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POWER SERIES ANALYSIS OF EQUATION OF STATE FOR NANOMATERIALS

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ABSTRACT

The compression behavior of some nanomaterials at high pressure is critically analyzed by using power series approach of equation of state. The present equation of state (EOS) is developed with the help of simple concept of power series. Many EOSs for different solids are derived on the basis of different theories viz. Rydberg potential, finite stain etc. but it has been observed that EOSs can be obtained by power series expansion. It is shown that the power series method is capable enough to establish an excellent EOS for nanomaterial. The calculated results obtained by using present EOS is further compared with different frequently used EOSs and experimental results. Present EOS gives good agreement between theory and available experimental data which supports the validity of the simple power series model proposed for nanomaterials.

Keywords: Nanomaterials, Equation of State, Compression, Bulk modulus.

I. INTRODUCTION

In nature, a large number of systems operate under law of physics in nanoscale. Nature is a master in nano engineering. Nanoscale phenomena like Chemical reaction, catalysis action, surface properties, nano particle properties, condensation of water in raindrops or in ice, nanoparticle in dust, volcano, and factory smoke are witnessed all around the physical world. In biological processes like functioning of life, metabolic activity in body and cell, photosynthesis, functioning of chlorophyll, fertilization of ovum and various initial stages of development of zygote are the example of nanoengineering in nature.

It is possible to control fundamental properties like colour, electric conductivity, melting point, strength, modulus of rigidity, hardness, thermal expansion by applying nanotechnology in manufacturing of these materials. Nanoscience plays a key role in turning these concepts in reality. Researchers are investigating the applications of nanomaterials meanwhile the properties of these materials are also being studied by the different workers [1-4].

Nanoscience covers various branches of science viz. physics, chemistry, material science, and biology. Nanoscience deals with fabrication, characterizations and properties of matter in nano scale i.e. 1-100 nm. This scale is basically of the order of dimension of molecule; therefore it covers a wide range of physical and biological matter. The laws of Physics operate in a different ways due to complex type of interface of quantum mechanics, constraints in design a material. Nanomaterials have a large surface to volume ratio which is a significant property. But the different behaviors of nanometerial on nanoscale also open the door for new

research opportunity in the manufacturing and characterization of structural and physical properties of these materials. Now study of natural phenomena occurring in any material can be understood and explained by point of view of nanoscience. Nonomaterials like ceramic, composite, polymers always require to control over the structure of material on nanoscale so that the desired physical properties can be obtained[4,5].

Nanomaterials often require different production techniques. The main approaches for the construction are top to down and bottom to up approach. A large number of materials are now prepared and considered as nanomaterial but some materials are still in laboratory stage and only some of them are commercially available for different applications [6, 7]. The one dimension nanomaterials are thin films and other surfaces like silicon integrated circuited used in electronics industry. In this type of nanomaterial, the thickness of film approaches to atomic dimension. On the other hand, in two dimensional nanomaterials such as tubes and wires which have two nanoscale dimensions. Carbon nano tubes (CNT) are the best example of two dimensional nanomaterials. CNT are basically rolled arrangement of C atoms. CNT may be single walled or multi walled. Single walled CNT consist of just one tube. However, multiwalled CNT has several concentric tubes which have dimension of nanometer but its length may be in order of micrometer to centimeters [8-11]. Due to strong bonding among the specially arranged carbon atoms, they have noble physical and chemical properties. Mechanically these materials are very strong like diamond and have high melting point. The elastic constants of nanomaterials are different from other solids. The bulk modulus of CNT is in order of TPa which results small compression. In the present paper, compression of CNT is also studied on the basis of EOS. Sometimes single walled carbon nanotube has irregular horn like shape which is called nanohorn. Another type of structure of nanomaterial is dendrimer which is a highly branched tree like polymer molecule. Many biological materials like cells, cancer tumors have dendrimer shape. Researchers are working in the area of formation of such drugs which can affect surfaces. Now the measurements techniques like STM are capable better in these denrimer shaped surfaces. of analyzing and characterizing accurate arrangement of molecules. However, in nanoscales the physical properties are strongly influenced by quantum mechanical effects. Specially electronic and optical properties of these materials can be explained with the help of quantum mechanics. Sometimes semiconducting nano particles are called quantum dots [12-13]. Quantum dots play a significant role in optical and spectral behavior of these materials. The specific wavelength of optoelectronic device can be controlled by size and arrangement of the particle.

