Thermodynamic Consideration on Solid Transition of CdSe Nanocrystals Induced by Pressure

Q. Jiang,* J. C. Li, and M. Zhao

The Key Laboratory of Automobile Materials, Ministry of Education and Department of Materials Science and Engineering, Jilin University, Changchun 130025, China

Received: February 18, 2003; In Final Form: July 28, 2003

The thermodynamic amount of the pressure-induced solid transition between the wurtzite phase and the rock-salt phase and the melting thermodynamic amounts of the metastable rock-salt phase for CdSe nanocrystals are considered based on known thermodynamic data of the wurtzite phase. Moreover, the static hysteresis width of the above solid transition is also determined. The predictions are found to be reasonable and are in agreement with the present theoretical and experimental results.

As the first-order structural transition, many solids transform to denser structures under applied pressure, resulting in materials with novel properties without any change in the material composition.[1] The structural transitions are utilized for such applications as steel hardening by martensite transition,[2] shape memory effect,[3] high fracture toughness in ceramics of zirconia,[4] and diamond film formation.[5]

Despite the importance of the solid transition for materials science, the microscopic mechanisms of solid−solid phase transition processes are comparatively more complicated to understand due to the inhomogeneous kinetic effect, the complicated effect of grain boundaries, defect formation, and often irreversible transition characteristic.[1−4] Theoretical estimates for lifetimes of metastable states can be off by many orders of magnitude because they must include largely unknown details of microscopic transition pathways.[1,6] It is interesting that when the material size is in nanometer range, the study of phase transitions may be simplified because small crystals can behave as single crystals and reproducibly cycle the transition without appearance of lattice defects, such as dislocations and grain boundaries, where there is only a single transition interface between the parent phase and the formed phase.[1,3,6] The existence of the single interface leads to a constant static pressure hysteresis width $P_w(t{\rightarrow}\infty)$ (t denotes the time), and this value can be estimated.[3]

High-pressure phases can persist in a metastable state at ambient pressure if sufficiently large energetic barriers and low transition temperatures hinder transition to the more energetically favorable structure; both are characterized by a large kinetic transition hysteresis loop width, $P_w(t{\rightarrow}0)$.[7] Some known examples are the high-energy structures of martensite in carbon steel relative to that of ferrite plus carbide,[2] and that of diamond relative to that of graphite.[5] It is interesting that, as the size of materials decreases, the metastable high-pressure phases and some denser parking phases that have not been found in bulk state are easily formed at ambient pressure. This phenomenon has been found in CdSe,[1,6,8] HgS,[9] ZnO,[10] ZnS,[11] GaAs,[12] Fe,[13] Co,[13,14] Cr,[15] and In.[16] The essential reason is that there exists size-dependent internal pressure P_i for an isotropic spherical or quasi-spherical nanoparticle with a diameter D by surface stress

* Corresponding author: fax +86/431-5705876; e-mail jiangq@jlu.edu.cn.

f through Laplace−Young equation,[17]

$$P_i = 4f/D \tag{1}$$

In light of the characteristic of the single-crystal transition and eq 1, the study of the solid transition of nanocrystals offers a chance to deepen our understanding for the metastable high-pressure phases and related kinetic phenomena. Among the studied systems,[1,6,8−16] CdSe nanocrystals can be used as model systems for structural studies because a large amount of experimental details for the transition from a wurtzite-like phase to a rock-salt-like phase have been determined.[1,6,8] In this contribution, the solid transition thermodynamics of CdSe nanocrystals under pressure, the thermodynamic melting properties of the high-pressure phase, and the static hysteresis loop width are considered. It is found that the calculated thermodynamic amount is in agreement with the available theoretical and experimental results, which in return confirm our general thermodynamic consideration for the solid transition under pressure.

According to the Laplace−Young equation and some thermodynamic assumptions,[17]

$$f = [(3h\gamma_{sl})/(4\kappa)]^{1/2} \tag{2}$$

where $\kappa = -\Delta V/(VP) = 1/B$ is the compressibility, with B being the volume elastic modulus,[17] and h the mean diameter of atoms in a crystalline lattice. The solid−liquid interface energy, γ_{sl}, has been determined in terms of Gibbs-Thompson equation,[18]

