Study of Pressure-dependent Gruneisen Parameter for Different Nanosized Germanium materials

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Abstract: - Investigating the Gruneisen parameter of semiconductor materials holds significant relevance for their enhanced utilization in modern technology. The Grüneisen parameter possesses adaptability across multiple scientific and engineering domains, finding utility in a variety of applications. Its use allows for a more comprehensive comprehension of how materials react to alterations in temperature and pressure, thus facilitating enhanced precision in forecasting and offering valuable insights into material behavior.
This study delves into the impact of high pressure on the Gruneisen parameter for both bulk Germanium and various Germanium nanomaterial sizes, encompassing dimensions of 13nm, 49nm, and 100nm. The evaluation of volume compression ratios is facilitated by employing the Tait and Birch-Murnaghan equations of state (EOS) in this research. Notably, it was uncovered that the observed high-pressure effects are notably influenced by the particle size being considered. A comparative analysis between the 13nm and 49nm germanium particles highlights that the 100nm germanium particle experiences a more substantial reduction in volume.
Furthermore, the present study ventures into theoretical predictions of pressure-dependent Gruneisen parameters across diverse-sized germanium crystals at a reference temperature. Remarkably, the outcomes gleaned from this investigation align with trends observed for other metals in the existing literature, underscoring the consistency of the variation of Gruneisen parameters with volume compressions observed in germanium.

Key-Words: - Equation of state; Gruneisen parameter; Isothermal Bulk Modulus; High pressure Compressions; Structural properties; Volume collapse; Nanomaterials.

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1 Introduction

Substances characterized by clusters and crystallites within the diameter range of 10 to 1000 angstroms are categorized as nanostructured materials. The significant shifts in fundamental electrical, optical, and magnetic properties that manifest as one transitions from an "infinitely extended" solid to a material particle composed of a finite number of atoms have led to heightened attention from academia and industry towards these materials. This undertaking outlines the latest advancements in the examination of nanostructured materials, with a specific focus on pioneering investigations into size-dependent nanoscale semiconductors, metal assemblies, and colloids [1].

More intricate structures with distinct physical characteristics are being created by researchers. Many times, referred to as nanocrystals, crystalline semiconductors are a subset of the noteworthy instances of complicated structures. A substance in between tiny molecules and bulk crystalline limitations is a nanocrystal. Nanocrystals' optical and electrical features have drawn a lot of interest since they display unexpected quantum phenomena and might be used to create cutting-edge technology [2].

As it frequently appears in equations that explain the thermoelastic behavior of substances at high pressures and temperatures, the Gruneisen parameter is a significant number in geophysics. It has a minuscule description that relates to the atomic vibrational frequencies of a material and a minuscule one that relates to well-known thermodynamic features like heat capacity and thermal expansion. Although the form of and the equation of state are frequently selected autonomously of one another and slightly randomly, the Gruneisen parameter is intimately tied to the EOS [3].

The earth's germanium is a highly significant semiconductor material that is used in a variety of transistor and integrated circuit designs. Although its bulk characteristics have long been well known, research into the nano solid's properties has only recently been initiated. Nanotechnology is widely used and has numerous practical uses. To comprehend the thermoelastic characteristics of the nanomaterial, the impact of size and shape is crucial [4]. For any technological application of any materials perceptive, their properties must be known. Most of the properties, of bulk materials such as photosensitive, electrical, and updraft, are constant under fixed temperature and pressure, nano-scaled range crystal, size will powerfully distress these properties. The change of one or both two factors, (temperature and pressure) material structure is reformed. In general, a phase transition happens when a solid's crystal structure is subjected to changes in temperature or pressure [5].

Numerous size-dependent characteristics may be found in semiconductor nanocrystals. Controlling the crystal size allows for the induction of variations in basic properties, including electrical conductivity and phase transitions. Reviewing the current state and future directions for this field of materials physical chemistry research [6].

The glass network's structural units' thermal vibrations' anharmonicity is quantified by the Gruneisen parameter y. This parameter is crucial for describing a variety of methods; in particular, it may be used to forecast malleable twists in glassy polymers and interpret the characteristics of glass buildings [7]. Investigation of theoretical equations of state, geophysical models, ultrasonic measurement, and solid melting all greatly benefit from the study of the Gruneisen parameter. The reduction of shock wave data to isothermal data is greatly aided by knowledge of the pressure-dependent Gruneisen parameter [8]. There has been a long-standing fascination with how the Gruneisen parameter behaves under high compression, which provides a basic basis for researching thermoelastic characteristics of solids, due to the absence of a good theory and the challenges connected with experimental data [9].

