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Theoretical study of High-pressure compression of Nano Sized Germanium and Silicon

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ABSTRACT

High pressures have been employed to examine the pressure-induced structural and mechanical characteristics of nanocrystalline Ge and Si with different grain sizes in the current work. Volume collapse in nano and bulk phases at low and high pressures was determined by authors using the isothermal equation of states Vineet, Birch-Murnaghan, and Suzuki based on a molecular dynamic's simulation model. The acquired result was found that the high-pressure properties depend meaningfully on the particle sizes, the 4.1-nm Si nanoparticle skilled a higher decrease in volume value than the diameter of 10.3 nm but 13nm Ge particle shows a smaller reduction in volume than 49nm and 100nm sizes nanoparticles. The results of the various EOSs agreed with one another, suggesting that the EOSs of bulk materials may be used in the computations of nanoparticles.

Introduction:

Previous high-pressure studies of nanoparticles attracted a lot of attention to the fascinating features that emerged when these materials were subjected to great pressure. The influences of size and shape, in addition to crystal structures, have identified the high-pressure behavior of nanoscale materials in comparison to ordinary bulk materials [1, 2].

Due to their size-dependent optical characteristics and prospective use in optoelectronics, biological imaging and treatments, flash memory, and lithium-ion batteries, germanium nanoparticles, emphasize the advancements made in this area and offer details on the methods employed to create colloidal germanium nanoparticles with precise size and shape control [3].

Many disciplines have developed numerous branches as a result of high-pressure research. One of the most crucial results of high-pressure experiments is the P-V-T relationship, or equation of state (EOS), which allows for the determination of numerous crystal characteristics under various pressure and temperature settings[4].

It is essential to examine the structure of nanocrystalline constituents and gather useful information about their properties given that the study of nanocrystalline materials is under high- pressure. Since they exhibit physical and chemical characteristics that are dissimilar from those of the same bulk material due to their huge macroscopical size. Due to the rapid growth of nanomaterials of nanoparticles with a size of 1-100 nm and their widespread uses in various industrial, medicinal, life science, and electronics applications, draw interest due to their incredibly small size and strong sensitivity to external influences like pressure and temperature. Applying extreme pressure may be one way to cause changes in the form and structure of nanoparticles.

Due to their distinctive electrical, magnetic, mechanical, optical, and photonic properties—many of which are related to surface and volume effects and are critical in defining their phase change dynamics—semiconducting nanomaterials have garnered greater attention from researchers. When a substantial transitions from the bulk phase to the nanophase, the surface shape changes along with the drop in volume, producing more binding energy in nanomaterials than in their bulk counterparts. Hence, the rise in exterior energy is to blame for the rise in bulk modulus and phase transition pressure of nanomaterials, which results in a decrease in compressibility in these nanomaterials. It is crucial to conduct a theoretical investigation of the characteristics under high pressure of the crystal, in order to improve comprehend the intuition mechanism of the interaction mechanism [5]. Transparent electrodes in photovoltaic and display devices, phototransistors and diodes, gas, and chemical sensors, etc. are just a few of the numerous applications that have made transition metal systems a very fascinating field of study for both theorists and experimentalists[6].

Germanium nanoparticles' size-dependent optical characteristics and prospective use in the above fields have attracted scientists and engineers. Robust and simple synthetic methods are required to reliably produce Ge nanoparticles in order to further these applications and learn more about their size-dependent characteristics[3].

The research was conducted with the use of X-ray diffraction and synchrotron radiation, and the equation of state and the I-II transition of nanocrystalline Ge with crystallite sizes of 13, 49, and 100 nm have been investigated. Values of the bulk modulus and the transition pressure rise with decreasing particle size, however, the percentage volume collapse at the transition remains constant [7].

A recent study investigates the effect of high- pressure on the phonon frequency spectrum of silicon nanoparticles with two different diameters, 4.1 nm, and 10.3 nm indicating, the 4.1-nm particle experienced a higher reduction in volume and a more significant shift in phonon frequency spectrum under a specific pressure value than the nanoparticle of a diameter of 10.3 nm did [8]. The structural high-pressure behavior is shown through a model. The interface structure significantly influences the physical properties of nanocrystalline Ge because a considerable portion of the atoms is found in the grain borders.

The bulk modulus, an elastic property that is crucial for determining hardness and softness that measures resistance to volume change in bulk materials, is highly correlated with both pressure and temperature. The development of the nanoscale thermodynamic approach is critical for a deeper understanding of the thermodynamic characteristics and, consequently, the elastic behaviors of nanocrystals[9].