$$\gamma_{sl} = 2hS_{vib}H_m(T)/(3V_gR) \tag{3}$$

where S_{vib} is the vibrational part of the overall gram−atom melting entropy S_m, R is the ideal gas constant, V_g denotes the gram-atom volume, $H_m(T)$ is the temperature-dependent gram-atom melting enthalpy of bulk crystals. $H_m(T)$ is determined by Helmholtz function, $H_m(T) = G_m(T) - TdG_m(T)/dT$ where $G_m(T)$ denotes the temperature-dependent solid−liquid Gibbs free energy difference at $T < T_m$, with T_m being the melting temperature. For semiconductors, $G_m(T) = H_mT(T_m - T)/T_m^2$, with H_m being the bulk melting enthalpy at T_m.[19] This $G_m(T)$ function is obtained by assuming that the specific heat difference between solid and liquid ΔC_{psl} is a temperature independent

constant with its value equivalent to that at the isenthalpic temperature T_h, at which $H_m(T)$ goes to zero. T_h is expected to be close to T_k with T_k being the Kauzmann temperature or isentropic temperature where $\partial G_m(T)/\partial T = 0$.[18] Using $\Delta C_{psl} = H_m/(T_m - T_h)$, Hoffman has obtained the above $G_m(T)$ function. Thus, $H_m(T) = H_m(T/T_m)^2$ in terms of Helmholtz function and $T_k = T_m/2$.

When $T < T_k = T_m/2$, $H_m(T) = H_m(T_k)$.[17] This is because at $T < T_k$ the liquid can exist only in a glass form with a C_p value similar to that of the corresponding crystal, which leads to $\Delta C_{psl} \approx 0$ and $H_m(T)$ remains constant. Because the discussed solid transition of CdSe occurs at $T < T_k$,[1,6,8] $H_m(T) = H_m(T_k/T_m)^2 = H_m/4$ is taken.

In light of Mott's equation for semiconductors, $S_{vib} = (3R/2)\ln(\sigma_c/\sigma_l)$ where $\sigma_s/\sigma_l = (v_s/v_l)^2 = (\Theta_s/\Theta_l)^2$ with Θ_s, Θ_l, σ_s, σ_l, v_s, and v_l being the Debye temperatures, the electronic conductivities, and the vibrational frequencies of the crystal and the liquid, respectively, where the subscripts s and l denote the solid and liquid.[20] When v_s and v_l are unavailable, $S_m = R\{1 + 3\ln[\Theta_s/\Theta_l]\}$, or $S_{vib} \approx S_m - R$.[20] Substituting these relations for $H_m(T)$ and S_{vib} into eq 3,

$$\gamma_{sl} = h(S_m - R)H_m/(6V_gR) \tag{4}$$

To determine the thermodynamic amount of the solid transition, the thermodynamic amount of the high-pressure phase must first be known, which can be obtained from the available thermodynamic amount of the low-pressure phase. Let subscripts h and l denote the high-pressure and the low-pressure phases, respectively, and the pressure-dependent transition volume difference per gram atom $\Delta V_g(P)$ can be expressed approximately as $\Delta V_g(P) \approx \Delta V_{g0} + [\Delta V_h(P) - \Delta V_l(P)]$, where $\Delta V_{g0} = V_h(P = 0) - V_l(P = 0)$, $\Delta V_h = -V_hP_h\kappa_h$, and $\Delta V_l = -V_lP_l\kappa_l$. For CdSe crystals, the experimental evidences indicate that $\Delta V_g(P) \approx \Delta V_{g0}$,[6] or, $\Delta V_h(P) \approx \Delta V_l(P)$. Thus, $V_hf_h\kappa_h \approx V_lf_l\kappa_l$. In light of eq 2, this result implies that $f\kappa \propto H_m\kappa^{1/2} = c$, where c denotes a constant. Since H_m is related to the bond strength, $\kappa^{-1/2}$ thus is reasonably proportional to the bond strength. As result of the above approximation,

$$f_h \approx (V_l/V_h)(\kappa_l/\kappa_h)f_l \tag{5}$$

Because the specific heat difference between polymorphous solid phases of the same substance ΔC_{pss} is always small if no Curie transition between them occurs,[21] the melting entropies of such phases are approximately equal. Thus,

$$H_{mh} = H_{ml} - H_s \tag{6.1}$$

$$S_{mh} \approx S_{ml} \tag{6.2}$$

$$T_{mh} = H_{mh}/S_{mh} \tag{6.3}$$

where H_s denotes the solid transition enthalpy. Since H_{mh} may be determined through eqs 5, 2, and 4, H_s is given by eq 6.1.

According to the first thermodynamic law,

$$S_s = [H_s - P_e\Delta V_g(P)]/T \tag{7}$$

where S_s is the solid transition entropy and P_e shows the necessary pressure for the solid transition in thermodynamic equilibrium. Since the parent phase is the stable phase under ambient pressure, $H_s > 0$, $S_s > 0$, and $\Delta V_g < 0$.

