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Pressure induced phase transformation and instability of ZnS and ZnSe nanocrystals

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ABSTRACT: A simple theoretical approach has been proposed to study the compressional and elastic behavior of nanomaterials using the size dependent equation of state under high pressure. The volume compression, being the main factor to identify the change in transition pressure during transformation from zinc blende (ZB) structure to the rock salt (RS) structure, is determined as a function of pressure. The application of equation of state has also been extended to analyse the pressure dependence of second order elastic constants (SOECs) of ZnS and ZnSe nanosemiconductors in order to judge the mechanical instability at their respective transition pressures. A good agreement between the theory and experiment supports the suitability of the formulation used in the present study.

Keywords: Nanocrystals, volume compression, second order elastic constants, Equation of state.

I. INTRODUCTION:

All applied research consists of studying the pressure and temperature dependence of their physical properties with a view in preparing the material to exhibit the expected properties in specific conditions of thermal and mechanical stress environment. The pressure is attractive thermodynamical variable to explain several mechanical properties of most of the semiconductors and their alloys. High pressure studies of nanosemiconductors such as ZnS and ZnSe have attracted considerable attention due to their polymorphic structural transformation [1-6]. In an ambient condition, these nanosemiconducting crystals belong to the II-VI compounds and have the zincblende (ZB) structure. They have wide energy band gap and possesses the important applications in preparing illuminant film components and electronic devices at microscopic scale. Furthermore, this system is known to undergo a first-order phase transition from B3 (zinc blende) structure to B1 (rock salt) structure on application of mechanical pressure. In the experimental papers of Zhou et al [7] and Nemes et al [8], the pressure induced phase transition from B3 to B1 is documented as 15 GPa and 13.5 GPa in bulk ZnS and ZnSe crystals respectively whereas the experimental values of transition pressure (P_t) in ZnS and ZnSe nanocrystals are reported between (19- 23.1) GPa [5] and (10.6-13.6) GPa [6] respectively.

Not only the experiments but also some theoretical investigations with various model theories have been focused on their phase transitions [9-11]. Jaffe et al [9] reported that the ZB –RS phase transition in ZnS occurs at 16.1 GPa by using the Hartree-Fock linear combinations of atomic orbital method (LCAO). Miao and Lambrecht [10] reported the transition pressure (P_T) 14.5 GPa for ZnS using the pseudo potential and a plane wave method. For ZnSe, Smelyansky and Tse [11] obtained the ZB -RS transition pressure 20.8 GPa using the full potential linear augmented plane wave calculations whereas Varshney et al [12] obtained the ZB -RS transition pressure at about 18 GPa by using the Slater-Kirkwood variational method. However, in the present investigation the structural phase transition in ZnS and ZnSe nanocrystals are achieved at 19.5 GPa and 13.5 GPa respectively by using Kumar's Equation of state [18]. The present calculated values of transition pressure are found more close to experimental data as compared to those reported by previous theoretical investigators [9-12].

An understanding of the pressure dependence of elastic constants is the essential prerequisite to study the phase instability in materials. The elastic constants of the material play an important role in predicting and understanding the material response, strength, mechanical stability and phase transition. Only a few studies have been conducted on the mechanical properties of bulk materials ZnS and ZnSe at elevated pressures as well as pressure dependence of their elastic constants by using different experimental [13-14] and theoretical [15-17] methods. However, no theoretical studies are reported on the elastic properties of ZnS and ZnSe nanostructured crystals so far. For the first time, we have determined the pressure dependence of second order elastic constants of nanomaterials to study the instability behavior of these nanocrystals at transition pressure (P_t). The method of analysis is described in section 2 and results are discussed in section 3.

II. METHOD OF ANALYSIS

The equation of state (EOS) for nanomaterials in terms of the relative change in volume, V/V_0 , can be written as follows [18]:

$$P = a_1 \left(1 - \frac{V}{V_0}\right) + a_2 \left(1 - \frac{V}{V_0}\right)^2 \quad (1)$$

where P is the pressure, V/V_0 is the relative change in unit cell volume, a_1 and a_2 are the size dependent parameters, which may be determined from the definition of bulk modulus and its first order pressure derivative.