The study of elastic constants and phase transition of nanomaterials at high pressure and high temperature is one of the major areas of interest and it attracts the attention of many theoretical and experimental workers of this field. The study will be useful from the fabrication and application point of view. Many experimental and theoretical studies are going on in this field [14-23]. Some completely analytical equations of state are available but still there is lacking of theoretical work. The purpose of this study is to advance the new approaches for equation of state for nanomaterials. In the present study the compression and bulk modulus behavior of some nanomaterials are analysed with the help of a new mathematical approach of equation of state. A number of nano materials viz. MgO, CdSe, CNT bundle, Rb_3C_{60}, ε Fe (Hexagonal), α Fe filled MWCNT, Fe_3C filled MWCNT and 3C-SiC(30nm) are selected for this purpose.

II. METHOD OF ANALYSIS

The equation of state is a fundamental relation to analyze the elastic and physical properties of different class of solids and it plays a key role in basic and applied condensed matter Physics related research. A very little work has been done in the field of nanomaterials[24-26], however a lot of work has been done in other class of solids[27-30]. Most of the equations of state are not suitable to explain the properties of nanomaterials at high pressure due to their abnormal behavior in this particle size range. However, some widely used EOSs in recent literature are used for nanomaterial. Pasafar and Mason [31] have considered a relation for compressed solids on a physical basis by finding that the repulsive branch of binding energy curve can be fitted by a quadratic expression in density, given as

$$P\left(\frac{V}{V_0}\right)^2 = A_0 + A_1\left(\frac{V}{V_0}\right)^{-1} + A_2\left(\frac{V}{V_0}\right)^2 \quad (1)$$

Where P is pressure, V/V_0 is volume compression. Where V_0 is volume at zero pressure and A_0, A_1 and A_2 are constants for a given temperature. However, on the basis of different theories Hama and Suito [32], Shanker and Kushwaha [33] have pointed out some drawbacks of this equation. Shanker and Kushwaha[33] expended the power series of PV^2, and similarly Singh[34-35] expended the power series PV in powers of $(1-V/V_0)$. Further Kholiya [35] expand the series as

$$P = A_0 + A_1\left(\frac{V}{V_0}\right)^{-1} + A_2\left(\frac{V}{V_0}\right)^2 \quad (2)$$

Sharma and Kumar [25] modified Shanker's formulation which was originally derived from volume temperature relation and given as

$$P = A_1\left(1-\frac{V}{V_0}\right) + A_2\left(1-\frac{V}{V_0}\right)^2 \quad (3)$$

Similarly, other possible relations are

$$P = A_0 + A_1 \exp\left[A_2\left(1-\frac{V}{V_0}\right)\right] \quad (4)$$

$$P = A_0 + A_1\left(\frac{V}{V_0}\right)^{-A_2} \quad (5)$$

In all the above equations the values of constants A_0, A_1 and A_2 are obtained by applying boundary conditions i. e. at P=0; $V=V_0$; $B= B_0$; $B'= B'_0$ where B is bulk modulus and B' is pressure derivative of bulk modulus and subscript $_0$ represents value at zero pressure. Applying boundary conditions eq. (4) becomes

$$P = \frac{B_0}{B_0^{'}+1}\left[\exp\left\{\left(B_0^{'}+1\right)\left(1-\frac{V}{V_0}\right)\right\}-1\right] \quad (6)$$

This is basically Tait's EOS. Expanding the exponential term and neglecting the higher order term eq. (6) becomes