In eq 7, P_e being an energy barrier going from one phase to other, is related to the Gibbs free energy difference between two phases G_{ss}. In our consideration, any energetic contribution

to the phase, such as surface energy difference of two phases $\Delta\gamma$, is taken as a part of G_{ss}. Thus, $\Delta\gamma$ affects the size of P_e through G_{ss}. Since such parameters are unknown, P_e in this work is determined by considering the relationship between P_e and $P_w(t\rightarrow 0)$. Based on the experimental results, $P_w(t\rightarrow 0)$ is observed to be temperature dependent but size independent.[1,6,8] While the former is understandable due to the kinetic nature of the hysteresis formation,[7] the latter should be valid within a limited size range where only a single transition interface is present with the interface energy between both phases γ_{ss}, which is a thermodynamic quantity of a size $P_w(t\rightarrow\infty)$. If the remaining hysteresis width of $P_w(t\rightarrow 0) - P_w(t\rightarrow\infty)$ induced by the kinetic effect is contributed from both transition directions in the same size, the total transition barrier in the forward and reverse transition directions has the same size of $P_w(t\rightarrow 0)/2$ as a first-order approximation. Therefore, $P_e = P_f + P_{if} - P_w(t\rightarrow 0)/2 = P_r + P_{ir} + P_w(t\rightarrow 0)/2$, where P_f and P_r are the forward and the reverse transition pressures, respectively, and $P_w(t\rightarrow 0) = P_f - P_r$. In light of eq 1, $P_{if} = 4f_f/D$ and $P_{ir} = 4f_r/D$. With these relationships and simple mathematical treatment,

$$P_e = \bar{P} + 4\bar{f}/D \tag{8}$$

where $\bar{P} = (P_f + P_r)/2$ and $\bar{f} = (f_f + f_r)/2$. Since $\bar{f} > 0$, $P_e > \bar{P}$. With the calculated value of H_s and S_s in terms of eqs 6.1 and 7, the transition temperature at ambient pressure T_s is obtained as

$$T_s = H_s/S_s \tag{9}$$

After the determination of the above thermodynamic quantities, the static parts of the hysteresis width $P_w(t\rightarrow\infty)$ could be determined in light of the equation $P_w(t\rightarrow\infty) = -2\gamma_{ss}A_g/\Delta V_g$,[3] where A_g denotes the gram-atom interface area. According to the standard combining rule for this cross term, $\gamma_{ss} = (\gamma_{ssh} + \gamma_{ssl})/2$ is taken. Since the grain boundary energy is double the corresponding γ_{sl} value,[18] $\gamma_{ss} \approx \gamma_{slh} + \gamma_{sll}$. For a spherical or quasi-spherical nanocrystal with a unique transition interface, the maximal A_g value is $n\pi D^2/4$, with $V_g = n\pi D^3/6$ where n is the nanocrystal number of one gram-atom crystal, or $A_g = 3V_g/(2D)$. Substituting γ_{ss} and A_g values into the above equation,

$$P_w(t\rightarrow\infty) = -3V_g(\gamma_{slh} + \gamma_{sll})/(D\Delta V_g) \tag{10}$$

Since eq 10 is applicable only for the transition of a single-crystal having one transition interface without dislocations, $D < 20-30$ nm should be satisfied.[22] Note also that although P_e can be determined by $P_w(t\rightarrow 0)$ in terms of eq 8 with some assumptions, $P_w(t\rightarrow 0)$ itself as a complicated multiparameter function of the activation energy, the activation volume and the time[1,6,8] cannot be determined directly in this work.

According to the above equations, the determined thermodynamic quantities for the wurtzite and the rock-salt phases of CdSe and related parameters are shown in Table 1. As shown in the table, $T_{mh} < T_{ml}$ and $H_{mh} < H_{ml}$ are understandable due to the metastable nature of the high-pressure phase. $\gamma_{mh} > \gamma_{ml}$ and $f_{mh} > f_{mL}$ because, on the surface, there is a higher bond density of the high-pressure phase than that of the low-pressure phase.[17,18] The determined value of $H_s = 2.51$ KJ g-atom^{-1} has a size similar to that of the theoretical calculation of $H_s = 3.16$ KJ g-atom^{-1},[25] and is one order smaller than H_m. It is expected that the sum of the total bond strengths of two phases is similar.[21] According to the estimated H_s value, S_s and T_s values are also obtained in terms of eqs 7 and 9.