The transition metal systems have a wide range of uses, in optoelectronic devices, display devices, gas and chemical sensors, etc. This has made them a very intriguing area of study for both theoretical and experimental researchers [10]. In the present work the effect of high pressure on relative volume compression of Ge nanoparticles with three different sizes and Si with two different sizes will be investigated using three equations of states proposed by Vinit & Birch -Murnaghan and Suzuki [11][12][13].

Method:

Studies of nanocrystalline materials under pressure are currently of great interest due to the potential for significantly different behavior from that of the bulk. According to a review of the literature on the behavior of nanomaterials at high pressure, the Vinet, Birch Murnaghan (BM), and Suzuki EOS have been extensively employed in experimental and theoretical studies [14].

Recent studies indicate that high pressure has a significant impact on the material's structural characteristics, such as phonon frequency shift, phase transformation, and lattice volume contraction. Using experimental procedures to determine the variance in these traits is frequently challenging and expensive. At extremely high-pressure ranges, they can occasionally be impossible to predict. In some situations, using an equation of state may make it simpler to find a solution[15].

Various forms of equations of state based on assumptions of solids have been developed in the literature. The Vinet EOS is formulated on a relationship between the pressure derivative of binding energy and interatomic spacing [11].

$$P=3(1-x)B_0[\exp(\eta(1-x)]/x^2 \quad (1)$$

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

and $\eta = 3(B_0^{'} - 1)/2$

B_0 is the bulk modulus at ambient temperature and $B_0^{'}$ is the first pressure derivative of bulk modulus

Finite strain theory is used to develop third order Birch–Murnaghan (B–M) EOS [16]is given by

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

which was developed for bulk materials, is frequently used with nanostructures, and is very consistent with experimental evidence.

Suzuki equation of state (EOS) [13]have followed the Gruneisen theory of thermal expansion given by

$$P=B_0(1 - x^{-3}) + B_0\frac{\eta}{3}(1 - x^{-3})^2 \quad (3)$$

These equations are termed as nanomaterial EOSs.
In the present study, VinetEOS , B–M EOS and Suzuki EOS are used to investigate the compressional behaviors of Ge and Si nanoparticle with different sizes under high pressure.

Result and Discussion:

Nanomaterials	Size(nm)	B_0(GPa)	B_0'(GPa)
Germanium Ge	13	112	4
	49	92	4
	100	88	4
	Bulk	74.9	3
Silicon Si	4.1	67	4.1
	10.3	78	4.1
	Bulk	98	4.1

Table 1_ Input parameters utilized in this research[17][15]

The current approach for analyzing the effect of pressure on Ge and Si materials in both bulk and nano forms**.** From the equation (1) known Vinet EOS, the volume ratio (V/V_0) at different pressure have been calculated. Input parameters B_0& $B_0^{/}$ as listed in Table 1 was taken from literature. Similarly, with the same input parameters, volume ratio (V/V_0) have been calculated using equation (2) known as Birch-Murnaghan EOS equation and equation (3) called Suzuki EOS. The results obtained are are given in Table (2-3), and variation is shown in Figure (1-2).It should be highlighted based on the foregoing that the current method is capable of accurately expressing the compressional and elastic properties of nanomaterials at high pressure. Due of its practicality and simplicity, this may be of interest to researchers presently researching the elastic properties of nanomaterials under intense strain.

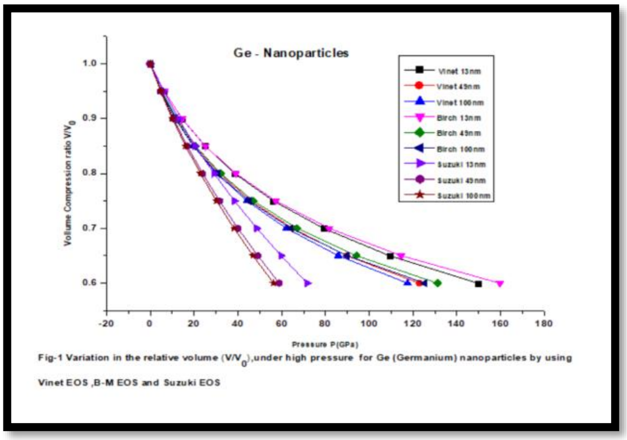

Fig-1_Variation in the relative volume of Bulk Ge in Comparison with nanoparticles using VinetEOS , Birch-Murnaghan EOS , Suzuki EOS

