



Compression Study of Nanomaterials Having Similar Pressure Derivative of Bulk Modulus

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Abstract: The current work uses a study of fundamental thermo dynamical features (product of thermal expansion coefficient and bulk modulus remains constant under pressure) to describe the behaviour of certain nanomaterial with equal first order pressure derivatives of bulk modulus under high pressure. Different Equation of states [EOS] have been applied and compared with the experimental result. An equation is formulated and is used to investigate the isothermal compression of nanomaterial i.e. γ -Fe₂O₃, CuO, AlN, TiO₂(anatase phase), Ni(20nm), Ge(49nm), CNT(single walled Corban Nanotube, CdSe (Rock salt Phase). Moreover the present EOS model specifies close conformity with the experimental data. This demonstrates the legitimacy of the current strategy, the obtained results are discovered to be in perfect agreement with the experimental data that is already known, proving the correctness of the formulation used in this study.

Index Terms - Nanomaterial, thermal expansion, pressure derivative of Bulk modulus, equation of State, carbon nanotubes.

I. INTRODUCTION

Nanomaterial have attracted a lot of attention in the last decade because these offers the applications for a wide range of industrial, biological, and electrical applications due to their incredibly tiny size. The behavior of nanomaterial under high pressure can provide important details about their fundamental microstructural properties. In physics, chemistry, and engineering, the study of nano materials with particle diameters smaller than 100 nm is a hot topic. External factors like as temperature and pressure are generally particularly sensitive to nanomaterial. Many of these materials' physical characteristics are highly influenced by their structures and interatomic distances. As a result, studying the thermodynamic characteristics of nano materials is one of the most exciting fields in Nano science.[1]

Magnetic particles with sizes in the nanometer scale are now of interest because of their many technological applications differs considerably from those of bulk materials. Magnetic ultrafine particles are applied in Ferro fluids, refrigeration systems, etc., and they have potential applications to storage devices, medical imaging, and catalysis. Recent researcher studies structural and magnetic properties of γ -Fe₂O₃ in isometric nanoparticles ranging from 3 to 14 nm with a narrow particle size distribution.[2]

Researcher used high-energy synchrotron radiation and Raman spectroscopic techniques to study nonmetric CuO, a key semiconductor, at a high pressure and It suggests that the contribution of size-induced surface energy to total inertial energy has no influence on the high pressure behavior of this class of nanomaterial.[3]

Recent researcher studies AlN Nano crystals begin to change into a rock-salt structure phase when compressed to 14.5 GPa. This pressure is significantly lower than the transition pressure of 22.9 GPa observed from the bulk AlN by using the same technique. Combination of the size-induced volumetric expansion and resulting softening of the Poisson ratio and shear modulus may explain the reduction of transition pressure in this type of nanomaterial [4]

The macro crystalline and Nano crystalline forms of TiO₂ are essential materials with a variety of recognized and future commercial uses, Pigments, plastics, cosmetics, electronics, and catalysts are just a few of the key technical applications of this material. Recent researcher have used TiO₂ as a model system to examine pressure-induced structural phase transitions of oxides found in the earth's mantle and found excellent result. [5]

Nano crystalline TiO₂ has lately been employed as a model system for studying the size-dependent phase transition behavior of Nano scale oxides in terrestrial settings.[6]

Researcher presents a study of pressure-induced alterations in Nano crystalline anatase (with a crystallite size of 30–40 nm) to 35 GPa using synchrotron X-ray diffraction. Found The bulk modulus of Nano crystalline anatase is approximately 35 percent higher than that of macro crystalline anatase.[7]

Recently X-ray diffraction experiments were carried out utilizing a synchrotron source under no hydrostatic compression of nano nickel (20nm) up to pressures of 37 and 56 GPa, respectively, no phase changes were discovered for compression over the pressure range of these experiments. It has been shown that when particle size decreases, compressibility decreases in system.[8]

The equation of state and the pressure of the I–II transition have been studied for Nano crystalline Ge using synchrotron x-ray diffraction. The bulk modulus and the transition pressure increase with decreasing particle size for both Ge-I and Ge-II, but the

percentage volume collapse at the transition remains constant. The interface structure plays a significant role in affecting the transition pressure and the bulk modulus.[9]

Carbon nanotubes (CNTs) have been studied extensively for their elastic properties, both for possible applications such as composite nanotube materials and to get a better understanding of this one-dimensional carbon-based material. The computations were done using the local-density approximation of density-functional theory. They determined that the 37 GPa! bundle bulk modulus is similar to that of graphite, which is between 34 and 42 GPa! The elastic properties of the individual tubes in the bundles are properly described by the elastic continuum approximation. The linear modulus is 1.5–2 times greater than the radial modulus for nanotube radii between 0.8 and 1.4 nm. [10]

