Indian Journal of Pure & Applied Physics
Vol. 54, April 2016, pp. 251-258

Effect of size with freedom of pressure and temperature for nanomaterials

Geeta Sharma & Munish Kumar*
Department of Physics, G B Pant University of Agriculture and Technology, Pantnagar 263 145, India

Received 12 February 2014; accepted 7 January 2016

A simple theoretical model is developed, which includes the effect of size, pressure and temperature on nanomaterials. The model is used to compute the variation of unit cell volume under different conditions of size, pressure and temperature of nanomaterials, viz., ε-Fe, Ni, Se and Zr. The results obtained are compared with the available experimental data. A good agreement is observed between model predictions and experimental data supporting the validity of the proposed model. Model predictions, reported in the absence of experimental data, may be interesting for the researchers engaged in the experimental studies of nanomaterials under varying conditions of size, pressure and temperature.

Keywords: Nanomaterials, Thermal expansion, Equation of states, Inverse Hall-Petch effect

1 Introduction

The continuous increasing interest in nanocrystalline materials for varied technological applications originates from the possibility to tune their properties, so that their performance in comparison to standard materials can be remarkably superior. In general, there is a critical grain size above which the properties of nanocrystalline materials overlap with those of the bulk and therefore, the advantage of nanomaterials disappear. It has been discussed that the crystallite size, the lattice strain build up and the lattice parameter evaluation are key factors to describe the size dependent property variation[1], which have to be measured as precisely as possible. The reduction in crystalline size is followed by the variation of lattice parameter or unit cell volume, which is consequently related to the modification of physical properties. An analysis of the experimental and theoretical work demonstrates that surface atoms dictate the performance of nanostructures, yet atoms of the interior remain as they are in bulk counterpart. Thus, the effect of size is very important to understand the behaviour of nanomaterials. In addition to this, nanomaterials are very sensitive to the external parameters, like pressure and temperature. Therefore, the study of pressure and temperature on nanomaterials may be more challenging, fascinating and rewarding. Chen *et al.*[2] performed X-ray diffraction measurements on the nanomaterial iron up to 46 GPa and reported the value of bulk modulus and its pressure derivative. No significant grain growth was observed to occur under pressure. Grant *et al.*[3] studied the compressibility of monolithic fully dense electrodeposited nanocrystalline Ni (29 nm) under both quasi-hydrostatic and non-hydrostatic conditions up to a nominal pressure of 50 GPa using angle-dispersion X-ray diffraction. They obtained an equation of state (EOS) from measured reflection. The apparent bulk modulus measured under non-hydrostatic condition is larger than that of corresponding coarse grained material under either type of compression, but nearly same under quasi-hydrostatic conditions. The high pressure studies have been reviewed by Sharma and Kumar[4].

Zhao and Lu[5] performed X-ray diffraction measurement in a temperature range 88-325 K on porosity free nanocrystalline element Se sample with hcp structure. Thermal expansion coefficients were determined according to the temperature dependence of lattice parameters and unit cell volume. It was found that with a reduction of grain size, the linear thermal expansion coefficient increases significantly, resulting in an evident increase in the volume thermal expansion coefficient that follows the D^{-1} rule. Bhagwat and Ramaswamy[6] synthesized nanocrystalline zirconia powder with a fairly narrow particle size distribution by the amorphous citrate route. Crystallite size determined from XRD was found to be 8 nm, which is in close agreement with the particle size determined by TEM; and thermal stability in tetragonal phase was found up to 1023 K. A linear increase in the lattice parameters and percent

*Corresponding author (E-mail: munish_dixit@yahoo.com)

thermal expansion as a function of temperature indicates a linear lattice thermal expansion. Thus, many studies exist related to the pressure effects (compression) as well temperature effects (thermal expansion) of nanomaterials. Moreover, theoretical analysis is lacking. Thus, it is legitimate and may be useful to present some simple theoretical basis to understand the effect of pressure as well as temperature. Since the effect of size is also very important and useful for nanomaterials[7], therefore, the effect of size is also included in the model.