For the melting enthalpy and entropy of vanadium (V), silver (Ag), and copper (Cu) nanoparticles, the results of pure theoretical calculation are in good agreement with available molecular dynamic results. The effect of size on the melting enthalpy and entropy of nanoparticles is greater compared to that of shape effect. The melting enthalpy and entropy decrease with particle size decreasing and the smaller the particle size, the greater the size and shape effects[10].

Three EOSs (The modified Lenard Jones EOS, Birch-Murnaghan (3rd) EOS, and Vinet-Rydburg EOS) were used to study the thermo elastic properties of carbon nanotubes under high pressure and different values of V/V_0 were found. These results show that these EOSs can also be used to calculate nanomaterials. The bulk modulus rises as the pressure rises, but the first order pressure derivative of the isothermal bulk modulus falls as the pressure rises [11- 12]. The compression characteristics of C_{60} crystalline solid in the face-centered cubic shape in the pressure range ranging from 0-11 GPa at room temperature using the best fit values of B_0 and $B_{0'}$ was studied. Tait's EOS has been further developed to study how the thermal expansivity and bulk modulus of C_{60} crystalline solid change with temperature [13].

In this article, we present a simple theoretical approach to study the compression behaviour of germanium nanoparticles with three different sizes (13nm, 49nm, and 100nm) using a two-equation of state Tait EOS [14] and well-known Birch Murnaghan [15]. The pressure-dependent Gruneisen parameter for bulk germanium and nano germanium sizes (13nm, 49nm, and 100nm) at the high-pressure range was theoretically predicted in the current work.

2 Methods and Analysis

The Gruneisen parameter's concise definition lies in its representation of the volume-related behavior of the ith lattice vibration mode [16], and this is furnished by

$$\gamma_i = -\frac{\partial\, ln\omega_i}{\partial\, lnV} \tag{1}$$

However, without a lattice dynamical model evaluation of γ_i across the Brillouin zone is not possible. It can be demonstrated that the first Brillouin zone is total γ_i results in macroscopical or thermodynamical description of γ_i, which can be expressed [17] .

$$\gamma_{th} = \frac{\alpha VB}{C_V} \tag{2}$$

Where α is the thermal expansion coefficient and B is the isothermal Bulk modulus and C_V is the heat capacity at constant volume.

Many researchers have developed many approximation expressions to examine the theoretical fluctuation of the Gruneisen parameter with high pressure using various methodologies [18].

The free volume expression for the Gruneisen parameter was derived by Savchenko and Zubarev [19] followed by the path suggested by Brillouin, who demonstrated that the thermal pressure may be thought of as the pressure necessary to maintain the volume constant when the temperature increased and derived the following formula.

$$\gamma_{VZ} = \frac{\frac{1}{2}B' - \frac{5}{6} + \frac{2P}{9B}}{1 - \frac{4P}{3B}} \quad (3)$$

Where VZ refers to vaschenko and Zubarev approach, P is a pressure and B is isothermal bulk modulus and B' is the first order pressure derivative of bulk modulus.

In our work computation of the Gruneisen parameter of Germanium using two phenomenological forms of isothermal equation of states Tait [14] and Birch -Murnaghan [20] as derived from Lattice potential theory. The Tait's EOS is best used when there is a nonlinear relationship between pressure and compression for various classes of solids and liquids [21].

$$P = \frac{B_0}{B_0'+1}\left[exp\left\{(B_0'+1)\left(1-\frac{V}{V_0}\right)\right\} - 1\right] \quad (4)$$

$$P = \frac{B_0}{B_0'+1}[exp\{(B_0'+1)(1-x^3)\} - 1] \quad (5)$$

Where $x = \left(\frac{V}{V_0}\right)^{\frac{1}{3}}$

The above equation derived on the fact that the product of thermal expansion coefficient ($\propto$) and Bulk modulus (B_T) is constant under the effect of pressure[22] i.e.

$$\propto B_T = \text{constant}$$

Third order Birch-Murnaghan is the most used EOS for the investigation of high-pressure compression in nanomaterials.

$$P = \frac{3}{2}B_0[x^{-7} - x^{-5}]\left[1 + \frac{3}{4}(B_0' - 4)(x^{-2} - 1)\right] \quad (6)$$

Where V is the volume of solid at pressure P and $V_0$is the Vollume of solid at zero pressure. Expression for isothermal Bulk modulus corresponding to equation (4) and (6) is obtained by using the relationship

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T \quad (7)$$

By Tait EOS

$$B = B_0 x^3[exp\{(B_0' + 1)(1 - x^3)\}] \quad (8)$$

By Birch-Murnaghan EOS

$$B = \frac{B_0}{2}(7x^{-7} - 5x^{-5}) + \frac{3}{8}B_0(B_0' - 4)(9x^{-9} - 14x^{-7} + 5x^{-5}) \quad (9)$$