Researcher found Bulk CdSe is known to undergo a wurtzite to rock salt transition at 2.0 GPa. . Structural transformations in CdSe nanocrystals are studied using high pressure x-ray diffraction and high pressure optical absorption at room temperature. The nanocrystals undergo a wurtzite to rock salt transition analogous to that observed in bulk CdSe. The nanocrystal phase transition pressures vary from 3.6 to 4.9 GPa for crystallites ranging from 21 to 10 Å in radius, respectively, in comparison to a value of 2.0 GPa for bulk CdSe. Surface energies calculated is used to understand the dynamic microscopic path followed by atoms during the phase transition . X-ray diffraction data also shows that unlike bulk CdSe, crystalline domain size is conserved upon multiple transition in the nanocrystals, indicating that the transition only nucleates once in each nanocrystal.[11]

II. RESEARCH METHODOLOGY

Previous workers in high pressure research demonstrates that the product of the coefficient of volume thermal expansion (α) and bulk modulus (B) remains constant under the effect of pressure [12][13] we can write

$$\alpha B = K \quad (1)$$

Where K is a constant for a given solid. On diff. Isothermally respect to volume Eq. (1) gives

$$\alpha \left(\frac{\partial B}{\partial V} \right)_T + B \left(\frac{\partial \alpha}{\partial V} \right)_T = 0 \quad (2)$$

Isothermal Anderson parameter is used researcher [13]

$$\delta_T = \frac{V}{\alpha} \left(\frac{\partial \alpha}{\partial V} \right)_T = -\frac{V}{B} \left(\frac{\partial B}{\partial V} \right)_T \quad (3)$$

At constant temperature

$$\frac{dB}{B} = -\delta_T \frac{dV}{V} \quad (4)$$

Integration with boundary condition $B = B_0$ when $V = V_0$ assuming that δ_T is independent of V gives

$$\ln \left(\frac{B}{B_0} \right) = -\delta_T \ln \left(\frac{V}{V_0} \right)$$

Or

$$\frac{B}{B_0} = \left(\frac{V}{V_0} \right)^{-\delta_T} \quad (5)$$

Now since isothermal bulk modulus $B = -V(\partial P/\partial V)_T$, Eq. (5) becomes

$$-\frac{V}{B_0} (\partial P/\partial V)_T = \left(\frac{V}{V_0} \right)^{-\delta_T}$$

Or

$$\frac{dV}{V^{\delta_T+1}} = -\frac{1}{B_0 V_0^{\delta_T}} dP \quad (6)$$

In view of Eq. (3) with isothermal bulk modulus $B = -V(\partial P/\partial V)_T$,

$$\delta_T = (dB/dP)_T = B'_0$$

The integration of Eq. (6) gives the following relation

$$P = \frac{B_0}{B'_0} \left[\exp \left\{ -B'_0 \ln \frac{V}{V_0} \right\} - 1 \right] \quad (7)$$

Eq. (7) is the same relation as given by Murnaghan [14] in a slightly different way assuming that bulk modulus depends linearly on pressure.

Due to the simplicity of Eq. (7) it has been widely used in the literature. On the other hand the more recent studies in high pressure research demonstrate that Anderson parameter δ_T is related to $\eta = V/V_0$ (where V_0 is the initial volume) as given below [15]:

$$(\delta_T + 1)/\eta = A$$

Where A is a constant for a given crystal. Thus Eq. (4) takes the following form

$$\frac{dB}{B} = \left[-\frac{A}{V_0} + \frac{1}{V} \right] dV \quad (8)$$

Integration of Eq. (8) yields

$$\frac{B}{B_0} = \frac{V}{V_0} \exp A \left[1 - \frac{V}{V_0} \right] \quad (9)$$

Now since $B = -V(dP/dV)_T$, Eq. (9) may be written as

$$\frac{B_0}{V_0} \exp A \left(1 - \frac{V}{V_0} \right) dV = -dP.$$

Upon integration gives

$$P = \frac{B_0}{A} \left[\exp A \left(1 - \frac{V}{V_0} \right) - 1 \right] \quad (10)$$

Here B_0 is the zero pressure value of bulk modulus and the constant A is determined from the initial condition, viz., at $V = V_0$, $A = \delta_T^0 + 1$. Now since $\delta_T^0 = (dB/dP)_T = B'_0$, thus $A = B'_0 + 1$ thus Eq. (10) needs only two parameters, viz. B_0 and A at zero pressure, and it is entirely free from the derivatives of bulk modulus B''_0 which are hardly available and their determination is quit uncertain and involves heavy computational work [16].