2 Theoretical Formulations

The equation of state (EOS) of nanomaterials has been developed as[4]:

$$P = a_1(1-\frac{V}{V_0}) + a_2(1-\frac{V}{V_0})^2 \quad \ldots (1)$$

where, P, is the pressure; V/V_0, the relative change in volume; and a_1 and a_2, the size dependent parameters, which may be determined from the definition of the bulk modulus and its first order pressure derivative as[4]:

$$a_1 = B_{0n} \quad \ldots (2)$$

$$a_2 = \frac{B_{0n}(B'_{0n}+1)}{2} \quad \ldots (3)$$

where, B, is the bulk modulus; B', the first order pressure derivative of the bulk modulus; and 0 refers to their initial value; and n, the nanomaterials. The Eq. (1) may be derived in different ways[4]. Moreover, Eq. (1) may be rewritten and completed as:

$$P = \frac{B_{0n}}{A}\left[\left\{1 + A(1-\frac{V}{V_0}) + \frac{A^2}{2}(1-\frac{V}{V_0})^2 + \ldots\ldots\ldots\ldots\infty\right\} - 1\right] \quad \ldots (4)$$

or

$$P = \frac{B_{0n}}{A}\left[\left\{\exp A\left(1-\frac{V}{V_0}\right)\right\} - 1\right] \quad \ldots (5)$$

where, A, may be taken as $(B'_{0n} + 1)$. Equation (5) has also been derived independently using the thermodynamic analysis[8] for bulk materials and has the power to predict many other EOS as discussed in detail by Kumar[8-10]. In Eq. (5), B_{0n} and B'_{0n}, are the parameters, which may be regarded as size dependent for nanomaterials. Therefore, to make Eq. (5) size dependent, one can proceed as:

Qi[11] presented a simple method for the cohesive energy of the nanosolids (E_{Tot}). According to this model, if the total atoms of a nanosolid are denoted by n and total number of surface atoms are N, then the number of interior atoms is (n-N). If the relaxation of the nanosolid is not considered, the interior structure is the same as the corresponding bulk materials. Let E_0 be the cohesive energy per atom for bulk material, then contribution to the interior atoms to the cohesive energy of nanosolid is $E_0(n\text{-}N)$. Since the half of the total bonds of each surface atom is dangling bonds, the contribution of each surface atom to cohesive energy of nanosolid is equal to $E_0/2$. Then total atoms contribution is $NE_0/2$. The value of E_{Tot} is the sum of the contributions of surface atoms and interior atoms as discussed earlier[11] is:

$$E_{Tot} = E_0\,(n-N) + \frac{1}{2}E_0 N \quad \ldots (6)$$

or

$$E_P = E_b\,(1-\frac{N}{2n}) \quad \ldots (7)$$

Here, E_{p} , is the cohesive energy per mole of nanosolid, which is given by:

$$E_P = \frac{A_v E_{Tot}}{n} \quad \ldots (8)$$

where A_{v} is the Avogadro constant and E_{b}, the cohesive energy per mole of the corresponding bulk material ($E_{\mathrm{b}} = A_{\mathrm{v}}E_0$). It is well known that both the cohesive energy and elastic moduli are the parameters to describe the rigidity or bond strength of materials. Thus, Kumar and Kumar[12] argued that the relation for bulk modulus may be written as:

$$B_{0n} = B_b\,(1-\frac{N}{2n}) \quad \ldots (9)$$

where B_{b} is the bulk modulus of bulk material and $N/2n$ may be evaluated for a nanosolid[11] which depends on the size of the nanomaterial. The method to find $N/2n$ has already been discussed by Qi[11]. According to this model, $N/2n$ is $2d/D$ for spherical

nanosolids with d as the diameter of atom and D the diameter of spherical nanosolid. Thus, combining Eqs (5) and (9), one gets the following relation for a spherical nanosolid:

$$P=\frac{B_b}{A}(1-\frac{2d}{D})\left[\left\{\exp A\left(1-\frac{V}{V_0}\right)\right\}-1\right] \quad \ldots (10)$$

