CONDENSED MATTER PHYSICS
An International Journal
Full Paper
CMPAIJ, 1(1), 2016 [018-022]

Behaviour of nanomaterials under pressure

Neetu Sorot[1], B.R.K.Gupta[1], Jeewan Chandra[2]*
[1]Department of Physics, G.L.A.University Mathura, U.P., (INDIA)
[2]Department of Applied Science, G. B. Pant Engineering College, Uttarakhand, (INDIA)
E-mail: jeewan25may@rediffmail.com

ABSTRACT

Equation of state model is used to study the compression behaviour of nanomaterials. The well known Suzuki's EOS is shown to be mathematically inconsistent and hence modified by applying the initial boundary conditions. Thermodynamically and mathematically consistent, modified Suzuki's EOS is applied to study the compression behaviour of various nanomaterials (Zr0.1Ti0.9O2, 3C-SiC, ε- Fe, CuO, The results obtained using the thermodynamically consistent formulation (modified Suzuki's EOS) are found to be in better agreement with the experimental data in comparison to the Suzuki EOS.

KEYWORDS

Nanomaterials;
Compression behaviour;
Equation of state.

INTRODUCTION

It is evident from the exiting literature that during past years several experimental studies have been performed to understand the high pressure behaviour of nanomaterials. Studies of compressibility and pressure induced phase transitions for nanocrystalline materials can improve our understanding of the stable state of materials down to nanometer scale. Most high pressure research on nanocrystalline materials has been on semiconductor, although some work on insulators and metals has been reported recently. On applying the high pressure on nanomaterial, many effects may occur, such as (i) transformation of nano-constitutive elements (ii) transformation of the interaction between nano objects (iii) modification of interactions between the nano-objects and pressure transmitting medium. Due to such applications, the effects of pressure on nanomaterials have attracted the attention of the researchers.

The compression behaviour of Zr-doped nanoanatse $Zr_{0.1}Ti_{0.9}O_2$ synthesized by the sol gel method was studied by Holbig et al.[1] using a diamond anvil cell (DAC) and found no evidence of phase transition up to a pressure of 13 GPa. Lie et al.[2] have synthesized the nanocrystalline 3C-SiC (30 nm) by laser induced vapour phase reactions and performed the energy dispersive X-ray diffraction (EDXRD) experiment at room temperature using silicon oil as a pressure transmitting medium to obtain quasi hydrostatic condition. They observed a decrease of the Born's transverse effective charge of these nanocrystals with increasing pressure, in contrast to its bulk counterpart. Chen et al.[3] have performed X-ray diffraction measurements on nanocrystalline ε-Fe up to 46 GPa and determined the value of bulk modulus and its pressure derivative from the analysis of lattice parameter data. The EOS of nanocrystalline CuO (24 nm) has been studied by Wang et al.[4], using high energy Syncroton radiation and Raman spectroscopic techniques. The study based on the equation of states at high-pressure permits interpolation and extrapolation in to the regions in which the experimental data is not available adequately and hence may be helpful in planning future high pressure experiments[5-12]. In the present paper our aim is to develop a simple theoretical model to study the high pressure elastic properties of nanomaterials. To develop the theoretical model we have chosen the well known Suzuki's EOS[13-14] as a base. It is shown that the Suzuki EOS is mathematically inconsistent and does not follow the basic thermodynamic conditions. Therefore, to make Suzuki's EOS mathematically consistent some modifications are required and in the present paper it is modified by using the basic thermodynamic relations and initial boundary conditions as mentioned in method of analysis section. The obtained results with the Suzuki and the modified Suzuki EOS along with the experimentally obtained data are given and discussed in results and discussion section.

Method of analysis

In the literature Mie-Gruneisen Debye theory is being widely used. Using Mie-Gruneisen Debye theory Suzuki[13] reported what became known as the Suzuki relation for thermal expansivity. This reads as follows[13-14].

$$\frac{V}{V_0} = \frac{\left[1 + 2k - \left(1 - \frac{4kE_{Th}}{Q}\right)^{1/2}\right]}{2k} \quad \textbf{(1)}$$

Where $k = \frac{(B_0' - 1)}{2}$, $Q = \frac{B_0 V_0}{\gamma_0}$, γ_0 is the Gruneisen ratio and E_{Th} is the thermal energy.

