High Pressure Effects on Thermo Elastic Properties of Germanium with Different Nanoparticle Size

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Received: 15.07.2024 Revised: 14.08.2024 Accepted: 24.09.2024

ABSTRACT
In the current work, the pressure equation of state of "Ge-Nano particles with dimensions 13, 49 and100 nm" were studied using two equations of state (EOS) from the literature: the Birch-Murnaghan EOS and the Dodson EOS.The Birch-Murnaghan EOS is based on the concept of finite strain in solid mechanics, while the Dodson EOS is based on interstellar atomic potentials. Namely thermodynamic properties of Ge "bulk modulus B, Debye temperature θ_D, lattice constant a, and phonon frequency spectrum" were determined by processing the tow EOSs. Finally, An equitable analogy was made between the current findings and the generalized gradient approximation approach as well as the first principle approximation, and it was discovered that there was perfect agreement. It was demonstrated that Ge EOS can be used to calibrate high pressure for chemical compound Ge nanoparticles at 49 and 100 nmWhile the equations gave slightly different descriptions of the thermodynamic properties when the dimensions of the germanium particles were 13 nm.

Keywords: Equation of state; Ge- nanoparticles; High pressure; First Grüneisen parameter; bulk modulus. Lattice vibrations

1. INTRODUCTION

Previous high-pressure research on nanoparticles comes into play someattention was given to the intriguing characteristics that show themselves when these materials undergo extreme stress. This size and shape and effects of crystals, the structure has defined high-pressure behavior comparing Nanoscale Materials to Ordinary Matter materials [1, 2]. Previous studies have revealed a variety of interesting phenomena. These include increasing phase transition pressure and shape adjustment as the particle size of Ge nanoparticles [3] decreases. Nonetheless, the impact of size and shape on nanomaterial's' high-pressure performance varies depending on the system.Therefore, further study of the effects of high pressure on various nanomaterial's as a function of size and shape is needed, which has important implications for understanding the physical and chemical properties of nanomaterial's. Ge nanoparticles highlight the progress made in this field and provide information on the techniques used to produce colloidal germanium nanoparticles with precise size and shape control. This is due to their size-dependent optical properties and their uses in flash memory, lithium-ion batteries, biological imaging and treatment, and optoelectronics. [4]. Scientists and engineers are drawn to germanium nanoparticles because of its size-dependent optical properties and potential applications in the aforementioned sectors. To further these uses and learn more about Ge nanoparticles' size-dependent characteristics, robust and straightforward synthetic methods are needed[5,6].

2. Method of the study

The thermodynamic characteristics of nanomaterials have been examined using the molecular dynamics (MD) modeling technique. Because these characteristics are connected to interatomic distances between atoms, it allows for the simulation of atom and molecular motion interacting with certain interatomic potentials [7,8] and the investigation of the system dynamics at finite temperatures, It makes it possible to examine the system's dynamics at limited temperatures because these characteristics are connected to atoms' interatomic distances. The surface and volume effects of nanomaterials influence many of their properties, and changes in their dimensions are directly correlated with changes in the associated

temperature and/or pressure,From this presentation, equations of state will be used to describe these changes on germanium (with specific nanometer dimensions) through the following equations of state:

2.1 Dodson EOS

Dodsondeveloped an empirical EOS that suits all metals, metal alloys, ionic crystals, and semiconductors based on two basic parameters[9, 10]. The following gives the equation:

$$P_{Do}=\frac{27}{8}B_0B_0'^{2}\left[(\eta)^{-2/3}-1+4\left\{1-\frac{2}{3B_0'}\right\}\times\left\{1-(\eta)^{-1/3}-\frac{1}{6}\left(1-\frac{2}{3B_0'}\right)Ln\eta\right\}\right] \quad (1)$$

Where, P_{Do}refers to the pressure due to the Dodson EOS, B_0 is bulk modulus at ambient pressure, $B_O^{'}$ indicates the first pressure derivative of bulk modulus, and

$$\eta=\frac{V_p}{V_o} \quad (2)$$

η: is the volume compression ratio.