It may be mentioned that Eq. (10) is size dependent isothermal EOS for spherical nanosolids, which does not include the effect of temperature. To circumvent this difficulty, one can proceed in the following way. The thermal pressure, P_{Th}, is defined as[4]:

$$(\frac{\partial P_{Th}}{\partial T})_V = \ _{0n}\ B_{0n} \quad \ldots (11)$$

where α_{0n} is the coefficient of volume thermal expansion of nanomaterial and T is the temperature. Using the Hildebrand approximation[13], the integration of Eq. (11) gives the following relation:

$$P_{Th}=\int_{T_0}^{T}(\ _{0n}\ B_{0n})\,dT \quad \ldots (12)$$

or

$$P_{Th} = \ _{0n}\ B_{0n}(T-T_0) \quad \ldots (13)$$

Now, including the effect of temperature in Eq. (10), one gets the following relation:

$$P=\frac{B_b}{A}(1-\frac{2d}{D})\left[\left\{\exp A\left(1-\frac{V}{V_0}\right)\right\}-1\right]+P_{Th} \quad \ldots (14)$$

or

$$P=\frac{B_b}{A}(1-\frac{2d}{D})\left[\left\{\exp A\left(1-\frac{V}{V_0}\right)\right\}-1\right]+\ _{0n}\ B_{0n}(T-T_0) \quad \ldots (15)$$

Equation (15) includes the effect of size, pressure and temperature. When applied pressure, P = 0, Eq. (15) gives the following relation:

$$T=T_0-\frac{B_b}{A\ _{0n}\ B_{0n}}(1-\frac{2d}{D})\left[\left\{\exp A\left(1-\frac{V}{V_0}\right)\right\}-1\right] \quad \ldots (16)$$

In the present paper, Eqs (15) and (16) are used to study the effect of pressure and temperature on nanomaterials of different sizes. These equations also need the values of α_{on} as input data, which are readily available[3,6]for Ni and Zr. However, for the nanomaterials for which the values of α_{on} are not available, the following relation[12] is used:

$$_{0n} = \ _b(1-\frac{2d}{D})^{-1} \quad \ldots (17)$$

where α_b is the coefficient of volume thermal expansion for bulk material.

3 Results and Discussion

A simple theoretical model is, thus, developed to understand the effect of pressure, temperature and size on nanomaterials. To demonstrate the suitability of the model, four nanomaterials, viz., ε-Fe, Ni, Se, and Zr are selected based on their importance in the field of nanoscience and technology as well as the availability of some experimental data so that the model predictions may be judged in the light of the experimental informations[2-6]. The input data required are given in Table 1. To study the effect of pressure on volume of ε-Fe (10 nm) at different temperatures, viz., 300 K, 400 K and 500 K, Eq. (15) is used. The results obtained are reported in Fig. 1 along with the available experimental data[2] at 300 K. There is a good agreement between the model predictions and experimental data[2] at 300 K. The effect of

Table 1—Values of input parameters used in the present work[2-6]

Sr No.	Nanomaterials	B_{0n} (GPa)	B'_{0n}
1	ε-Fe (10 nm)	179.0	3.6
2	Ni (29 nm)	170.6	4.0
3	Se (13 nm)	7.6	4.0
4	Zr (8 nm)	84.6	4.0

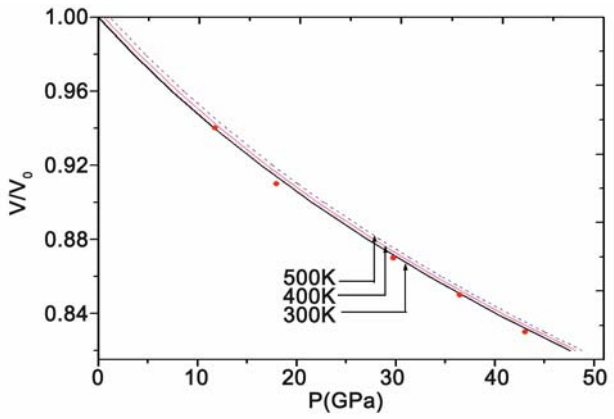

Fig. 1 — Pressure dependence of V/V_0 for ε-Fe (10 nm) at different temperatures [• represents experimental data[2] at 300 K]