The bulk modulus B_T , is defined as,

$$B_T = V \left(\frac{\partial P}{\partial V} \right)_T \quad (2)$$

In view of equation (1), equation (2) can also be written as

$$B_T = \frac{V}{V_0} \left[a_1 + 2a_2 \left(1 - \frac{V}{V_0} \right) \right] \quad (3)$$

Using equation (2), the first order pressure derivative of bulk modulus B'_T can be obtained as

$$B'_T = \left(\frac{\partial B_T}{\partial P} \right)_T = - \frac{V}{B_T} \left(\frac{\partial B_T}{\partial V} \right)_T \quad (4)$$

which can be written in terms of size dependent parameters a_1 and a_2 as follows:

$$B'_T = - \frac{1}{B_T} \left(\frac{V}{V_0} \right) \left[a_1 + 2a_2 \left\{ 1 - 2 \left(\frac{V}{V_0} \right) \right\} \right] \quad (5)$$

Applying boundary conditions in equations (3) and (5), i.e. $B_T = B_0$ and $V = V_0$, we get

$$a_1 = B_0 \quad , \quad \text{and} \quad a_2 = B_0 \left(\frac{B'_0 + 1}{2} \right) \quad (6)$$

Substituting the values of a_1 and a_2 from equation (6) into equation (1), the pressure P in equation (1) takes the following form

$$P = B_0 \left(1 - \frac{V}{V_0} \right) + B_0 \left(\frac{B'_0 + 1}{2} \right) \left(1 - \frac{V}{V_0} \right)^2 \quad (7)$$

Equation (7) thus relates pressure and volume compression (V/V_0).

Assuming the thermal pressure zero ($P_{Th} = 0$), and using the Mie-Gruneisen theory of EOS [19], the relation for thermal expansion reads as follows [20]:

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 + 2 \left(\frac{B'_0 + 1}{B_0} \right) P \right]^{\frac{1}{2}}}{(B'_0 + 1)} \quad (8)$$

To analyze the elastic behavior and phase instability of the nanocrystals, we have determined the second order of elastic constants (SOEC) of ZnS and ZnSe nanocrystals as the function of pressure. It is found that the values of SOEC obtained in the present study satisfy the instability condition [25] at transition pressure (P_t). To determine the pressure dependent relation of elastic constants for nanomaterials we have considered the approximation that Anderson-Gruneisen parameter δ is equal to the first order pressure derivative of bulk modulus [21] at constant temperature, that is

$$\delta = \left(\frac{\partial B}{\partial P} \right)_T = B'_0 \quad (9)$$

$$\text{Or } \delta = - \frac{V}{B} \left(\frac{dB}{dV} \right)_T \quad (10)$$

Integration of equation (10) at constant temperature gives the following relation

$$\frac{B}{B_0} = \left(\frac{V}{V_0} \right)^{-B'_0} \quad (11)$$

However, the equation (11) may be generalized as follows [22]:

$$\frac{E}{E_0} = \left(\frac{V}{V_0} \right)^{-\delta_{ij}} \quad (12)$$

where E represents any of the elastic moduli, such as $C_{11}, C_{12}, C_{44}, (C_{11} - C_{12})/2$ or B . E_0 refers to their initial value at zero pressure. Using equation (12), the expression relevant to C_{11}, C_{12}, C_{44} can be written collectively as:

$$\frac{C_{ij}}{C_{0ij}} = \left(\frac{V}{V_0} \right)^{-\delta_{ij}} \quad (13)$$

where δ_{ij} are the constants corresponding to C_{ij} and defined as [23]:

$$\delta_{ij} = \left(\frac{dC_{ij}}{dP} \right) \quad (14)$$

Equation (13) can be used to determine the pressure dependence of C_{ij} provided that the corresponding values of V/V_0 are known. The values of V/V_0 as the function of pressure are estimated from equation (8) and used in equation (13) to predict the values of pressure dependence of SOECs of both of the nanocrystals under study.