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

If boundary conditions are applied in eq. (3), the same eq. is obtained. Similarly applying boundary condition on eq. 5, Murnaghan EOS is obtained and reads as

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

Power series represented by eq. (1-5) are fully analytical and no physical and mathematical justifications are available for proposing these series, however, eq.(1) to (5) provide different EOS which are available in literature [35] and frequently used . On the basis of interatomic potential energy Vinet considered the following expression for pressure and known as Vinet universal EOS and widely used in recent literature [27].

$$P = 3B_0\left\{1-\left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right\}\left(\frac{V}{V_0}\right)^{-\frac{2}{3}}\left[\exp\frac{3\left(B_0^{'}-1\right)}{2}\left\{1-\left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right\}\right] \quad (9)$$

In the present paper, the author proposes a physical and mathematical explanation behind the pressure volume relation. Starting from the original power series concept, it is a well known fact that power series can approximate any function especially when the parameters are small. The approximation techniques are frequently used in Physics and many a times, the series give unexpected useful result. The power series is generally expressed as

$$f(x) = A_0 + A_1(x-c)+A_2(x-c)^2+A_3(x-c)^3+\ldots\ldots \quad (10)$$

Where f(x) is any function, x is variable, A_n are constants and c is the center around which the series expands. It is pointed out that series is centered at c, and in case of pressure, it can be assumed that pressure is function of density ρ and series is centered around the density ratio $\rho/\rho_0=1$ i.e. at zero pressure. Power series give good approximation if the variable is small i.e. ρ/ρ_0 centered at 1. Therefore the expansion is centered on zero pressure. On the basis of this concept, the correct power series can be proposed as

$$P(\rho) = A_0 + A_1\left(\frac{\rho}{\rho_0}-1\right)+A_2\left(\frac{\rho}{\rho_0}-1\right)^2 \quad (11)$$

The series is extended up to quadratic term only because higher order terms involve higher order derivatives of bulk modulus which are presently not available in the literature. However by including the higher order term results may improve. Volume and pressure are related as $\frac{\rho}{\rho_0}=\frac{V_0}{V}$

Above equation reads as

$$P(\rho) = A_0 + A_1\left(\frac{V_0}{V}-1\right)+A_2\left(\frac{V_0}{V}-1\right)^2 \quad (12)$$

Applying boundary condition and using the definition of bulk modulus i.e. $B = -V\frac{dP}{dV}$ and its first pressure derivative, the constants become $A_0 = 0$, $A_1 = B_0$ and $A_2 = \frac{1}{2}B_0\left(B_0^{'} - 1\right)$

Now the above equation becomes

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

By using eq. (12), bulk modulus is given as

$$B = B_0\frac{V_0}{V} + B_0\left(B_0^{'} - 1\right)\frac{V_0}{V}\left(\frac{V_0}{V} - 1\right) \quad (14)$$

Further by using eq. (14) the pressure derivative $B^{'} = \frac{dB}{dP}$ is given as

$$B^{'} = \frac{V_0}{V}\frac{B_0}{B}\left[1 + \left(B_0^{'} - 1\right)\left(2\frac{V_0}{V} - 1\right)\right] \quad (15)$$

It should be mentioned here that the above equations of states are mathematically and thermodynamically consistent. However, some equations used for nanomaterials viz. Suzuki equation of state [36, 37], Kumar and Kumar formulation [35] are not mathematically and thermodynamically consistent. Further eq. (13) can be extended for the effect of temperature on nanomaterials by introducing concept of thermal pressure.

The thermal pressure P_{Th} is expressed as

$$P_{Th} = \int_{T_0}^{T} \alpha_0 B_0 dT \quad (16)$$

where α_0 is thermal expansion coefficient at zero pressure. Using Hiderbrand approximation [38] eq. (11) becomes

$$P_{Th} = \alpha_0 B_0 (T - T_0) \quad (17)$$

If pressure is fixed and the temperature changes, then the eq. (13) becomes

$$P = B_0\left(\frac{V_0}{V} - 1\right) + \frac{1}{2}B_0\left(B_0^{'} - 1\right)\left(\frac{V_0}{V} - 1\right)^2 + \alpha_0 B_0 (T - T_0) \quad (18)$$

This equation can be used for the study of temperature in nanomaterials.