As our result has been shown in comparison with these standard EOS given in literature [17] [18] [19] in the following form:

Birch – Murnaghan EOS

$$P = \frac{3}{2} B_0 \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left[1 + \frac{3}{4} (B'_0 - 4) \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\} \right]$$

Since $B'_0 + 1 = A$

$$\text{So } P = \frac{3}{2} B_0 \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left[1 + \frac{3}{4} (A - 5) \left\{ \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right\} \right] \quad (11)$$

Vinet EOS

$$P = 3 B_0 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} \left\{ \left(\frac{V}{V_0} \right)^{\frac{1}{3}} - 1 \right\} \exp \left[\frac{3}{2} (B'_0 - 1) \left(1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right) \right]$$

Or

$$P = 3 B_0 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} \left\{ \left(\frac{V}{V_0} \right)^{\frac{1}{3}} - 1 \right\} \exp \left[\frac{3}{2} (A - 2) \left(1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right) \right] \quad (12)$$

Shanker EOS

$$P = \frac{B_0}{2A} \left\{ \left(1 + A \left[1 - \frac{V}{V_0} \right] \right)^2 - 1 \right\} \quad (13)$$

III. RESULTS AND DISCUSSION

The current approach for analyzing the effect of pressure on Nanomaterials is based on the quasi-harmonic approximation that the product of the thermal expansion coefficient α and Bulk modulus B_T remains constant under pressure [33]. Using the same approximation, in this study we have investigated the required pressure on different nanomaterials γ -Fe₂O₃, CuO, AlN, TiO₂ (anatase phase), Ni(20nm), Ge(49nm), CNT(single walled Corban Nanotube, CdSe (Rock salt Phase) for different required compression ratio (V/V_0) such that From the equation (10), have been calculated. Input parameters B_0 & B'_0 & constant A as listed in Table 1 was taken from literature. The results obtained are shown in Figures. 1-2. Similarly, with the same input parameters, pressure for different volume ratio (V/V_0) have been calculated using equation (11) also known as Birch-Murnaghan equation and equation (12) called as Vinet EOS & equation (13) called as Shanker EOS. Experimental data as referenced in the figures (1-2) was taken from the various literature and compared with the result obtained by our derived equation and different EOS. We found that there is very good agreement between theory and experiment.

On the basis of the above, it should be noted that the current method is capable of properly describing the compressional and elastic characteristics of nanomaterials under high pressure. This may be of current interest to researchers studying the elastic characteristics of nanomaterials under high pressure because of its simplicity and applicability.

Table 1 - Input parameters utilized in this research

Nanomaterials	B_0	B'_0	$A = B'_0 + 1$	Ref.
γ - Fe ₂ O ₃	374	4	5	[20]
CuO	81	4	5	[3]
AlN	321	4	5	[21]
TiO ₂ (anatase)	243	4	5	[22]
$N_i(20nm)$	185	4	5	[23]
$G_e(13nm)$	92	4	5	[9]
CNT	230	4	5	[24]
<i>CdSe(Rock salt phase)</i>	74	4	5	[25]