Corresponding Isothermal Pressure derivative of Bulk modulus

$$B' = \left(\frac{\partial B}{\partial P}\right)_T = \left(\frac{\partial B}{\partial V}\frac{\partial V}{\partial P}\right)_T = -\frac{V}{B}\left(\frac{\partial B}{\partial V}\right)_T \quad (10)$$

Eq. (8) and (9) results in the following form after substitution from equation (10)

$$B' = \frac{V}{V_0}(B_o' + 1) - 1 \quad (11)$$

$$B' = \frac{B_0}{8B_T}(B_0' - 4)[81x^{-9} - 98x^{-7} + 25x^{-5}] + \frac{B_0}{6B_T}[49x^{-7} - 25x^{-5}] \quad (12)$$

3 Results and Discussion

In this study two equation of states Tait, Birch-Murnaghan EOS with Only two parameters B_0 and B_0' are taken from literature as shown in Table-1. The values of pressure P for different sizes of Ge were computed for varying values of V/V_0 by using Tait and Birch- Murnaghan EOS (Fig.1-2). Pressure P was computed using equations (5-6) and isothermal Bulk Modulus(B) and first pressure derivative of bulk modulus (B') at constant temperature was determined by using equations (8-12). Gruneisen Parameters (Υ) at varying compression ratio was derived by substituting these values in equation (3). As shown in Fig. 1-2, as compression ratio increased from 0-1 then pressure decreased exponentially. The bulk germanium curves exhibit proximity between the two equations of state

(EOS) throughout various compression levels. However, when it comes to germanium nanomaterials, the results from both EOSs show a significant convergence in the vicinity of 10 GPa pressure. As the pressure values exceed 10 GPa, there is a noticeable increase in the divergence of the curves. The trends in relative volume variation at high pressures for germanium particles of sizes 49 nm and 100 nm closely resemble those predicted by the Birch-Murnaghan EOS (B-M EOS) and the Tait EOS. Conversely, for germanium particles of size 13 nm, there is a marked discrepancy. The data for relative volume (V/V_0) obtained through the B-M EOS gradually decreases to reach 0.6 for nanoparticles with diameters of 49 nm and 100 nm at a pressure of around 130 GPa. This divergence in relative volume behavior between the B-M EOS and the Tait EOS contrasts with the latter's prediction that the results will decrease, reaching the lowest value around 120 GPa for the same nanoparticle sizes. Utilizing the Tait EOS, Figures 1 and 2 portray the stiffness of both the bulk phase and nano-germanium particles of various sizes. These illustrations reveal that as pressure increases, the relative volume values of nanoparticles with smaller diameters exhibit a slower reduction compared to those of the bulk phase of Ge. For instance, the relative volume (V/V_0) values for the bulk material reach their minimum (0.6) around 80 GPa, whereas this minimum occurs at 120 GPa for diameters of 100 nm and 49 nm, and at 150 GPa for a diameter of 13 nm. Consequently, the compressibility of nanoparticles diminishes as their sizes decrease. This discrepancy can be attributed to the influence of nanoparticle size on factors like bulk modulus and Debye temperature.

In accordance with the nanoparticle size dependence formula, the bulk modulus B_0 for bulk Ge is 74.9 GPa. However, for nanoparticles with sizes of 100 nm and smaller, values of 92 GPa, 88 GPa, and 112 GPa have been sourced from the literature (as presented in Table 1). This variation in bulk modulus is significant due to the increase in repulsive forces between neighboring atoms within the nanoparticles at shorter distances. While repulsive forces exist between neighboring atoms, attractive forces act among all atoms within the particle. Figure 3 and 4 illustrate a graphical representation of the Gruneisen parameter (Y) plotted against V/V_0 for both the bulk material and various sizes. From these graphs, a noteworthy observation can be made: the Gruneisen parameter (Y) versus V/V0 variation obtained using both the Tait EOS and the Birch-Murnaghan EOS for bulk Ge shows similarities up to low compression, with slight divergence at higher compression. On the other hand, in the case of size-dependent variations, the Birch-Murnaghan EOS yields straight-line trends, whereas the values derived from the Tait EOS result in curved trends.