2.2 Birch-Murnaghan EOS

The Birch-Murnaghan equation of state (EOS) is a widely used equation of state that has gained significant popularity among scholars. Its derivation is grounded in the solids finite strain model. The following gives B-M EOS in eq. 1.[11](Birch, 1947):

$$P_{\text{B-M}}=\frac{3K_0}{2}\left(\eta^{-7/3}-\eta^{-5/3}\right)\left(1+\frac{3}{4}\left(K_0'-4\right)\left(\eta^{-2/3}-1\right)\right) \quad (3)$$

Where

$P_{\text{B-M}}$: Is the pressure due to Birch–Murnaghan equation of state EOS.

3. Bulk modulus

Studying equations of state has an advantage because of their association with bulk modulus (B), which makes it possible to determine how the bulk modulus depends on pressure. The mathematical definition of a material's bulk modulus is the pressure that must be applied to a substance in order to create a relative change (reduction) in the material's volume.:

$B=-\Delta P/(\Delta V/V)$ (4)

This equation is rearranged to get the form of eq.5,

$$B=-V\frac{\partial P}{\partial V} \quad (5)$$

Equation 6 illustrates the bulk modulus's dependence on pressure and shows that it rises when pressure rises or the volume of a solid material unit cell decreases. Experiments have demonstrated that the bulk modulus is dependent on the material's generated compression at a certain temperature [12].High pressure causes the lattice spacing to contract, which introduces a strong repulsive interatomic force against the external agent. Therefore, using Eq. (5), the bulk modulus corresponding to each equation of state is determined.The following equations can be used to determine the bulk modulus at high pressure by taking the derivative of Dodson EoS and B-M EoS (eqs. 1 and 3) with respect to volume:

$$\frac{dP_{Do}}{dV}=\frac{27}{8}B_0B_0'^{2}\left[\frac{-2}{3}\frac{V^{\frac{-2}{3}-1}}{V_0^{\frac{-2}{3}}}+4\left(1-\frac{2}{3B_0'}\right)\times\left\{\frac{1}{3}\frac{V^{\frac{-1}{3}-1}}{V_0^{-1/3}}-\frac{1}{6}\left(1-\frac{2}{3B_0'}\right)\frac{1}{V}\right\}\right] \quad (6)$$

Eq. 7 is arranged tobecome

$$\frac{dP_{Do}}{dV}=\frac{27}{8}B_0B_0'^{2}\left[\frac{-2}{3}\frac{V^{\frac{-5}{3}}}{V_0^{\frac{-2}{3}}}+4\left(1-\frac{2}{3B_0'}\right)\times\left\{\frac{1}{3}\frac{V^{\frac{-4}{3}}}{V_0^{-1/3}}-\frac{1}{6}\left(1-\frac{2}{3B_0'}\right)\frac{1}{V}\right\}\right] \quad (7)$$

Where, $\frac{dP_{Do}}{dV}$ is pressure derivatives of Dodson EoS.

Then, substituting Eqs. (8) into the bulk modulus definition in Eq. 6, one can fine the Dodson EoS in terms of isothermal bulk modulus, as shown in Eq. 8:

$$B_{Do}=\frac{27}{8}B_0B_0'^{2}\left[\frac{2}{3}(\eta)^{\frac{-2}{3}}-4\left(1-\frac{2}{3B_0'}\right)\times\left\{\frac{1}{3}(\eta)^{\frac{-1}{3}}-\frac{1}{6}\left(1-\frac{2}{3B_0'}\right)\right\}\right] \quad (9)$$