Shanker[15] used $P_{Th} = \frac{\gamma_0 E_{Th}}{V_0}$ and rearranged Eq. (1) as follows

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 - 2\left(\frac{B_0' - 1}{B_0}\right) P_{Th}\right]^{1/2}}{(B_0' - 1)} \quad \textbf{(2)}$$

Where P_{Th} is the thermal pressure. Eq (2) is valid at P=0. Following the arguments of Kushwaha and Shanker[16] when P is not equal to zero, Eq. (2) may be rewritten as follows

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 - 2\left(\frac{B_0' - 1}{B_0}\right)(P_{Th} - P)\right]^{1/2}}{(B_0' - 1)} \quad \textbf{(3)}$$

Now, when thermal pressure is zero (P_{Th}=0), Eq. (3) gives the following simple relation.

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 - 2\left(\frac{B_0' - 1}{B_0}\right) P\right]^{1/2}}{(B_0' - 1)} \quad \textbf{(4)}$$

Or

$$P = B_0\left[\left(1 - \frac{V}{V_0}\right) + \left(\frac{B_0' - 1}{2}\right)\left(1 - \frac{V}{V_0}\right)^2\right] \quad \textbf{(5)}$$

Eq. (5) is widely used Suzuki's EOS, which gives the compression curve quite close to the experimental values, but Suzuki's EOS given by Eq. (5) is found to be mathematically inconsistent and does not follow the basic thermodynamic conditions. Mathematical inconsistency in the Suzuki EOS may be shown as follows:

The expression for bulk modulus, i.e. $B = -V\left(\frac{dP}{dV}\right)$, obtained from Eq. (5) comes out as:

$$B = \left(\frac{V}{V_0}\right) B_0 \left[1 + 2\left(\frac{B_0' - 1}{2}\right)\left(1 - \frac{V}{V_0}\right)\right] \quad \textbf{(6)}$$

From Eq. (6), the first order pressure derivative of bulk modulus, $B' = \frac{dB}{dP}$ comes out to be:

$$B' = -\left[\frac{1 + (B_0' - 1)\left(1 - \frac{2V}{V_0}\right)}{1 + (B_0' - 1)\left(1 - \frac{V}{V_0}\right)}\right] \quad \textbf{(7)}$$

Now, from the thermodynamic boundary condition at P=0; V=V_0 and one should have B=B_0, but at P=0; V=V_0 Eq. (7), gives $B' = B_0' - 2$, therefore, the Suzuki EOS is mathematically and thermodynamically inconsistent. So we have to modify Suzuki's EOS in such a way that it follows the basic thermodynamic relations. Therefore, the aim of the present paper is to redefine the Suzuki EOS and formulate an EOS which is mathematically consistent and explains the compression behaviour of different solids. In the present paper, to modify the Suzuki EOS, the expansion method, have been considered and the product *PV* is expended in powers of 1-(V/V_0) up to the quadratic term, as:

$$P\left(\frac{V}{V_0}\right) = A_0 + A_1\left(1-\frac{V}{V_0}\right) + A_2\left(1-\frac{V}{V_0}\right)^2 \quad (8)$$

where A_0, A_1 and A_2 are constants and may be determined from the initial boundary conditions as used by Shanker and Kushwah[4] i.e. at initial pressure P=0; V=V_0 and therefore, from Eq. (8), we have A_0=0.

The expression for bulk modulus, i.e. , obtained from Eq. (8) comes out as:

$$B = \left(\frac{V_0}{V}\right)\left[A_1 + A_2\left\{1-\left(\frac{V}{V_0}\right)^2\right\}\right] \quad (9)$$

The expression for first order pressure derivative of bulk modulus, i.e. $B' = \frac{dB}{dP}$ by differentiating Eq. (9) with respect to pressure is as follows:

$$B' = \frac{A_1 + A_2\left[1+\left(\frac{V}{V_0}\right)^2\right]}{A_1 + A_2\left[1-\left(\frac{V}{V_0}\right)^2\right]} \quad (10)$$

At P=0; V=V_0; Eqs. (9) and (10) give A_1=B_0 and, $A_2 = B_0\left(\frac{B_0'-1}{2}\right)$ where B_0 and B_0' are the values of bulk modulus and first order pressure derivative of bulk modulus at zero pressure, respectively.