Letters

J. Phys. Chem. B, Vol. 107, No. 50, 2003 **13771**

TABLE 1: Necessary Parameters for the Calculation of the Transition Behavior of CdSe

parameters	results	ref
h_l (nm)[a]	0.219	7,24
h_h (nm)[b]	0.286	7,25
V_{gl} (cm^{3}g-atom^{-1})[c]	16.90	
V_{gh} (cm^{3}g-atom^{-1})[c]	14.01	
ΔV_g(cm^{3}g-atom^{-1})[c]	−2.89	
$\Delta V_g/V_g$[c]	−0.171	
T_{ml} (K)	1525	23
H_{ml} (KJg-atom^{-1})	22.78	23
S_{ml} (Jg-atom^{-1}K^{-1})	14.94	23
S_{vibl}(Jg-atom^{-1}K^{-1})	6.624	23
κ_l (10^{-12}Pa^{1-})	21.9	24
κ_h (10^{-12}Pa^{1-})	17.4	25
γ_{sll} (mJm^2)	39.20	eq 4
γ_{slh}(mJm^2)	54.94	eqs 5, 2, 4
f_l (Jm^2)	0.542	eq 2
f_h (Jm^2)	0.823	eq 5
H_{mh} (KJg-atom^{-1})	20.27	eqs 5, 2, 4
S_{mh} (Jg-atom^{-1}K^{-1})	14.94	23
S_{vibh}(Jg-atom^{-1}K^{-1})	6.624	eq 6.2
T_{mh} (K)	1357	eq 6.3
H_s (KJg-atom^{-1})	2.51	eq 6.1
S_s (Jg-atom^{-1}K^{-1})	31.3−40.9	eq 7
P_e(GPa)[d]	4.59−5.15	eq 8
T_s (K)	62−80	eq 9
$P_w(t\rightarrow\infty)$ (GPa×nm/nm)	1.65/D	eq 10

[a] $h_l = a^2/(6c) + c/4$ where $a = 0.430$ nm and $c = 0.701$ nm are the lattice constants of the wurtzite structure.[7,24] [b] $h_h = a/2$ where $a = 0.571$ nm is the lattice constant of the rock-salt structure.[7,25] [c] $V_g = N_0 v_a$ where N_0 is the Avogadro's constant and v_a the mean atom volume in the corresponding crystalline structure. $v_{al} = \sqrt{3}\ a^2c/8 = 0.02806$ nm^3 and $v_{ah} = a^3/8 = 0.02327$ nm^3. [d] To minimize the error during the estimation of $\bar{P}$ in eq 8, due to the uncertainty of the measured $P_w(t\rightarrow 0)$ values, the smallest value of $D = 2.5$ nm and $T = 425$ K and $T = 504$ K are taken,[6] where $P_f(425K) = 7.52$ GPa, $P_r(425\underline{K}) = 0.59$ GPa, $P_f(504K) = 6.01$ GPa, $P_r(504K) = 0.99$ GPa. Thus, $\bar{P}(425$ K$) = 4.09$ GPa and $\bar{P}(504$ K$) = 3.50$ GPa.

Under the assumption that the kinetic transition resistance in two transition directions has the same size, S_s and T_s values are determined by two sets of experimental data at different T.[1,6] It is found that $S_s > S_m$, which implies that structural change between two solid phases is larger than that between the solid and liquid. The obtained T_s value is much lower than room temperature. This result confirms the above assumption that the ΔC_{pss} value is small ($\Delta C_{pss} > 0$ since the high-pressure phase is metastable at the ambient pressure). The larger values of S_s and $\Delta T = T - T_s$ may be the reason that P_e value for the solid transition of CdSe is several orders larger than that for the usual martensite transition.[1,3,21]

In the size range of 2.5 nm $< D < 12.5$ nm,[6] 0.66 GPa $> P_w(t\rightarrow\infty) > 0.13$ GPa in terms of the result of $P_w(t\rightarrow\infty) = 1.65/D$. This result implies that the static hysteresis is size-dependent, although eq 10 is valid only for single crystals up to a value about $D = 20-30$ nm. Since $P_w(t\rightarrow 0) \approx 6$ GPa at room temperature and decreases as temperature increases,[6] which is one order larger than $P_w(t\rightarrow\infty)$, the size of $P_w(t\rightarrow 0)$ is mainly induced by the kinetic effect.

