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Factors to determine the pressure change tendencies in pressure-induced phase transition of semiconductor nanocrystals

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HIGHLIGHTS

- Size-dependent phase transition pressure for nanocrystals is discussed.
- Variation tendencies of phase transition pressure can be determined.
- Surface energy, surface stress and gram-atom volume are the decisive parameters.
- Individual contributions of surface energy and surface stress are clarified.
- Model predictions agree well with the experimental and theory results.

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ABSTRACT

A critical rule without free parameters to estimate the size-dependent enhancement or reduction of phase transition pressure $\Delta P_e(D)$ for phase transitions of nanocrystals is established where D denotes the size of nanocrystals. $\Delta P_e(D)$ function is determined by D, surface energy γ, surface stress f and gram-atom volume V_g of the two transition phases. Also, the individual contributions of γ and f on $\Delta P_e(D)$ can be separated. Our model predictions agree well with the corresponding experimental and theoretical results. This model is of fundamental significance in understanding the essence of size-dependent pressure induced phase transition and guiding the experimental scientists to estimate their results.

1. Introduction

Pressure-induced phase transition of nanocrystals has attracted much interest in recent years since the produced nanophases show different physical and chemical properties from the original phases, there are new applications in various industrial fields [1–3]. However, an important new phenomenon, what the external pressure needed to trigger phase transition of nanocrystals $P_e(D)$ could be larger or smaller than the corresponding bulk one $P_e(\infty)$, remains physically to be unclear.

It is well known that for the pressure-induced phase transitions the density of metastable high pressure phase is larger than that of the corresponding stable phase under ambient pressure, or their gram-atom volume V_g, obtained as dividing the mole volume by the atom number per unite, which denotes the corresponding volume per mol atom, follows $V_L > V_H$ with subscript L and H denoting the ambient stable phase and metastable high pressure phase respectively. This is also the case of nanocrystals. However, $P_e(D)$ is size-dependent [4–19] and could be larger or smaller than $P_e(\infty)$. The former case includes transitions of Fe_2O_3 from γ to α (γ–α) [4], ZnS from cubic sphalerite to hexagonal wurtzite (s–w) [5,6] and CdSe [7], ZnO [8–10] from wurtzite to rocksalt (w–r) transitions, etc. However, in the transitions of CeO_2 from cubic fluorite to orthorhombic α-$PbCl_2$ (c–o) [11], AlN from wurtzite to rocksalt (w–r) [12], and ZrO_2 from monoclinic to tetragonal (m–t) [13], Fe and $Fe_{90}Cu_{10}$ from bcc to hcp [14], a depression of $P_e(D)$ is observed. The inhibition of $P_e(D)$ has been attributed to be the contribution of size-induced volumetric expansion and the softening of both the Poisson ratio and shear modulus [12]. Moreover, cubic bixbyite to hexagonal corundum transition (bcc–rh) of In_2O_3 [15,16] and rutile to fluorite transition of SnO_2 [17] show that $P_e(D) \approx P_e(\infty)$, while reduction for In_2O_3 and enhancement for SnO_2 of $P_e(D)$ have also been reported recently [18,19]. Such a variety of results always puzzled experimental scientists and theoretical workers. Consequently, exploring

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the origin of these differences and finding a uniform rule to describe these phenomena become a significant work.

Thermodynamic theories can accurately describe the energy transfer and change for the pressure-induced phase transition. Several thermodynamic models have been proposed to investigate the size-dependent phase transition of nanocrystals. As considering the contributions of surface, edge, and corner to the Gibbs free energy (G) within different shapes, Barnard et al. successfully described the phase transition behaviors of group IV [20] semiconductors and TiO_2 nanocrystals [21,22]. The D–T phase diagram of Hf nanoparticles was established on the basis of the Debye model of the Helmholtz free energy, well fitting to experimental data [23,24]. In addition, the P- and D-induced phase transition temperatures for CdSe, Fe_2O_3, CdS and SnO_2 nanocrystals have been estimated by incorporating the bond-order-length-strength (BOLS) correlation mechanism [25,26], showing that the competition between the effects of P and D dominates the phase transition of nanocrystals. Since D of nanocrystals decreases, the surface/volume ratio of nanocrystals is large, and the influences of the surface stress f and the surface energy γ on the phase transition become significant [27–31]. Moreover, $P_e(D)$ value can be separated roughly into three parts, i.e. the ratio of the volume collapse, the surface energy difference of two phases, and the bulk internal energy difference [9]. However, the effect of f on $P_e(D)$ in the above consideration is neglected. Note that γ describes the reversible work per unit area to form a new solid surface, whereas f denotes the reversible work per unit area due to the elastic deformation, which equals the derivative of γ with respect to the strain tangential to the surface. Although the above experimental and theoretical results have enriched our understanding on $P_e(D)$ functions, a thermodynamic model is needed to quantify the functions.

In this paper, the contributions of f and γ on $P_e(D)$ of nanocrystals are discussed based on our early model for solid transition of nanocrystals [27–31], and a simple rule for $P_e(D)/P_e(\infty)$ is proposed to estimate the variation trends of $P_e(D)$ function. The results will help us to understand why there exists pressure increasing or decreasing during a pressure-induced transition of nanocrystals.