III. RESULTS AND DISCUSSION:

A simple theory has been thus presented to predict the effect of pressure on nanomaterials. The equation of state employed in the present study consists of only two input parameters, viz. B_0 and B'_0 . We have compiled these data in table 1 along with their proper references. Since the studies on compression behavior of ZnS and ZnSe nanocrystals have attracted much attention in experimental studies [5, 6], we have, therefore, considered these materials in the present study. Equation (8) is used to study the compression behavior of these two nanomaterials. The pressure at which the ZB structure into RS structure is the phase transition pressure (P_t). The estimated values of the P_t at which the zincblende (ZB) structure of ZnS and ZnSe nanocrystals transform into

rocksalt structure (RS) are achieved as 19.5 GPa and 13.5 GPa respectively are consistent with those of the experimental values [5,6]. The consistency is attributed to the properly formulated effective equation of state (7) as well as use of input parameters (B_o, B'_o) in both ZB and RS structures. The trend of variation of compression (V/V_o) in both nanocrystals are shown in fig. 1 and fig. 2. It is clear from the figures that the phase transformation from zincblende structure to rocksalt structure occurs at 19.5 GPa in ZnS and 13.5 GPa in ZnSe nanocrystal.

To analyze the mechanical instability of ZnS and ZnSe nanocrystal under transformation, we have determined the values of pressure dependent second order elastic constants (SOEC) associated with various compressions by using the equation (13). The pressure dependence of SOECs need the corresponding values of V/V_o as input. For this purpose, we have used equation (8) to compute V/V_o at different pressures for both ZnS and ZnSe nanomaterials. The input data used to calculate the phase transition pressure and pressure dependence of elastic constants are given in tables 1- 2 respectively. The variations of elastic constants with pressure are shown in figure 3 and figure 4. Employing the mechanical stability criteria; one can study the mechanical stability of ZnS and ZnSe. Sinko and Smirov [25] deduced the conditions of mechanical stability from elastic constants. As is known, for a cubic crystal, the mechanical stability under isotropic pressure is judged from the following conditions: (a) $\tilde{C}_{44} > 0$, (b) $\tilde{C}_{11} > \tilde{C}_{12}$, (c) $\tilde{C}_{11} + 2\tilde{C}_{12} > 0$, where $\tilde{C}_{\alpha\alpha} = C_{\alpha\alpha} - P$ ($\alpha=1,4$), $\tilde{C}_{12} = C_{12} + P$. We have plotted the mechanical stability of ZnS and ZnSe versus pressure in figures 5-6. When one of the above condition is no longer fulfilled, it indicates that the crystal is not stable at transition pressure (P_t) or above the transition pressure. In the present investigation it is found that the stability condition $\tilde{C}_{11} > \tilde{C}_{12}$ is not satisfied at the transition pressure 19.5 GPa in ZnS and 13.5 GPa in ZnSe as evident from figure 5 and figure 6 respectively. At both transition pressure values, the stability condition produces negative value instead of positive and that is the reason that ZnS and ZnSe nanocrystals undergo phase transition from ZB structure to RS structure at their respective critical pressures.

On the basis of overall descriptions, it may thus be emphasized here that a simple and straightforward theoretical method is capable of explaining the phase transformation properties of nanomaterials under high pressure satisfactorily. Due to simplicity and applicability, this may be of the current interest to the researchers engaged in the study of the induced phase transformation and elastic properties of nanomaterials under high pressure.

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TABLE CAPTIONS

Table: 1 Input data used to calculate the phase transition pressure in ZnS and ZnSe nanocrystals are given.

Table: 2 The values of SOECs of ZnS and ZnSe nanocrystals at zero pressure used in the present work as input data are given.