Substituting the values of A_0, A_1 and A_2 in Eq. (8) becomes:

$$P = B_0\left[\frac{V_0}{V}\right]\left[\left(1-\frac{V}{V_0}\right) + \left(\frac{B_0'-1}{2}\right)\left(1-\frac{V}{V_0}\right)^2\right] \quad (11)$$

Eq. (11) can be regarded as the modified Suzuki EOS and is thermodynamically and mathematically consistent.

RESULTS AND DISCUSSION

To study the high pressure behaviour using equation of states, we requires two input parameters 'B_0' and '', these parameters are given in TABLE 1 along with corresponding references. The results obtained for the pressure dependence of the volume compression for 4 nanomaterials (Zr0.1Ti0.9O2, 3C-SiC, ε-Fe, CuO, using Suzuki's EOS [Eq. (5)] and modified Suzuki's EOS [Eq. (11)] are shown in Figures (1 to 4) along with the experimental data. From these figures, it is clear that the Eq. (11) modifies the results of Suzuki's EOS (Eq. 5), for the compression behaviour of nanomaterials. The reason for this may be attributed to the mathematical consistency of the modified Suzuki EOS which was missing in the Suzuki EOS. Thus, it is convenient to use Eq. (11) i.e. modified Suzuki's EOS to study the high pressure behaviour of nanomaterials. The theory may also be extended to study the pressure dependence of bulk modulus for these nanomaterials. The pressure dependence of bulk modulus can also be calculated from Eq. (9). It is pertinent to mention here that Kumar and Kumar[17] have also modified Shanker's EOS on the empirical basis to study the compression behaviour of nanotubes (individual and bundles). Although, the results obtained by modified Shanker's EOS were close in the range up to where

TABLE 1 : Values of input parameters used in the present work (B_0 is the bulk modulus in GPa at P=0 and B_0' is the first order pressure derivative of bulk modulus at P=0)

Sr.No.	Material	*B0* (GPa)	B_0'	References
1	Zr0.1Ti0.9O2	213	17.9	[1]
2	3C-SiC	245	2.9	[2]
3	ε- Fe	179	3.6	[3]
4	CuO	81	4	[4]