III. RESULTS AND DISCUSSION

In the present study we have fully analyzed compression behavior of some nanomaterials. The compression and bulk modulus of nanomaterials are obtained by using presently proposed eq. (13) and compared with some frequently used EOSs viz. Shanker modified equation by Sharma and Kumar [eq. (7)], Murnaghan EOS [eq. (8)] and Vinet EOS [eq.(9)]. In the present study almost all important nanomaterials have been selected (MgO,

CdSe, CNT bundle, Rb_3C_{60}, ε Fe (Hexagonal), α Fe filled MWCNT, Fe_3C filled MWCNT and 3C-SiC(30nm)). Since nanomaterials are used for device fabrication so it is very important to know about compression and bulk modulus of these materials for their utility at high pressure and high temperature range. The input parameters for calculations are given in table 1 with their references in square brackets. The compression behaviors obtained by using different equations are graphically represented in figures 1 to 8 and their experimental data are given in square brackets [39-43]. In all cases of selected nanomaterials, it is found that the calculated results show good agreement with available experimental data. Further, the results obtained by eq.13 are also compared with some frequently used EOS like Vinet [27] and Sharma and Kumar [25]. It is noticed that results are very close to Vinet universal EOS. In some cases of nanomaterials like 20 nm Ni, GaN, Si results are better than Vinet's EOS. The bulk modulus and pressure derivative of bulk modulus of nanomaterials can be calculated by using eq.14 and 15, but experimental data are not available, therefore, results are not given in the present paper. Thus, it is found that the present equation is capable to predict compression as well as bulk modulus behavior of nanomaterials. The pressure range selected is such that the experimental data are available for comparison, although it can be calculate in all possible range.

Thus, good results are obtained for the compression behavior of nanomaterial solids by using eq. (13). It can be emphasized that simple concept of power series introduced in EOS seems to be applicable for the study of nanomaterials under high pressure and high temperature.

IV. CONCLUSION

An equation of state is proposed to analyze compression behavior of some important nanomaterials like MgO, CdSe, CNT bundles, Rb_3C_{60}, ε Fe, αFe filled MWCNT, Fe_3C filled MWCNT and 3C-SiC(30 nm) under high pressure and high temperature. The input parameters used in this work have been shown in Table 1. It has been shown that the compression at high pressure can be successfully explained using presently proposed EOS. In present study, this equation is further extended for a high temperature and high pressure range by introducing the concept of thermal pressure. After the study it is found that the results obtained by new equations of state show good agreement between calculated and available experimental data. The overall study demonstrates the validity of proposed equation.

Table 1: Input Parameters with their Corresponding References. The Square Brackets Show the Reference Sources.

Solids	B_0 (GPa)	B_0'	Reference
MgO	179	1.5	[11]
CdSe	74	4	[14]
CNT bundle	37	11	[15]
Rb_3C_{60}	17.35	3.9	[16]
ε Fe (Hexagonal)	179	3.6	[17]
α Fe filled MWCNT	167	4	[18]
Fe_3C filled MWCNT	135	4.05	[19]
3C-SiC(30nm)	245	2.9	[20]