Table. 1 Input parameters [19-20]

Nanomaterial	B_0(GPa)	B_0'
Ge(13nm)	112	4
Ge(49nm)	92	4
Ge(100nm)	88	4
Ge Bulk	74.9	3

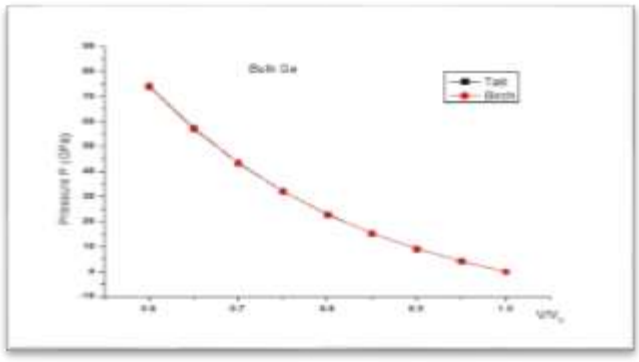

Fig. 1 Variation in the relative volume of Bulk Germanium by using of Tait EOS and Birch-Murnaghan EOS

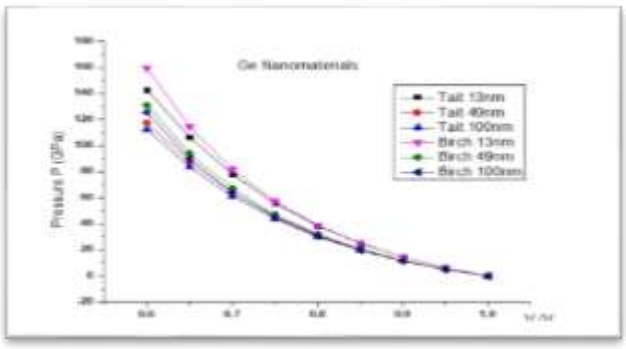

Fig. 2 Variation of relative volume for germanium nanomaterials with different sizes by Tait and /birch Murnaghan EOS

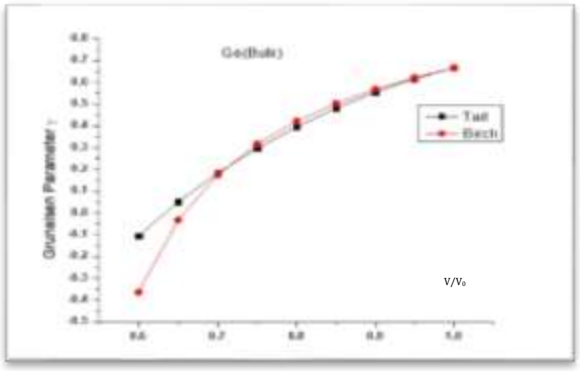

Fig. 3 Variation of Gruneisen parameter of Bulk Germanium by Tait and Birch Murnaghan EOS

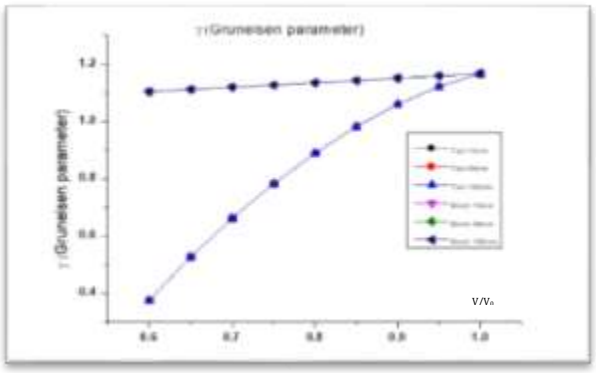

Fig. 4 Variation of Gruneisen parameter of Germanium nanomaterials by Tait and Birch-Murnaghan EOS

4 Conclusion

The Grüneisen parameter is a versatile parameter with applications in various scientific and engineering disciplines. It helps us gain a deeper understanding of how materials respond to thermal and pressure changes, enabling more accurate predictions and insights into material behavior. By employing the Tait and Birch-Murnaghan equations of state (EOS), investigations have been carried out to examine the relative volume and Gruneisen parameter of both bulk and nanomaterials (13nm, 49nm, and 100nm) subjected to high pressure conditions. The reduced compressibility of smaller-sized germanium nanoparticles when subjected to elevated pressures is attributed to their higher Bulk modulus values in comparison to their larger counterparts in the bulk form. In comparison to B-M EOS, Tait EOS forecasts more drastic changes during the entire study, therefore it is determined that Tait EOS is more dependable to apply on Nanomaterials. According to both EOS's results and the data on nanoparticles, materials with a nanoscale size can be used for more beneficial purposes than their bulk counterparts.

In the current study, a novel theoretical prediction was made concerning the pressure-dependent Gruneisen parameter within the high-pressure range. This prediction pertains to both bulk germanium and varying nano germanium sizes (13nm, 49nm, and 100nm), and interestingly, no prior research has documented this aspect.

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