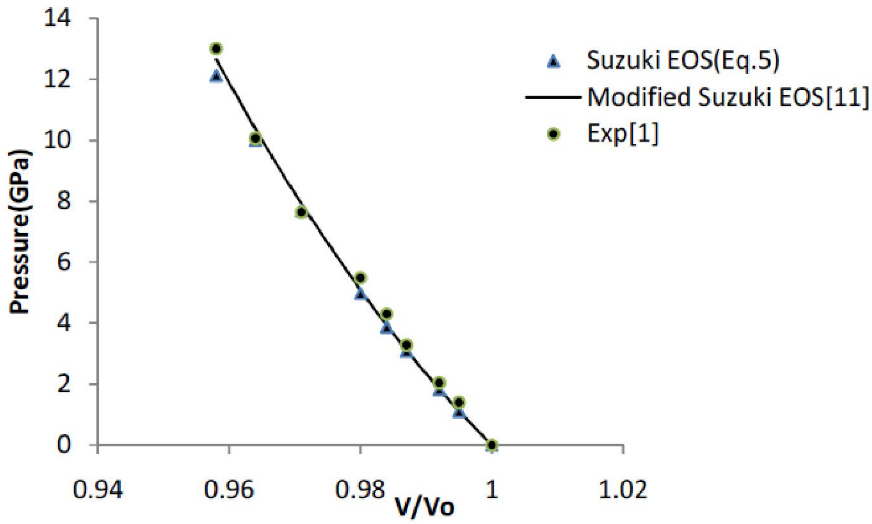

Figure 1 : Compression behavior of nano-Zr0.1Ti0.9O2

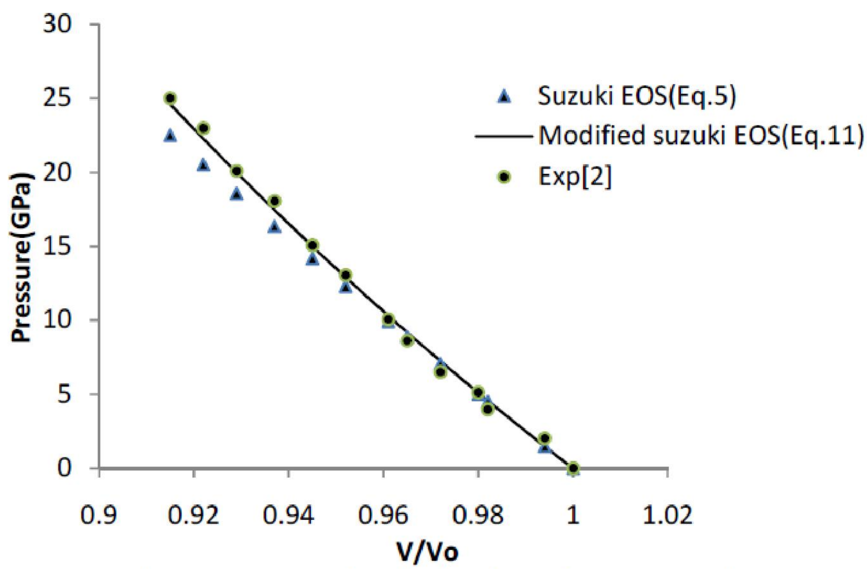

Figure 2 : Compression behavior of nano-3C-SiC

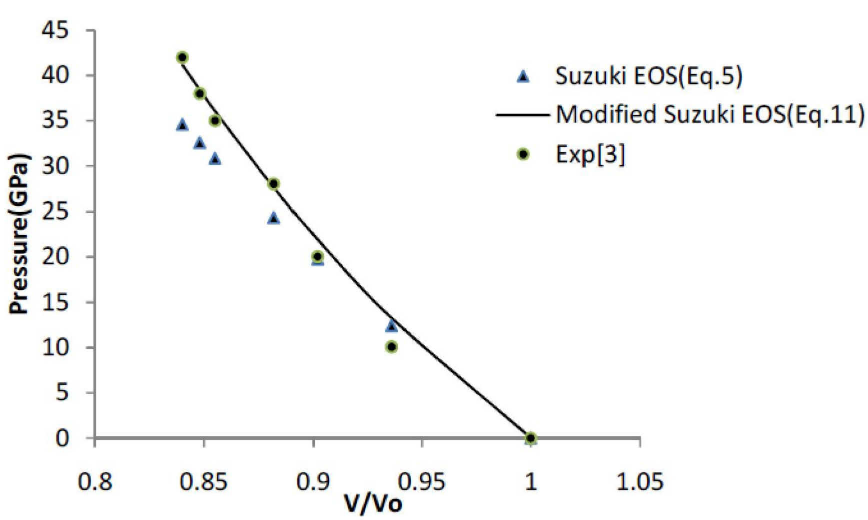

Figure 3 : Compression behavior of nano-õ Fe

the experimental data is available but Kholiya[18] have shown that their used EOS is thermodynamically and

