nanocrystals occurs at a much higher pressure than in the bulk solid. This elevation of phase transition pressure in finite size is general and has been observed in all nanocrystals studied here as well as CdS$_x$Se$_{1-x}$ nanocrystals in glass matrices (Silvestri and Schroeder, 1995) and small Sn particles (Kapitanov et al., 1986).
3.2. Single Nucleation

In order to understand the hysteresis, X-ray diffraction was collected on the samples at high pressure, as shown in Fig. 2A for InP nanocrystals (Herhold et al., 1996). The nanocrystals are stable above the bulk phase transition at 10.8 GPa. In addition, after transformation, the nanocrystal size is maintained, as indicated by the same peakwidths before and after the phase transition shown in Fig. 2B. Therefore, each nanocrystal transforms coherently from one phase to the next. The phase transition nucleates only once in each crystallite, since the time required for the entire nanocrystal to transform is less than the time between successive nucleation events (Turnbull, 1950).

This is in contrast to what occurs in a typical bulk semiconductor in a pressure-induced phase transition, as shown for a powder of bulk InP in

![Graph showing X-ray diffraction data](image)

**FIGURE 2** (A) X-ray diffraction on 50 Å InP nanocrystals showing the phase transition from zincblende to rock salt with increasing pressure. The 200 zincblende peak is very weak and not visible in these scans. (B) The zincblende (111) peak (solid line) at ~0.5 GPa and the rock salt 200 peak (dotted line) at >15 GPa centered at ΔQ = 0 and scaled to the same height.
Fig. 3A. Here, the peakwidths broadened dramatically after the phase transition (Fig. 3B), demonstrating that the initial single crystals (approximately 10 microns in size) had fractured into several smaller domains. Evidence for domain fracture in bulk semiconductors is seen in transmission electron microscopy (TEM) taken of GaAs single crystals after cycling through the phase transition (Besson et al., 1991). This fracturing is the result of multiple heterogeneous nucleation of the phase transition at defects or other catalytic sites in the initial crystals. In the case of bulk InP, additional effects such as strain and domain shapes may be causing the peaks corresponding to different lattice reflections to have different widths (Wright et al., 1993). For example, the shape of the resulting crystalline domains may reflect which directions are favored for growth of the phase transition. Analysis of the high pressure X-ray and TEM of recovered bulk samples can
provide some insight into the preferred orientation for propagation of the phase transition, but the interpretation is often difficult (Besson et al., 1991; Rubie and Brearley, 1994; Wright et al., 1993).

The peakwidths of the different lattice reflections of rock salt InP nanocrystals are the same, thus transformation-induced strain is not present. However, nanocrystals are still affected by the transition path, as will be discussed in the following sections. Single nucleation of the phase transition indicates that nanocrystals are below the critical size for nucleation of the high pressure phase. This agrees with data collected on bulk-like GaAs and AlAs epilayers which find that the domain size in the recovered zincblende phases after pressurization are ~65 Å for GaAs and ~175 Å for AlAs (Venkateswaran et al., 1992). X-ray diffraction of pressure-induced phase transitions in 20–45 Å CdSe nanocrystals (Tolbert and Alivisatos, 1995b) and 492 Å Si clusters (Section 4) demonstrate that they also transform via single nucleation. Therefore, nucleation of the phase transition in nanocrystals is simpler than the behavior of the bulk solid.

3.3. High Temperature Kinetics

In many cases, it is not known what determines the barrier to nucleation. There are many theories on nucleation kinetics (Turnbull, 1956), and it would be useful to compare the theories to quantitative measurements of the barrier. Kinetics are most readily measured by varying the temperature. High temperature experiments on a few pressure-induced phase transitions have yielded estimates of the kinetic barriers and also of the Clapeyron slope between the two structures (which depends on the thermodynamic changes in entropy and volume between the two phases) (Jeanloz, 1987; Xiaoyuan and Jeanloz, 1987), but the majority of materials have not been studied.