FIGURE CAPTIONS

Figure 1: Variation of V/V_o vs P for ZnS nanocrystal

Figure 2: Variation of V/V_o vs P for ZnSe nanocrystal

Figure 3: Variation of C_{11} , C_{12} , C_{44} vs P for ZnS nanocrystal

Figure 4: Variation of C_{11} , C_{12} , C_{44} vs P for ZnSe nanocrystal

Figure 5: The mechanical stability $\tilde{C}_{11} > \tilde{C}_{12}$ of ZnS versus pressure

Figure 6: The mechanical stability $\tilde{C}_{11} > \tilde{C}_{12}$ of ZnSe versus pressure

Table: 1 Input data used to calculate the phase transition pressure

Crystals	ZB Phase B_0 (GPa)	RS Phase B_0 (GPa)	B_0 (ZB)	B_0 (RS)	$\Delta V/V_0$	P_t (GPa) calculated	P_t (GPa) Exp.
ZnS [5]	72±7 [5]	103.6 [24]	9±3	4	17.5±1% [5]	19.5	19-23.1 [5]
ZnSe [6]	56±2.6 [6]	116±2.6 [6]	4	4	13% [6]	13.5	10.6-13.6 [6]

Table: 2 The values of SOECs of ZnS and ZnSe nanocrystals at zero pressure used in the present work as input data

Crystals	C_{11}	C_{12}	C_{44}	Ref.	C_{11}'	C_{12}'	C_{44}'	Ref.
ZnS	104.0	65.0	46.2	[27]	3.88±0.25	4.76±0.25	1±0.25	[26]
ZnSe	91.2	58.2	42	[26]	4.44±0.3	4.93±0.3	0.43±0.3	[13,26]