2. Methodology

Under a certain conditions of P, T (temperature in Kelvin), and D, a phase having the smallest Gibbs free energy (G) value in this system should be the stable one. As the system reaches an equilibrium state between two phases, their Gibbs free energy difference disappears, namely $\Delta G = 0$. At constant T, P and D are thermodynamic variants for ΔG function, which consists of roughly three components: the bulk Gibbs free energy difference $\Delta G(\infty)$; the size dependence of surface energy difference $\Delta G_s(D)$; as well the size and pressure dependences of elastic energy difference $\Delta G_e(P,D)$ [29], namely,

$$\Delta G(P,D) = \Delta G(\infty) + \Delta G_s(D) + \Delta G_e(P,D) \tag{1}$$

where $\Delta G(\infty)$ is expressed as [28],

$$\Delta G(\infty) = -P_e(\infty)\Delta V \tag{2}$$

with $\Delta V = V_H - V_L$ where subscripts H and L denote the phases after and before the transition under pressure. $\Delta G_s(D)$ has been deduced by γ and V_g [27–31],

$$\Delta G_s(D) = 6(\gamma_H V_H - \gamma_L V_L)/D. \tag{3}$$

$\Delta G_e(P,D)$ function is influenced both by P_{in} (the internal pressure induced by f) and P_e, namely $P = P_{in} + P_e$. When $P_e \approx 0$, $P = P_{in}$. According to the Laplace–Young equation,

$$P_{in} = 4f/D \tag{4}$$

with f being approximately taken as the solid–liquid interface stress f_{sl} [28–31],

$$f_{sl} = (hD_0 S_{vib} H_m B/16VR)^{1/2} \tag{5}$$

where h is atomic diameter, B is the bulk modulus, $D_0 = 3h$ for ideal spherical particles, R is the ideal gas constant, H_m is the bulk gram-atom melting enthalpy at T_m, S_{vib} is the vibrational part of the overall gram-atom melting entropy S_m and $S_{vib} \approx S_m$ for the oxides and semiconductors. Considering Eq. (4) and the definition of ΔG_e, there is [27–31],

$$\Delta G_e(P,D) = P_H V_H - P_L V_L = 4(f_H V_H - f_L V_L)/D + P_e(D)\Delta V \tag{6}$$

At equilibrium, $\Delta G(P,D) = 0$. In terms of Eqs. (1)–(3) and (6), we have,

$$P_e(D) = P_e(\infty) - \frac{6(\gamma_H V_H - \gamma_L V_L)}{D\Delta V} - \frac{4(f_H V_H - f_L V_L)}{D\Delta V}, \tag{7.1}$$

or,

$$\frac{P_e(D)}{P_e(\infty)} = 1 - \frac{6(\gamma_H V_H - \gamma_L V_L)}{DP_e(\infty)\Delta V} - \frac{4(f_H V_H - f_L V_L)}{DP_e(\infty)\Delta V} \tag{7.2}$$

In light of Eq. (7.1), if $\Delta P_e = P_e(D) - P_e(\infty) > 0$, if we define $\Delta(\gamma V) = \gamma_H V_H - \gamma_L V_L$, and $\Delta(fV) = f_H V_H - f_L V_L$, we have,

$$3\Delta(\gamma V) + 2\Delta(fV) > 0 \tag{8.1}$$

Against that, if $\Delta P_e < 0$, then,

$$3\Delta(\gamma V) + 2\Delta(fV) < 0. \tag{8.2}$$

We note that Eq. (7.1) can also be rewritten as,

$$\Delta P_e D = -\frac{[\Delta 6(\gamma V) + \Delta 4(fV)]}{\Delta V} = \kappa \tag{9}$$

where the right part of Eq. (9) is size-independent, κ is a constant for a certain two phase system, denoting a strong (or weak) increasing (or decreasing) trend of $P_e(D)$ as D drops.

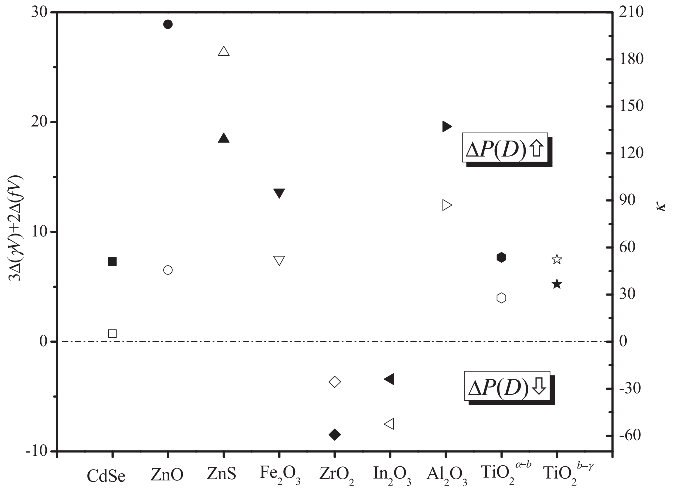

Fig. 1. The rule to estimate enhancement or reduction of $P_e(D)$ is determined by γ, f and V_g between two phases in terms of Eqs. (8.1) and (8.2), and the κ value based on Eq. (9) describe the intensity of dependence of ΔP_e on D. The dot-dash line denotes $3\Delta(\gamma V) + 2\Delta(fV) = 0$ where $\Delta P_e(D) = 0$. The closed and open symbols corresponding to the left and right coordinate respectively.