temperature is also studied. The results are computed at higher temperatures, viz., 400 K and 500 K and reported in Fig. 1. A small shift in isotherm is found, which shows the effect of temperature on compression. This demonstrates that more pressure is required at higher temperature for same compression of the nanomaterials. Actually, by increasing the temperature of the solid, thermal pressure increases and therefore, more pressure is required for same compression. Moreover, a simple theoretical model is developed for this purpose. It may be mentioned that at higher temperature, the experimental data are not available. The present results are reported in the absence of experimental data. It may be of good interest to researchers engaged in the high pressure - high temperature study of nanomaterials. Also, Eq. (15) is used to study the effect of pressure on ε-Fe at different sizes, viz., 10 nm and 80 nm at different temperatures, viz., 300 K, 400 K and 500 K. It seems very interesting because with the help of present model, one can predict the behaviour of a nanomaterial with all possible variables, viz., pressure, temperature and size. The results obtained are reported in Figs 2-4. A shift in the isotherm is observed by increasing the size at all the temperatures considered in the present work. In low pressure range, the effect of size is very small, but it increases as pressure increases. Thus, it may be concluded from Figs 2-4 that the shift in the isotherm depends upon the temperature as well as size.

The size dependent thermal expansion of nanomaterials is of current interest. Therefore, Eq. (16) is also used to study size dependence of thermal expansion. The results obtained are reported in Fig. 5. It is found that V/V_0 depends linearly on temperature. It may be mentioned that linear behaviour has also been obtained experimentally by Lu *et al.*[14] for nano-crystalline Ni-P alloy. Thus, the present results are consistent with the experimental observations of Lu *et al.*[14]. The effect of size is also studied, which shows that temperature dependence of V/V_0 decrease as size increases. To confirm the model predictions, the present computational work is repeated for Ni. The results are reported in Figs 6-10.