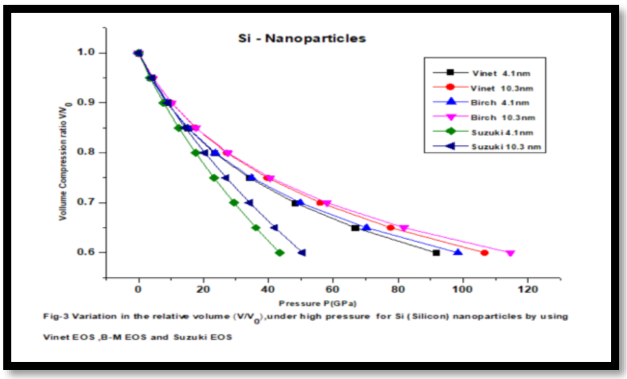

Fig-2 _Variation in the relative volume of Bulk Si in Comparison with nanoparticles usingVinet EOS, Birch-Murnaghan EOS , Suzuki EOS

Germanium Nanomaterials												
v/v_0	Pressure (P)											
	Vinet				Birch-Murnaghan				Suzuki			
	13 nm	49nm	100nm	Bulk	13nm	49nm	100nm	Bulk	13nm	49nm	100nm	Bulk
1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0	6.4	5.2	5.0	4.1	6.4	5.2	5.0	4.1	6.0	4.9	4.7	3.9
0.9	14.5	11.9	11.4	9.2	14.6	12.0	11.4	9.2	12.9	10.6	10.1	8.2
0.9	25.0	20.6	19.7	15.5	25.2	20.7	19.8	15.4	20.6	16.9	16.2	12.9
0.8	38.6	31.7	30.3	23.2	39.1	32.1	30.7	23.0	29.1	23.9	22.9	18.0
0.8	56.2	46.1	44.1	32.7	57.4	47.1	45.1	32.3	38.5	31.6	30.3	23.4
0.7	79.1	65.0	62.2	44.7	81.7	67.1	64.2	43.6	48.7	40.0	38.3	29.2
0.7	109.3	89.8	85.9	59.8	114.6	94.1	90.0	57.5	59.8	49.1	47.0	35.4
0.6	149.6	122.9	117.5	79.1	159.7	131.2	125.5	74.3	71.7	58.9	56.3	41.9

Tables-2: Calculated values of pressure P(GPa) of germanium (Ge) bulk and nanomaterials by using VinetEOS , Birch-Murnaghan EOS and Suzuki EOS

Silicon Nanomaterials									
v/v_0	Pressure P								
	Vinet			Birch-Murnaghan			Suzuki		
	4.1nm	10.3nm	Bulk	4.1nm	10.3nm	Bulk	4.1nm	10.3nm	Bulk
1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0	3.8	4.4	5.6	3.8	4.4	5.6	3.6	4.2	5.3
0.9	8.7	10.2	12.8	8.8	10.2	12.8	7.7	9.0	11.3
0.9	15.1	17.6	22.1	15.2	17.7	22.2	12.4	14.4	18.1
0.8	23.3	27.2	34.1	23.7	27.5	34.6	17.6	20.4	25.7
0.8	34.1	39.7	49.8	34.9	40.6	51.0	23.2	27.1	34.0
0.7	48.1	56.0	70.4	49.9	58.1	72.9	29.4	34.3	43.1
0.7	66.7	77.7	97.6	70.3	81.8	102.8	36.2	42.1	52.9
0.6	91.6	106.7	134.0	98.4	114.6	144.0	43.4	50.5	63.5

Tables3_ Calculated values of pressure P(GPa) of Silicon (Si) bulk and nanomaterials by using VinetEOS, Birch-Murnaghan EOS and Suzuki EOS

Conclusion:

Utilizing VinetEOS , B-M EOS and Suzuki EOS studies of the relative volume of bulk and nanomaterials of Ge (13nm, 49nm, and 100nm) & Si (4.1nm and 10.3 nm)under high-pressure have been conducted.It is obvious that the phase transition pressure is directly impacted by the change in particle size. The parent phase's volume collapse and equilibrium cell volume are closely related to the materials' grain size. Smaller size germanium nanoparticles are less compressible when high pressure is applied and are relevant to large value of their Bulk modulus compare to their Bulk form ,but Smaller size Si nanoparticles to be more compressible when high pressure is applied are relevant to smaller value of their Bulk modulus and compare to their Bulk form[9]. The volume thermal expansion of nano solids increases with decreasing size for all distinct geometries, and nano germanium gradually hardens with an increase in pressure. The current findings and the experimental data are well congruent. At different temperatures and pressures, the model is successful in explaining these thermodynamic characteristics.

Two-parameter equations of state, which are the basis of the "universal" equation of state presented by Vinet, B-M, and Suzuki. It is noteworthy because it agrees with the Birch-Murnaghan equation, which is derived from Eulerian finite-strain theory [18] , and is therefore applicable to condensed matter involving any sort of bonding. The outstanding success of the Eulerian finite-strain formalism in characterizing the compressional behaviour of materials at high pressures is widely known.

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