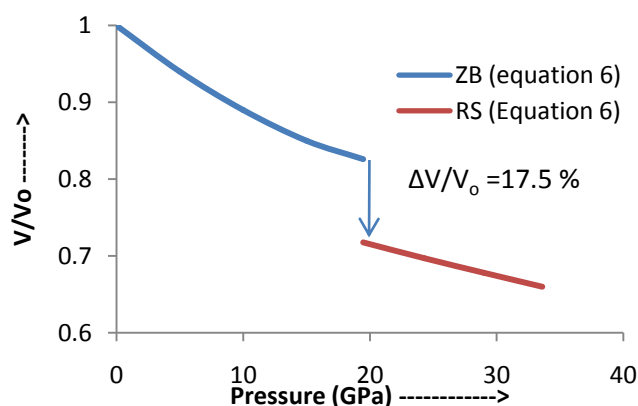


Figure 1: Variation of V/V_0 vs P for ZnS nanocrystal

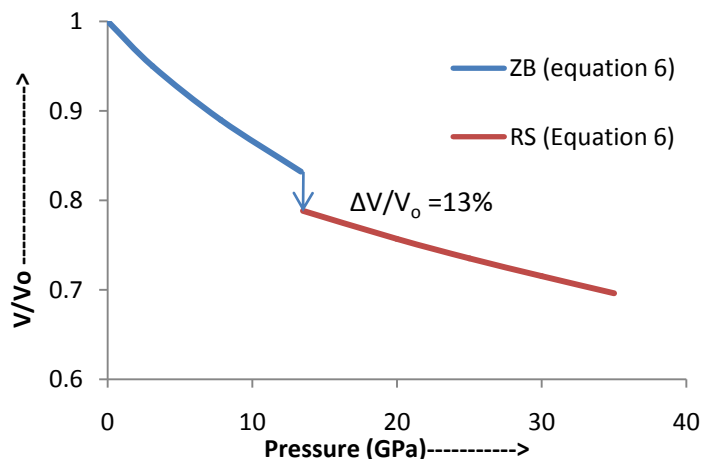


Figure 2: Variation of V/V_0 vs P for ZnSe nanocrystal

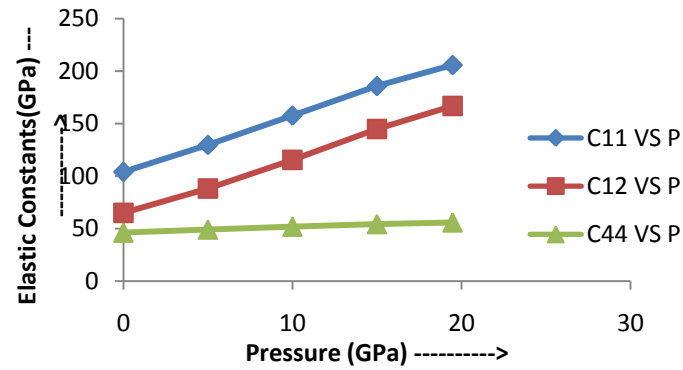


Figure 3: Variation of C_{11} , C_{12} , C_{44} vs P for ZnS nanocrystal

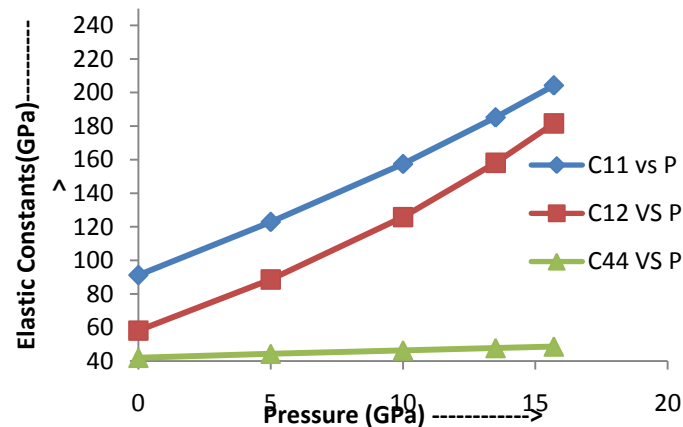


Figure 4: Variation of C_{11} , C_{12} , C_{44} vs P for ZnSe nanocrystal

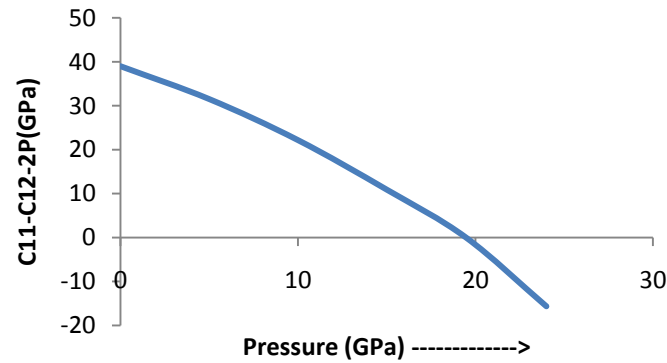


Figure 5: The mechanical stability $\tilde{C}_{11} > \tilde{C}_{12}$ of ZnS versus pressure

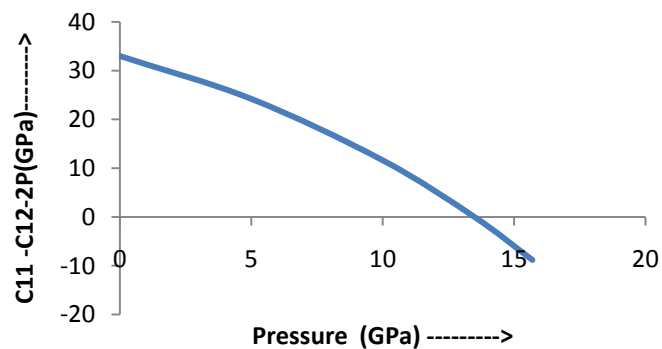


Figure 6: The mechanical stability $\tilde{C}_{11} > \tilde{C}_{12}$ of ZnSe versus pressure