CdSe nanocrystals were chosen for the high temperature kinetics study of pressure-induced phase transitions by Chen et al. due to the well-studied room temperature behavior (Tolbert and Alivisatos, 1995b). Figure 1 shows hysteresis curves for CdSe nanocrystals at two different temperatures. As the temperature increases, the hysteresis narrows noticeably. In these cases, the measurement time is on the order of 10 min. However, as the temperature is raised even higher while maintaining a constant pressure above the midpoint of the hysteresis
curve, the rate of conversion from wurtzite to rock salt becomes comparable to the observation time, and the kinetics can be measured directly. An example of the wurtzite to rock salt transformation in 34 Å CdSe nanocrystals versus time is shown for two temperatures in Fig. 4. The forward phase transition follows unimolecular kinetics, as to be expected if the dominant step in the phase transition is homogeneous single nucleation.

Transformation rates at multiple temperatures can be used to estimate the kinetic barrier height from a simple Arrhenius model. Barrier heights have been calculated for the forward wurtzite to rock salt phase transition in CdSe nanocrystals at 4.9 GPa with two temperature points for each size. These results are shown in Fig. 5. The barrier height increases from 0.5 to 2.3 eV as the size increases from 23 to 43 Å. Note that 4.9 GPa is not the midpoint of the hysteresis (see Fig. 1). In addition, as will be discussed in Section 5, the midpoint (approximately

![Graph](attachment:image.png)

**FIGURE 4** Transformation from wurtzite to rock salt with time for 34 Å CdSe nanocrystals at a constant pressure of 4.9 GPa and two temperatures. The differential of optical density (O.D.) was calculated by subtraction of the first absorption feature in the wurtzite phase in two consecutive spectra. The linear fits shown are used to calculate the rate constant at each temperature.
FIGURE 5 Changes in kinetic barrier height versus size (number of unit cells) for TOPO coated CdSe nanocrystals in ethylcyclohexane at 4.9 GPa. The number of unit cells was calculated using the sizes obtained from optical absorption measurements and TEM. The volume of a unit cell is $1.124 \times 10^{-28} \text{m}^3$ obtained from Tolbert and Alivisatos (1995b).

taken to be the thermodynamic transition pressure) shifts with size. These issues complicate the determination of the kinetic barrier at the actual thermodynamic transition point. However, the shift in thermodynamic transition point is small, and thus the observed trend in size for the kinetic barrier at 4.9 GPa is still meaningful. This trend with size will not extrapolate to the bulk solid, because in the bulk, nucleation is heterogeneous and therefore has a lower barrier than in nanocrystals (see Fig. 1).

The data shown in Fig. 5 scale roughly with the number of atoms, which is proportional to the cluster volume. This trend with number of atoms was theoretically predicted for the conversion of the beta-Sn structure to the diamond structure in Si nanocrystals at atmospheric pressure by Brus et al. (1996). They propose that the energy required for
transformation per unit cell is constant, and therefore the total barrier height per cluster increases with increasing cluster size. This makes the transformation barrier an extensive property of the system. If transformation in a bulk solid occurred as homogeneous nucleation of the phase transition in the entire crystal at once, the kinetic barrier would be very large and transformation would only occur at very high pressures, as predicted for Si by Mizushima et al. (1994).

4. TRANSITION PATH

Single nucleation of the phase transition in nanocrystals allows for a study of the actual transition path. Nucleation of the phase transition is predicted to occur as a cooperative motion of the atoms along a specific transition coordinate (Brus et al., 1996), analogous to the diffusionless transformations observed in martensitic materials (Christian, 1975). Since nanocrystals remain intact during the phase transition, motion along the transition path will cause a shape change. Nanocrystals are synthesized at high temperatures so that each cluster has the same well-defined shape that is determined by minimizing the surface energy. Therefore, given a unique transformation path, each nanocrystal will convert to the same final shape in the high pressure phase. Structural transformations in nanocrystals are thus analogous to molecular isomerizations. Shape changes have been observed in macroscopic single crystals in temperature-induced phase transitions (Fraser and Kennedy, 1972; 1974), however, pressure-induced shape changes are obscured in bulk crystals due to multiple nucleation effects (Besson et al., 1991; Venkateswaran et al., 1992).