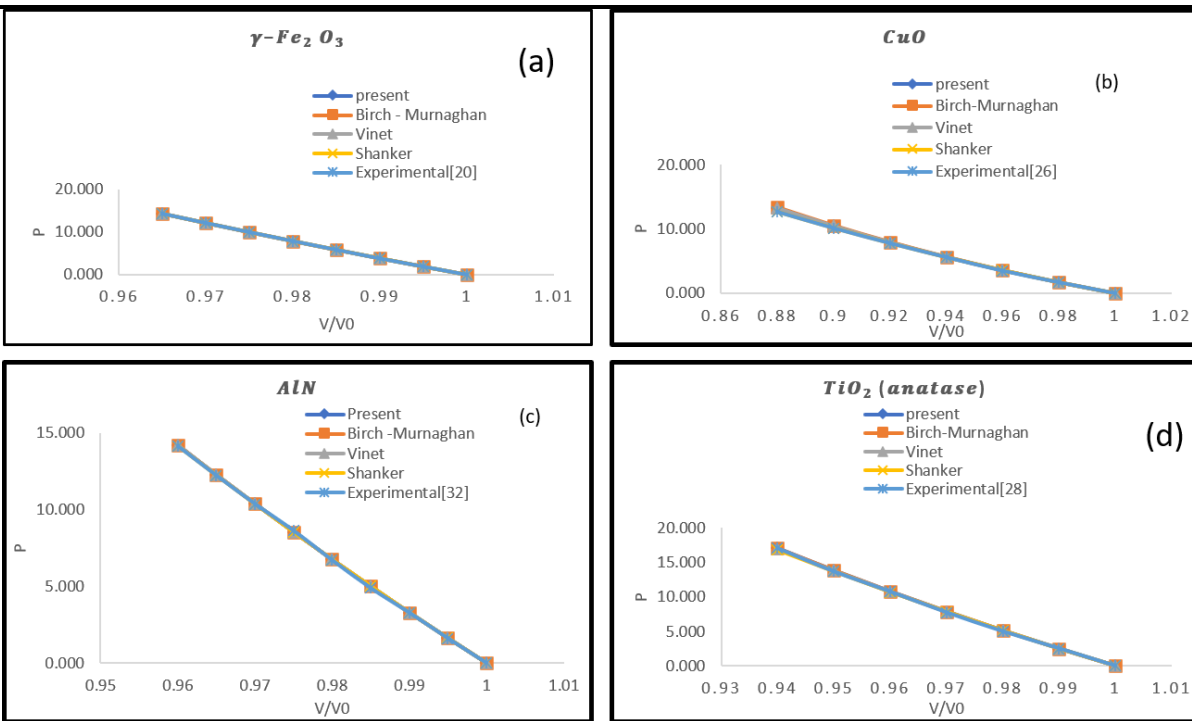


Fig. 1 Variation of pressure with required V/V_0 for (a) $\gamma\text{-Fe}_2\text{O}_3$ with Exp. [20] (b) CuO with Exp.[26](c) AlN with Exp.[32](d) TiO_2 (anatase) with Exp.[28]

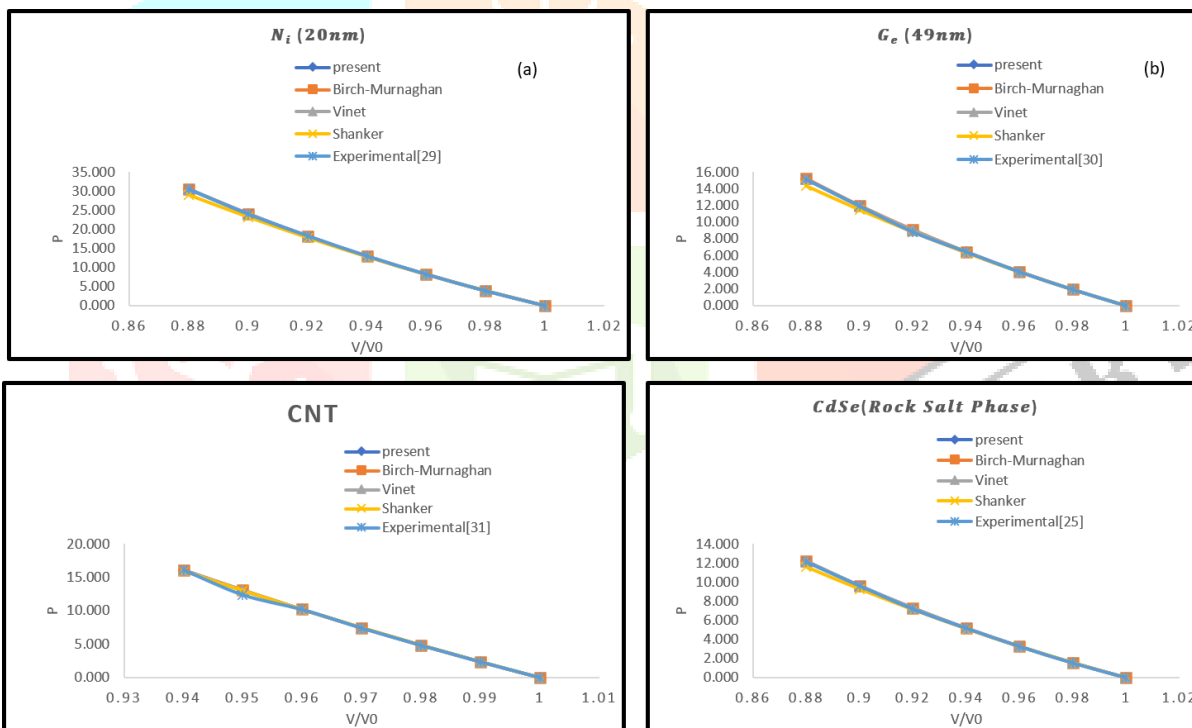


Fig.2 Variation of pressure with required V/V_0 for (a) Ni(20nm) with Exp.[29](b)Ge(49nm)with Exp.[30](c) CNT with Exp. [31](d) CdSe (Rock salt phase)with Exp. [25]

IV. Conclusions

The current formulation, which results from the fact that for nanoparticles, αB_T is constant, may be especially helpful for figuring out the necessary high-pressure for a certain compression ratio of solids, especially nanomaterials with similar first order pressure derivative of bulk modulus, given that its results are fairly close to those of nanomaterials' experimental data. For the current state equation to work, all nanomaterials only need one fixed parameter and one variable. The new approach may thus be helpful in developing future high-pressure testing on the compression behavior of nanomaterials.

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