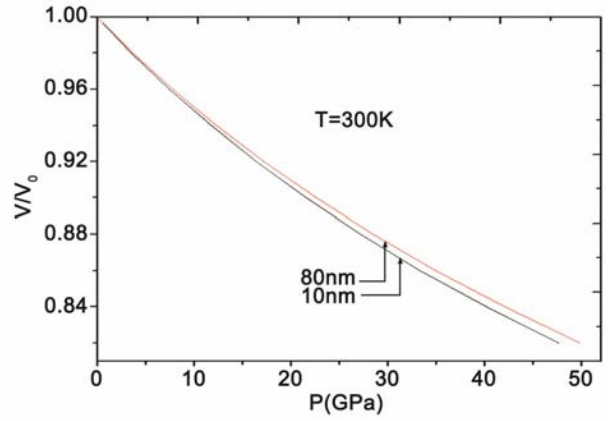

Fig. 2 — Pressure dependence of V/V_0 for different size of ε-Fe

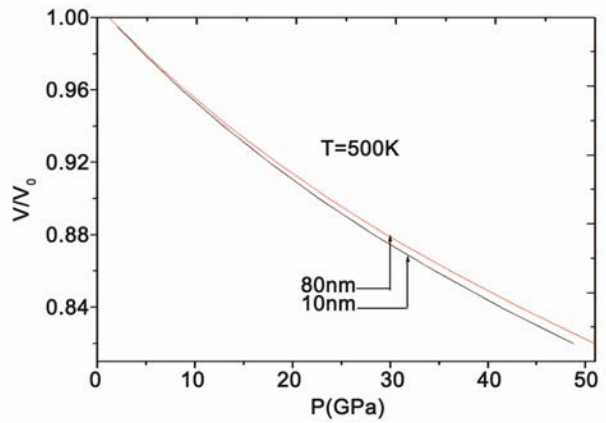

Fig. 4 — Pressure dependence of V/V_0 for different size of ε-Fe

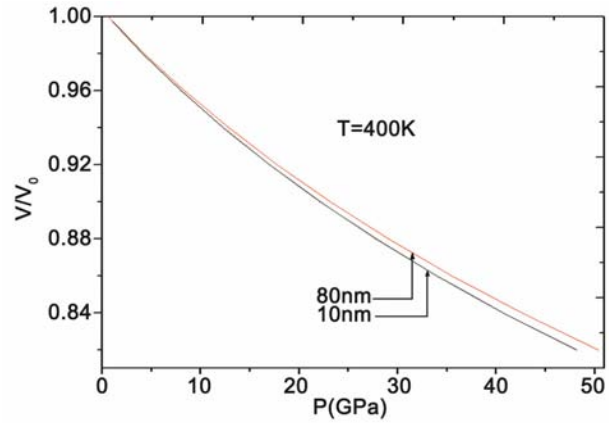

Fig. 3 — Pressure dependence of V/V_0 for different size of ε-Fe

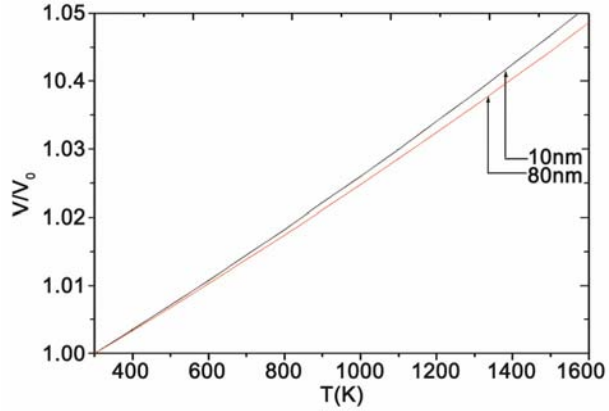

Fig. 5 — Temperature dependence of V/V_0 for different size of ε-Fe

A similar trend of variation confirms the model predictions. The available experimental data indicates that thermal properties of nanomaterials differ significantly from those of their conventional coarse-grained counterparts. However, a simple theoretical model is not available for the size dependence of thermal properties of nanomaterials with a wide grain range. Therefore, the present model is applied to study the temperature dependent properties for a wide range of grain size. Selenium nanomaterial is selected for this purpose and because of the fact that the experimental data[5] are available and comparison can be made. Equation (15) is used to compute the pressure dependence of V/V_0 for selenium (10 nm) at different temperatures, viz., 300 K, 400 K and 500 K. The results obtained are reported in Fig. 11. A shift

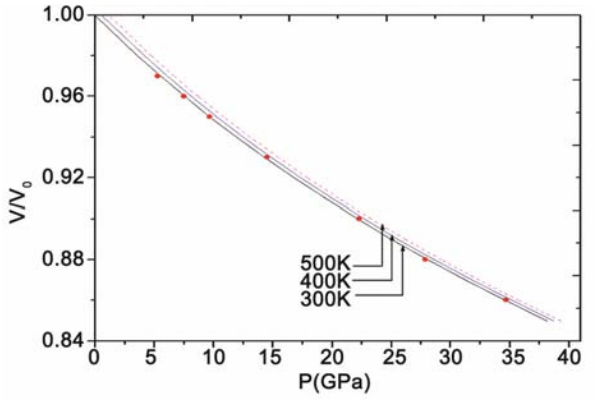

Fig. 6 — Pressure dependence of V/V_0 for Ni (29 nm) at different temperatures [• represents experimental data[3] at 300 K]