Evidence for this path-induced shape change can be observed in the high pressure X-ray diffraction collected on 492 Å Si nanocrystals (Tolbert et al., 1996), where the diamond phase nanocrystals were stable well above the bulk transition pressure to beta-Sn. This large elevation of the phase transition pressure in a sample with a significantly large number of atoms (~10^7) is a result of the dependence of kinetic barrier on size as discussed in the previous section.

An expanded view of the diffraction pattern for the 492 Å Si nanocrystals in the primitive hexagonal phase at 21 GPa is given in Fig. 6, and it reveals that the peakwidths differ for the [001] and [100] directions.
These peakwidths describe a cluster that is 549 ± 68 Å in the [001] direction and 267 ± 10 Å in the [100] direction, and thus has an aspect ratio of 2.1 ± 0.3. As-synthesized diamond phase Si nanocrystals are spherical as determined by TEM (Littau et al., 1993). By deforming the spherical cluster according to the proposed changes in the unit cell in order to reach the primitive hexagonal phase, the resulting particle should have an aspect ratio of approximately 1.9 (Chang and Cohen, 1985; Lewis and Cohen, 1993; Needs and Martin, 1984; Yin and Cohen, 1982), which agrees well with the experimentally observed aspect ratio. Therefore, the X-ray diffraction pattern in Fig. 6 agrees with that expected for a Si cluster that has coherently changed shape during the phase transitions according to the predicted atomic motions.

5. SURFACE EFFECTS

The presence of a large fraction of atoms on the surface will affect both the kinetics and the thermodynamics of the phase transition. Breaking
and rearrangement of surface bonds is most likely occurring during the phase transition. Early data on 45 Å CdS clusters demonstrated that changing the surface from a more labile ligand to a thicker coating of a more rigid ligand increased the upstroke phase transition pressure from 6.5 to 8.0 GPa (Haase and Alivisatos, 1992). To further investigate the question of surface effect, very small clusters are ideal for study since surface effects are most pronounced in the smallest sizes.

Shown in Fig. 7 are hysteresis curves for the zincblende to rock salt phase transition in Cd$_{32}$S$_{50}$ clusters in two different pressure media by Chen et al. Note that there are actually two interfaces of importance: the interface between the bare surface of the semiconductor cluster and the organic capping ligands, and the interface between the ligands and the pressure medium. Both are important; in this experiment, the latter was changed.

Immediately noticeable are the widths of the two hysteresis curves, which are about a third of the width for the larger CdSe nanocrystals shown in Fig. 1. This small kinetic barrier is predicted from the trend of barrier height with size discussed in Section 3.3 for such a small number of atoms. In addition, the widths of the Cd$_{32}$S$_{50}$ curves change as the interface between the surface ligands and the surrounding pressure medium changes. Thus, there are several identifiable regimes for pressure-induced solid–solid phase transition kinetics. In very small clusters, the surface will dominate the kinetic barrier because there are so few atoms. As the cluster size increases, the interior term dominates, and the kinetics depend strongly on the number of atoms present. Finally, as the material approaches bulk-like dimensions, defects and other catalytic sites are more likely to be present, nucleation is heterogeneous, and the kinetics are dominated by other effects.

In addition to the effect on the kinetics, the surface also strongly affects the thermodynamic transition point in these small clusters. The entire hysteresis curve in Fig. 7 shifts to higher pressure as the pressure medium is changed. In order to understand the shift of the thermodynamic transition point, these results can be compared to the room temperature pressure behavior of larger CdSe nanocrystals.

The hysteresis at room temperature for the wurtzite to rock salt phase transition in CdSe nanocrystals has been investigated as a function of size (Tolbert and Alivisatos, 1995b), and the upstroke phase transition pressure was observed to shift to higher pressures in smaller sizes. This effect cannot be explained by the kinetics observed at high temperature,
which would suggest the opposite trend. Rather, this is the result of the shift of the entire hysteresis curve to higher pressure.