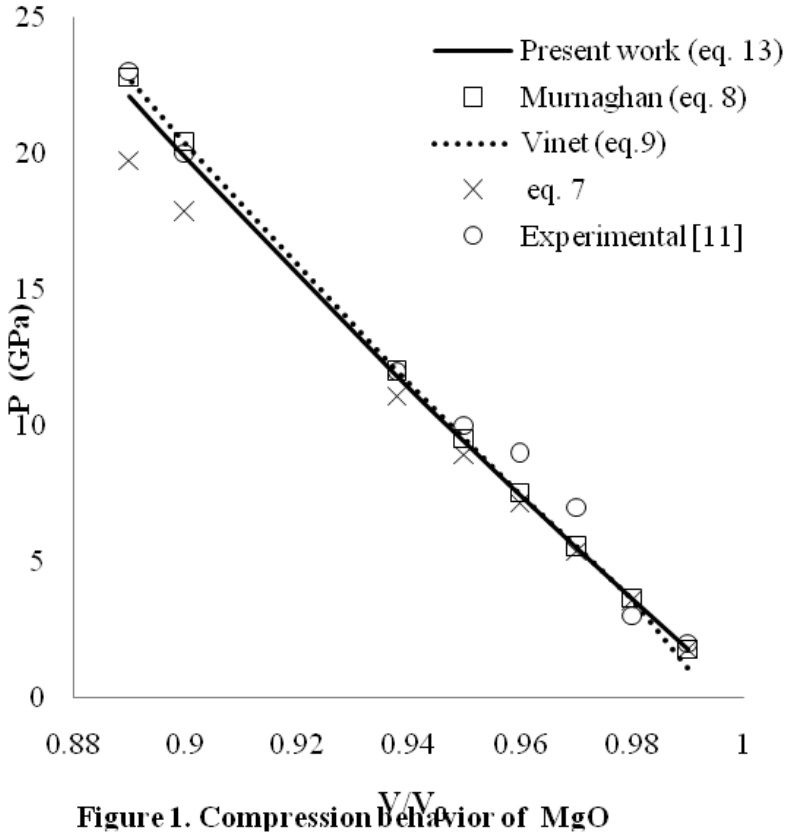

Figure 1. Compression behavior of MgO

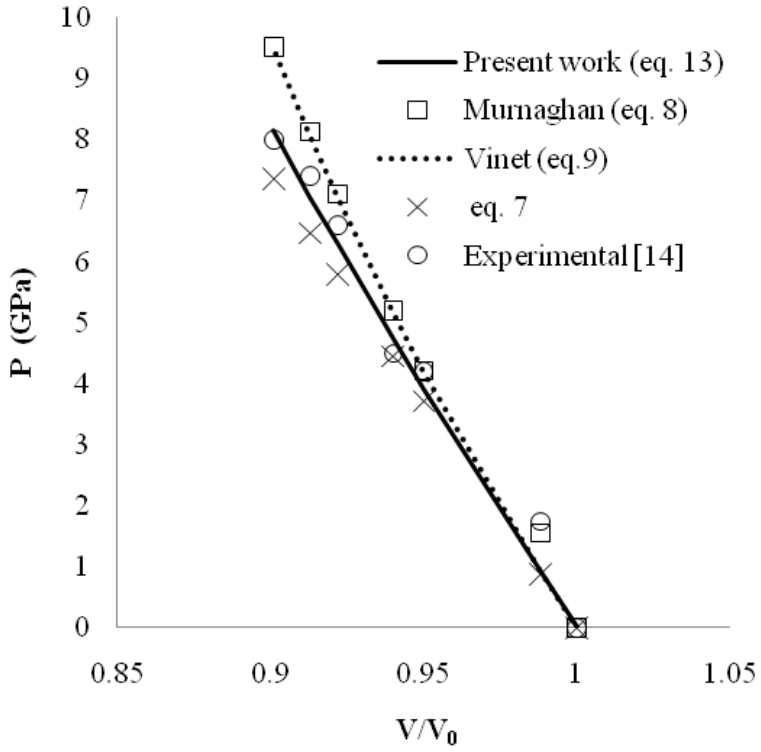

Figure 2. Compression behavior of CdSe

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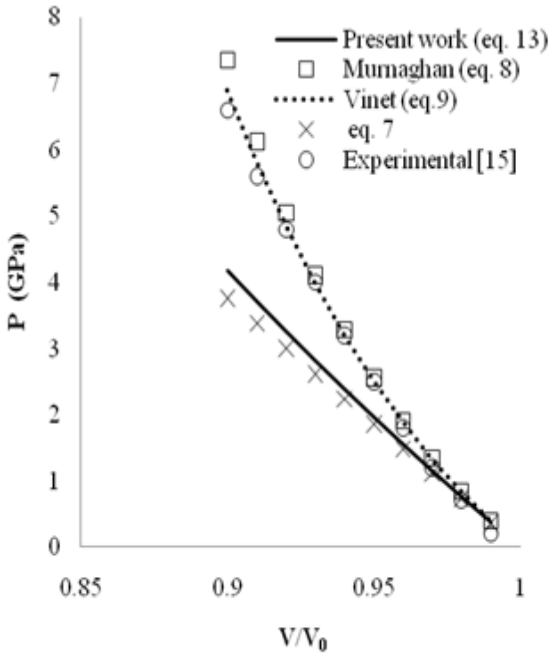