Where, B_{Do} denotes the bulk modulus as a function of relative volume/pressure , in terms of Dodson EoS. To express bulk modulus under high pressure by using an EOS, B-M EOS, given in eq.1, has been derived with respect to volume to obtain the next equation:

$$\frac{\partial P_{B-M}}{\partial V} = \frac{3}{2} B_0 [(\eta)^{\frac{-7}{3}} - (\eta)^{-5/3}] \left[\frac{3}{4} \left(B'_o - 4 \right) \left[\left(\frac{-2}{3} \right) \frac{V_p^{-5/3}}{V_0^{-2/3}} \right] \right] + \frac{3}{2} B_0 \left[\frac{-7}{3} \frac{V_p^{-10/3}}{V_0^{-7/3}} + \frac{5}{3} \frac{V_p^{-8/3}}{V_0^{-5/3}} \right] \left[1 + \left(\frac{3}{4} \right) (B'_o - 4) \left[(\eta)^{\frac{-2}{3}} - 1 \right] \right] \quad (10)$$

On substituting eq.(10) into eq.6, gets eq. 11which represents variation of bulk modulus under high pressure according to B-M EOS:

$$B_{B-M} = \frac{B_o}{2} \left[7\eta^{\frac{-7}{3}} - 5\eta^{\frac{-5}{3}} \right] + \frac{3}{8} B_o \left(B' - 4 \right) \left(9\eta^{\frac{-9}{3}} - 14\eta^{\frac{-7}{3}} + 5\eta^{\frac{-5}{3}} \right) \quad (11)$$

3.1 Grüneisen parameter and phonons

Phonons are a quantized form of energy that represent the vibrational motion of atoms in a solid phase. A broad variety of frequencies ω (modes) found in the crystal are described by the Debye theory in specific heat capacity. Therefore, density of state g(ω) equals the number of modes in the frequency range ω to ω +dω. According to Vocadlo et al. (2000)'s Grüneisen approximation theory[13], the volume V affects the vibrational frequencies of individual atoms in a solid, by the following relation:

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V} \quad (12)$$

Where: γ_i: Grüneisen parameter for the i^{th} mode.
ω_i: frequency of the i^{th} mode of vibration.
Equation (12) demonstrates how the application of high pressure can change the lattice volume, which in turn affects the vibrational frequency of atoms.
The Grüneisen parameter holds significant importance in the field of solid state matter due to its impact on the density of vibrational motion modes within crystals.

4. Calculations and results

4.1. Evaluation of V_p/V_0

The compressibility of Ge was calculated using (B.M and Dodson) EOS (eq.9 and 11) show in Fig. 1. Where the input parameters are; B and B', listed in Table 1.

Table 1. input parameter (bulk modulus and its derivative Ge nanoparticles[15-17]

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

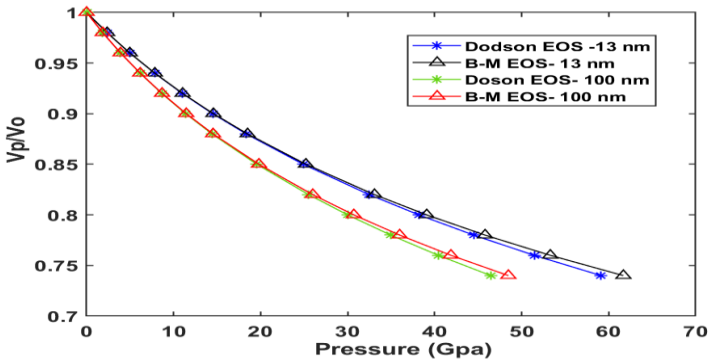

Fig 1. Compression of Ge nanoparticles using Dodson andBirch-M EOS

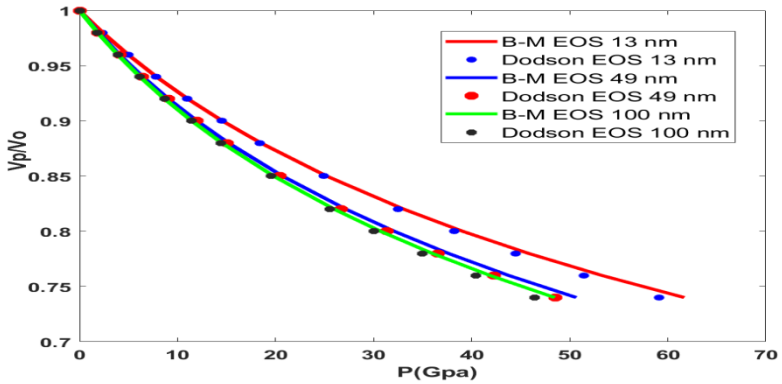

Fig 2. Compression of Ge nanoparticles usingBirch-M EOS

4.2 Grüneisen parameter and lattice vibrations

Pressure dependence of the Grüneisen parameter is caused by anharmonic properties of the solid. As a result, the following statement [14] represents the volume dependency of the Grüneisen parameter:

$$\gamma_p = \gamma_o(\eta) \qquad (13)$$

Where, γ_o and γ_p are the Grüneisen parameter at atmospheric pressure and under high pressure respectively. The following describes how pressure affects the density of states and phonon frequency spectrum:

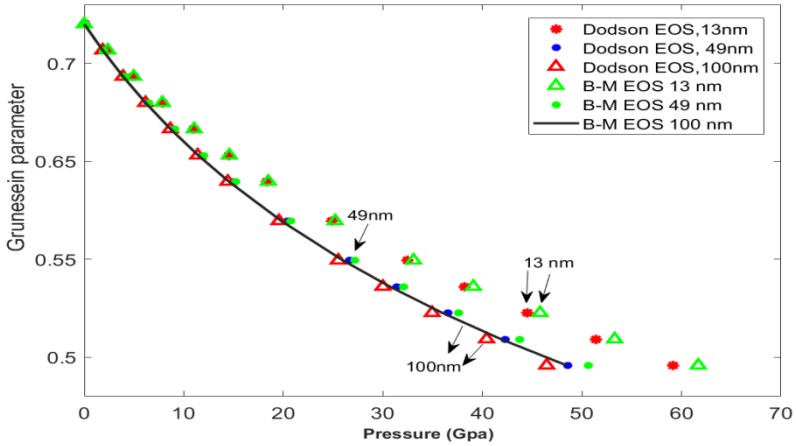

Fig 3: Grüneisen parameter variation in response to pressureusing Dodson Eos

5. Evaluation of bulk modulus for Ge nanoparticles under high pressure

Figure (2) displays the fluctuation of the bulk modulus B for Ge under high pressure corresponding to each EOS.

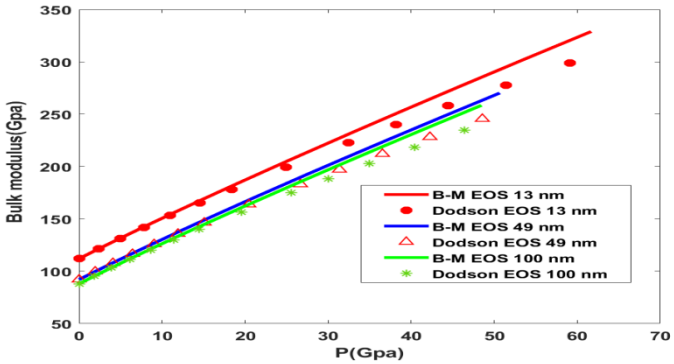

Fig 4: Variation of bulk modulus for Ge nanoparticles (13nm)

DISCUSSION AND CONCLUSION OF THE RESULT

According to this study, the equations of state (Dodson EOS andBirch-Murnaghan EOS) of germanium in dimensions of (13nm,100nm and 49nm) were tested. For the properties "bulk modulus B, Debye temperature θ_D, lattice constant a, under high pressure up to (60 GPa).

It gave very good appropriate results for Ge particles when they were of sizes (49 and 100nm) compared to the results that the literatures obtained from their experimental work, but when the particle sizes were (13nm) the results showed a divergence from the results obtained by the researchers. In previous literary articles, therefore, we can conclude that the above equations can be used for germanium under high pressure up to 60 GPa to calculate the thermodynamic properties when it has sizes (49 and 100nm), but we exclude these equations when the sizes are close to (13nm), and the reason for this may be due to the fact that the particle sizes are very small.

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