Because as D increases the reverse transition is absent,[8] it is plausible that $P_w(t\rightarrow\infty)$ is proportional to bond number on the transition interface, which is proportional to the interface area of D^2.[6] Thus, the size contribution on P_e through P_i is not evident, although $P_i \propto 1/D$.

In the above approach only general thermodynamic measurable quantities are utilized. Thus, the model seems to be applicable for other semiconductor compounds, such as GaAs, InAs, etc. However, since there is a lack of necessary experimental data used above, a comparison between the model prediction and experimental results fails. Thus, this work may provide only a possible thermodynamic way to determine the pressure-induced phase transitions.

In summary, the solid transition of CdSe nanocrystals and related thermodynamic amounts are considered. Moreover, the static hysteresis loop width is calculated. The obtained results are reasonable in comparison with theoretical and experimental results.

References and Notes

(1) Jacobs, K.; Zaziski, D.; Scher, E. C.; Herhold, A. B.; Alivisatos, A. P. *Science* **2001**, *293*, 1803.
(2) Salzbrenner, R. J.; Cohen, M. *Acta Metall.* **1979**, *27*, 739.
(3) Müller, I.; Xu, H. *Acta Metall. Mater.* **1991**, *39*, 263.
(4) Kelly, P. M.; Rose, L. R. F. *Prog. Mater. Sci.* **2002**, *47*, 463.
(5) Lu, W., Komvopoulos, K. *Appl. Phys. Lett.* **2003**, *82*, 2437.
(6) Jacobs, K.; Wickham, J. N.; Alivisatos, A. P. *J. Phys. Chem. B* **2002**, *106*, 3759.
(7) As T increases, $P_w(t\rightarrow\infty)$ dramatically decreases and $P_w(t\rightarrow\infty) \rightarrow P_w(t\rightarrow 0)$ in CdSe nanocrystals.[6] This temperature dependence of P_w will not be considered in this study.
(8) Wickham, J. N.; Herhold, A. B.; Alivisatos, A. P. *Phys. Rev. Lett.* **2000**, *84*, 923.
(9) Higginson, K. A.; Kuno, M.; Bonevich, J.; Qadri, S. B.; Yousuf, M.; Mattoussi, H. *J. Phys. Chem. B* **2002**, *106*, 9982.
(10) Decremps, F.; Pellicer-Porres, J.; Datchi, F.; Itié, J. P.; Polian, A.; Baudelet', F.; Jiang, J. Z. *Appl. Phys. Lett.* **2002**, *81*, 6.
(11) López-Solano, J.; Mujica, A.; Rodríguez-Hernández, P.; Muñoz, A. *Phys. Status Solidi B* **2003**, *235*, 452.
(12) Kodiyalam, S.; Kalia, R. K.; Kikuchi, H.; Nakano, A.; Shimojo, F.; Vashishta, P. *Phys. Rev. Lett.* **2001**, *86*, 55.
(13) Saito, Y.; Yoshikawa, T.; Okuda, M.; Fujimoto, N.; Yamamuro, S.; Wakoh, K.; Sumiyama, K.; Suzuki, K.; Kasuya, A.; Nishina, Y. *J. Appl. Phys.* **1994**, *75*, 134.
(14) Kitakami, O.; Sato, H.; Shimada, Y. *Phys Rev B* **1997**, *56*, 13849.
(15) Granqvist, C. G.; Buhrman, R. A. *J. Appl. Phys.* **1976**, *47*, 2200.
(16) Oshima, Y.; Nangou, T.; Hirayama, H.; Takayanagi, K. *Surf. Sci.* **2001**, *476*, 107.
(17) Jiang, Q.; Liang, L. H.; Zhao, D. S. *J. Phys. Chem. B* **2001**, *105*, 6275.
(18) Jiang, Q.; Zhao, D. S.; Zhao, M. *Acta Mater.* **2001**, *49*, 3143.
(19) Hoffman, J. D. *J. Chem. Phys.* **1958**, *29*, 1192.
(20) Zhang, Z.; Zhao, M.; Jiang, Q. *Semicond. Sci. Technol.* **2001**, *16*, L33.
(21) Jiang, Q.; Li, J. C.; Tong, J. *Mater. Sci. Eng. A* **1995**, *196*, 165.
(22) Lu, K. *Mater. Sci. Eng. R* **1996**, *16*, 161.
(23) Regel, A. R.; Glazov, V. M. *Semiconductors* **1995**, *29*, 405.
(24) Rabani, E. *J. Chem. Phys.* **2002**, *116*, 258.
(25) Rabani, E. *J. Chem. Phys.* **2001**, *115*, 1493.