Figure 3. Compression behavior of CNT Bundle

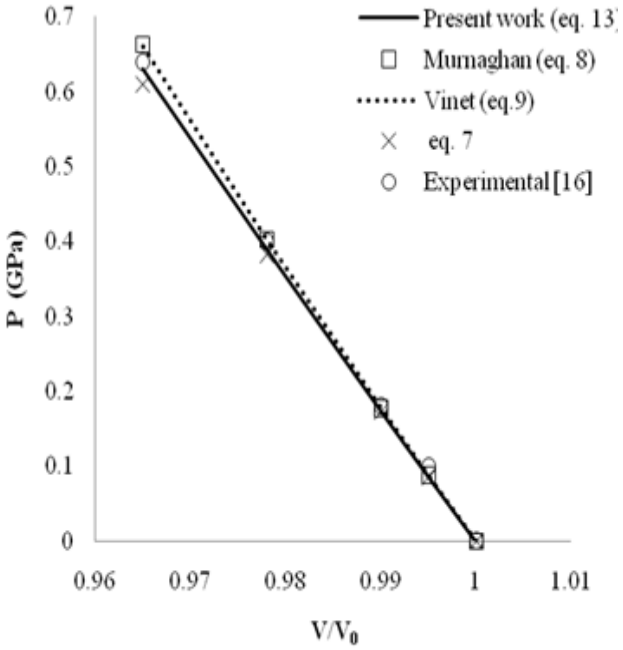

Figure 4. Compression behavior of Rb_3C_{60}

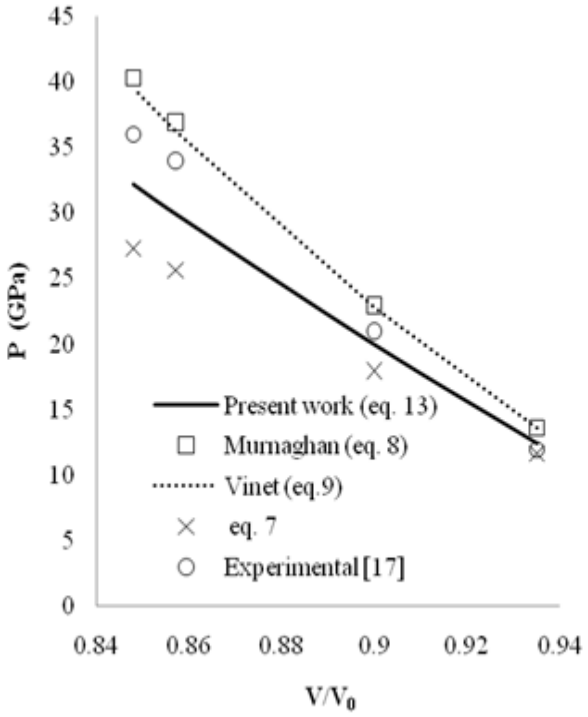

Figure 5. Compression behavior of ε Fe

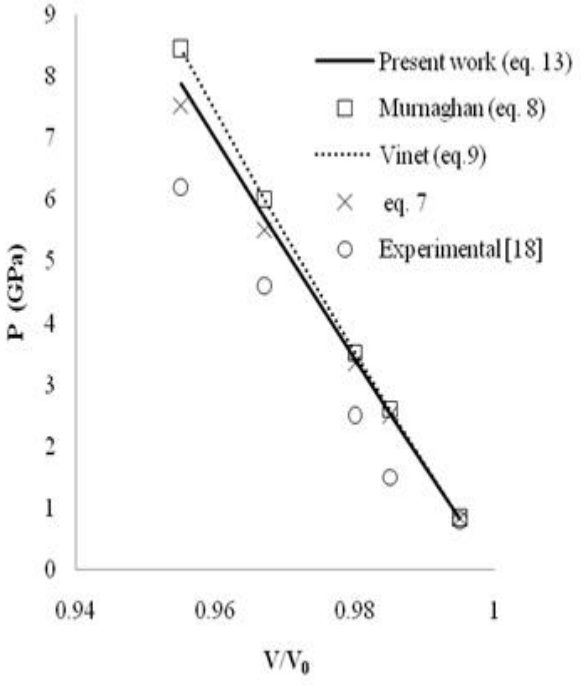