By taking the transition pressures as the midpoints of the hysteresis curves, it was found that the thermodynamic transition point shifts with size as $1/\text{radius}$, indicating that it depends on the surface to volume ratio. This is similar to the case of melting point depression in metal
(Buffat and Borel, 1976; Peppiatt and Sambles, 1975) and semiconductor (Goldstein et al., 1992) particles. The surface energy of the liquid is lower than that of the solid. Therefore, as the cluster size is reduced, the difference in energy between the solid and liquid phase increases, and the liquid is stabilized at lower temperatures. In the case of the pressure-induced wurtzite to rock salt phase transition, the surface energy of the rock salt nanocrystal must be higher than that of the wurtzite nanocrystal, resulting in the observed elevation of the phase transition pressure with decreasing cluster size.

Rock salt phases can form low energy surfaces such as the (100) surface which has only one dangling bond per atom (Oshcherin, 1976). However, the rock salt nanocrystal formed by the wurtzite nanocrystal undergoing a phase transition will not be the thermodynamically lowest energy structure of rock salt if the temperatures are low compared to diffusion of surface atoms. Rather, the rock salt nanocrystal will have a shape dictated by the transition path from wurtzite to rock salt and the initial wurtzite cluster shape. Note that the lower symmetry of the high pressure phases of Si allow observation of the shape change because the crystallographic directions are non-degenerate. However, in the case of CdSe and InP, the first high pressure phase is rock salt, which has cubic symmetry and thus all diffraction peaks are three-fold degenerate. As a result, the shape change is not enough to make a noticeable difference in the rock salt nanocrystal diffraction peaks.

The possible transformation path has been discussed previously, and a two-dimensional representation is depicted in Fig. 1. By transforming a wurtzite cluster with the known cluster shape (Shiang et al., 1995) into rock salt using the predicted transition path, an elongated rock salt structure is formed with a mixture of high and low index surfaces (Tolbert and Alivisatos, 1995b) and thus a higher surface energy than that of the initial thermodynamically formed wurtzite cluster. Note that the shift in thermodynamic transition point with size is small in this size range, and kinetics dominate the phase transition behavior.

6. METASTABILITY

The broad hysteresis in large nanocrystals gives them greater metastability than the bulk for both the low pressure and high pressure
phases. In fact, as observed in the hysteresis curves for CdSe nanocrystals, the rock salt phase is almost recovered at atmospheric pressure. There are examples of bulk solids where the high pressure phase is metastable at atmospheric pressure, such as MgTe (Li et al., 1995), AlN (Xia et al., 1993), and GaP (Itie et al., 1989). In addition, there are materials such as Si (You-Xiang et al., 1986) which transform to various metastable phases upon release of pressure that are different from both the high pressure phase and the thermodynamically stable atmospheric phase. However, most bulk materials recover to their initial phase at atmospheric pressure, and thus their denser phases only exist at high pressure.

The stability under pressure depends on the cluster size and surface, with the surface energy dominating in the smallest clusters and the number of atoms dictating the behavior as the size is increased. Lowering the temperature will possibly allow temporary recovery of the high pressure phase in nanocrystals, but a better, more permanent method may be to try different interfaces. The highest kinetic barrier will be in a large, defect free nanocrystal with a surface that stabilizes the nanocrystal against transformation. This surface is possibly one that provides a rigid environment which inhibits rearrangement of surface atoms. An example of using the surface for stabilizing novel materials is the synthesis of rock salt CdS nanocrystals at atmospheric pressure in an ionic polymer matrix, where the clusters are stable with respect to conversion back to the four-coordinate phase (Lin et al., 1994).

Additional methods of recovering the high pressure phase to atmospheric pressure may be first annealing the high energy surfaces of the transformed cluster at high pressure before releasing the pressure, or even synthesizing the nanocrystals in the high pressure phase. This latter idea has been demonstrated in GaN crystallites synthesized under modest pressures and high temperatures, where a small portion of the nanocrystals retained the high pressure rock salt phase (Xie et al., 1996).