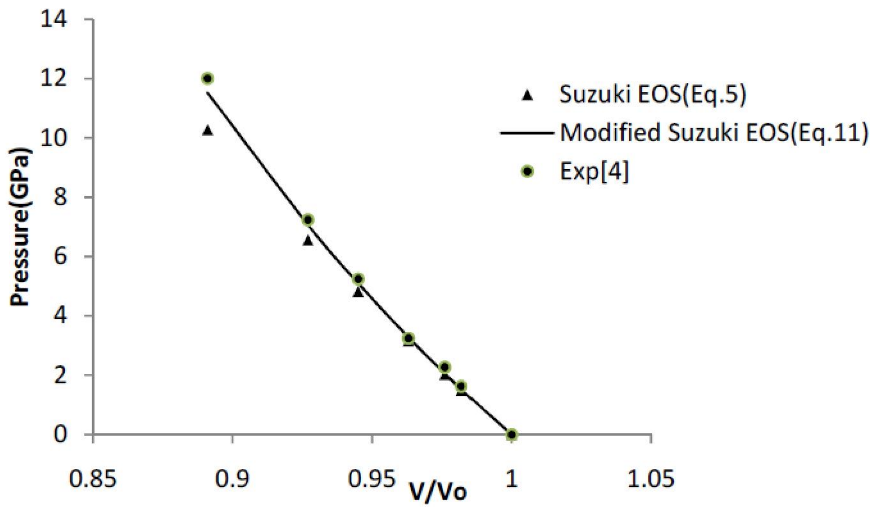

Figure 4 : Compression behavior of nano-CuO

mathematically inconsistent and hence may not be applicable for some other nanomaterilas as well as for interpolation and extrapolation in to the regions in which the experimental data is not available.

From the overall discussion, it may be concluded that the present formulation follows the fundamental thermodynamic conditions and modifies the results of Suzuki's EOS, which is mathematically and thermodynamically inconsistent also. Therefore, modified Suzuki's EOS, should be favoured over mathematically and thermodynamically inconsistent Suzuki's EOS.

REFERENCES

[1] E.Holbig, L.Dubrovinsky, G.S.Neumann, V.Prakapenka, V.Swamy, Z.Naturforsch; **61(b)**, 1577 **(2006)**.

[2] J.Liu, C.Jin, J.Chen, J.Hu; J.Am.Ceram.Soc., **87**, 2291 **(2004)**.

[3] B.Chen, D.Penwell, M.B.Kruger, A.F.Yue, B.Fultz; J.of Appl.Phys., **89**, 4794 **(2001)**.

[4] Z.Wang, V.Pischedda, S.K.Saxena, P.lazor; Solid State Commun., **121**, 275 **(2002)**.

[5] Jeewan Chandra, Pooja K.Bhatt, Kuldeep Kholiya; Journal of Nanotechnolog, Article ID 639068, **(2013)**.

[6] Jeewan Chandra, Deepika Kandpal, B.R.K.Gupta; Physica B, **404**, 1087 **(2009)**.

[7] Jeewan Chandra, Deepika Kandpal, B.R.K.Gupta; High Temperature-High Pressure, **37**, 325 **(2008)**.

[8] Jeewan Chandra, Deepika Kandpal, B.R.K.Gupta; High Temperature-High Pressure, **38**, 13 **(2009)**.

[9] Kuldeep Kholiya, Jeewan Chandra; Applied Physics A: Materials Science & Processing, **113**, 741 **(2013)**.

[10] U.D.Sharma, M.Kumar; Physica B, **405**, 2820 **(2010)**.

[11] Kuldeep Kholiya, Jeewan Chandra; Journal of Taibah University for Science, **8**, 137 **(2014)**.

[12] Jeewan Chandra, Kuldeep Kholiya; Ravindra Kumar ISRN Nanotechnology, Doi, http://dx.doi.org/10.1155/2013/404920, **(2013)**.

[13] O.L.Anderson; Equation of state for geophysics and ceramic science oxford university press, Oxford, **(1995)**.

[14] G.Helfrich; Phys.Earth Planet.Interiors, **116**, 133 **(1999)**.

[15] J.Shanker, S.S.Kushwah, P.Kumar; Physica B, **233**, 78 **(1997)**.

[16] S.S.Kushwaha, J.Shanker; J.Phys.Chem.Solids, **59**, 197 **(1998)**.

[17] M.Kumar, M.Kumar; Indian J Pure & Appl.Phys, **46**, 378 **(2008)**.

[18] Kuldeep Kholiya; Indian J Pure & Appl Phys, **51**, 94 **(2013)**.