Figure 6. Compression behavior of α Fe filled MWCNT

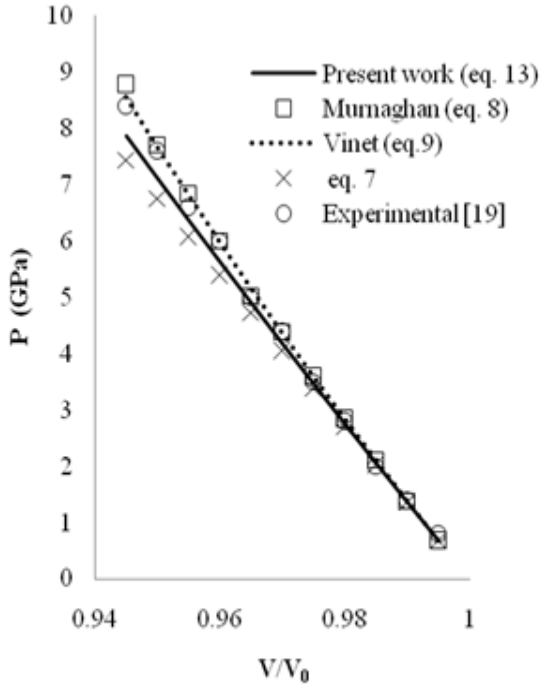

Figure 7. Compression behavior of Fe_3C filled MWCNT

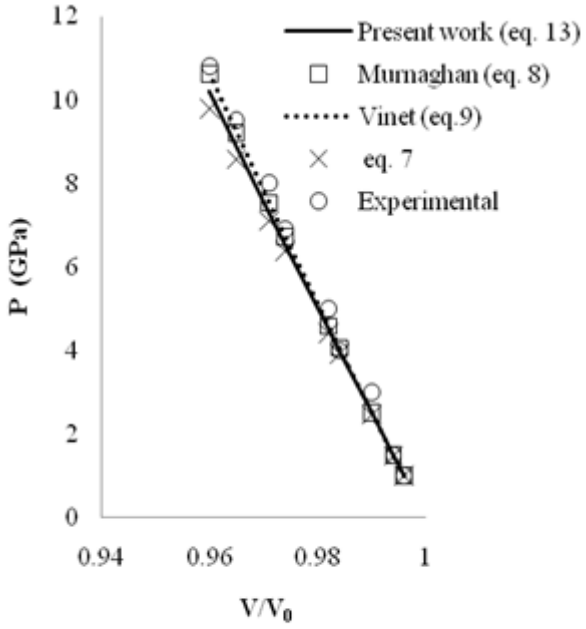

Figure 8. Compression behavior of 3C-SiC (30nm)

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