The extended phase stability of nanocrystals also allows the study of properties at conditions inaccessible to the extended solid. For example, shown in Fig. 8(a) is X-ray diffraction for InP nanocrystals with increasing pressure, with Fig. 8(b) depicting the corresponding change in unit cell volume versus pressure. Also shown is the Murnaghan equation of state (Murnaghan, 1944) fit with the bulk values for $B_0$ and $B'_0$ (Menoni and Spain, 1987) for comparison. Although the Murnaghan
FIGURE 8  (a) X-ray diffraction on 50 Å zincblende InP nanocrystals with increasing pressure. See Fig. 2 for indexing of the peaks. The extra peaks at 11.4 GPa are due to gasket diffraction. (b) Volume contraction of the unit cell with increasing pressure for the same sample. Unit cell volumes are calculated from the 111 (solid triangles), 220 (solid circles), 311 (solid squares) zincblende peaks and the 111 (open triangle), 200 (open circle) and 220 (open square) rock salt peaks. The solid line is a fit to the Murnaghan equation of state fit with bulk InP values.

equation of state is somewhat simplistic, the qualitative result is that the compressibility of the nanocrystals above the bulk phase transition deviates from that predicted by the bulk compressibility values. This is somewhat intuitive, as above the bulk phase transition, the atoms of the solid are experiencing an increased repulsive force and therefore the compressibility is lower than expected. This effect has also been observed in CdSe nanocrystals (Tolbert and Alivisatos, 1994a).

Enhanced stability also permits a study of electronic and optical properties of the material in a new regime. For example, under pressure, GaAs converts from a direct to an indirect gap without an accompanying structural transformation (Wolford and Bradley, 1984). This is the result of the different pressure coefficients of the direct and indirect gaps in the electronic band diagram. InP has a larger initial band gap, which delays the direct to indirect gap transition until higher pressure.
very close to the structural transformation to the high pressure metallic phase (Gorczyca et al., 1989; Menoni et al., 1986; Muller et al., 1980). As a result, it has been difficult to characterize and confirm the possible change in the electronic structure. However, since InP nanocrystals are stable well above the bulk structural phase transition, it may be possible to study the direct to indirect gap crossover more easily in nanocrystals than in the bulk solid.

Schroeder has utilized the extended pressure stability in finite size to study high pressure photoluminescence and Raman scattering in semiconductor nanocrystals at high pressures. Using this technique, he has measured electron-phonon coupling strengths (Silvestri and Schroeder, 1994) and electronic defect levels (Zhao et al., 1991) to pressures above the bulk structural transition.

7. CONCLUSIONS

Pressure-induced phase transitions in semiconductor nanocrystals ranging from the more ionic CdSe and CdS to the covalent InP and Si show similar results. Nanocrystals transform under pressure by homogeneous nucleation, with one nucleation event per nanocrystal. In fact, these transformations can be termed unimolecular isomerizations of a large number of atoms. The simplicity of the pressure behavior compared to the complicated kinetics observed in bulk solids suggests that nanocrystals are a good candidate for time-resolved studies of transition dynamics.

If the temperature is high enough to collapse the hysteresis, the transformation will be governed by thermodynamics alone, and it may be possible to measure the dynamics of the phase transition. This may be most easily accomplished in the smallest clusters where the room temperature hysteresis is already narrow. This experiment will require a structural or optical probe on a very short time scale. A current study of nanosecond time-resolved crystallography on the dissociation of carbon monoxide in myoglobin demonstrates that such structural work is possible (Srajer et al., 1996), and the time scales may soon be reduced to picoseconds. Given the pronounced change in optical properties, the dynamics of the phase change may also be followed with currently available techniques of femtosecond optical spectroscopy.
The number of atoms and the choice of interface between surface, organic capping ligands, and pressure medium can be used to tune the stability of a material through thermodynamics and kinetics. In these experiments, size and surface, combined with pressure, are used as tools for synthesis of new metastable materials. It should be noted that high pressure is already used as a synthetic tool. For example, rare earth elements display an altered reactivity at high pressures (Badding et al., 1995) and many unsaturated organic molecules undergo pressure-induced polymerization (Drickamer and Frank, 1973). With size and surface, however, denser phases of materials that are only accessible at high pressures may be present at ambient conditions, such as the metallic high pressure phases of many semiconductors.

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