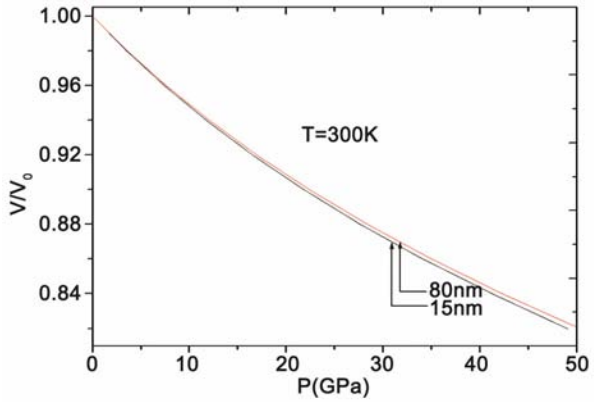

Fig. 7 — Pressure dependence of V/V_0 for different size of Ni

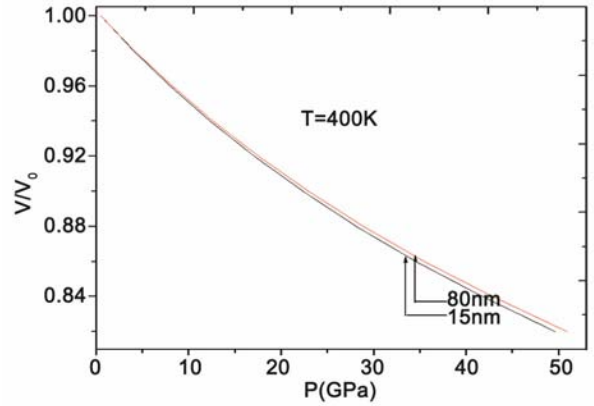

Fig. 8 — Pressure dependence of V/V_0 for different size of Ni

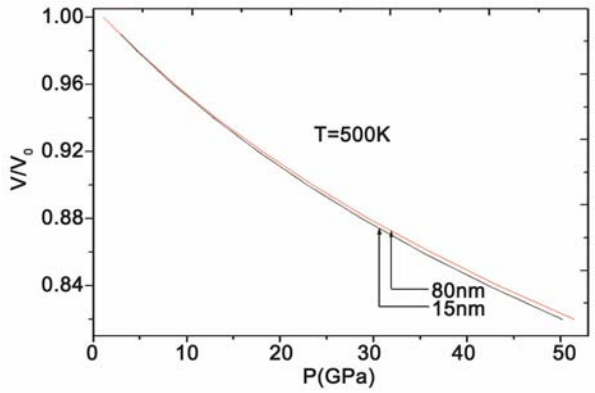

Fig. 9 — Pressure dependence of V/V_0 for different size of Ni

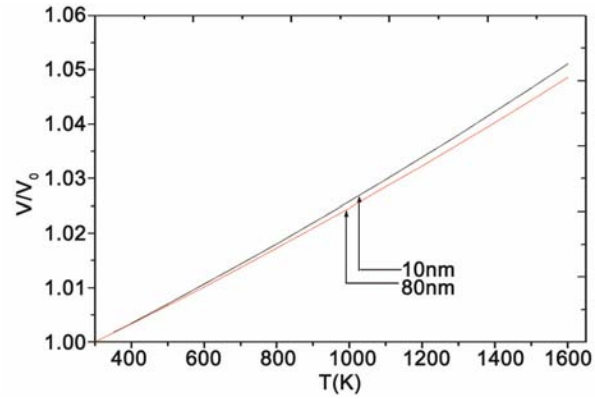

Fig. 10 — Temperature dependence of V/V_0 for different size of Ni

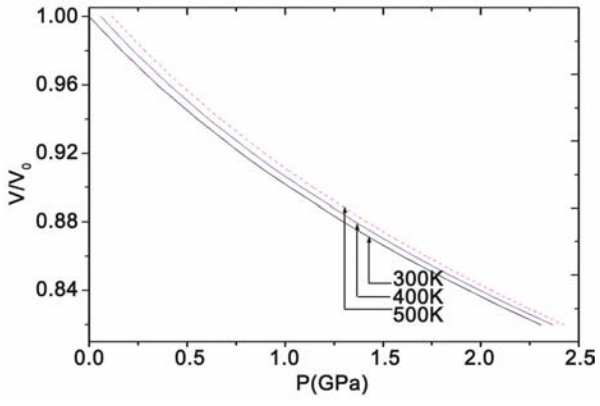

Fig. 11 — Pressure dependence of V/V_0 for Se (10 nm) at different temperatures

in the isotherm is observed by increasing the temperature. The temperature dependence of V/V_0 of Se for different sizes, viz., 13, 19, 21, 24 and 46 nm computed using Eq. (16) are reported in Figs 12-16 along with the experimental data[5]. There is a good agreement between the theory and experiment. This supports the model developed in the present work.

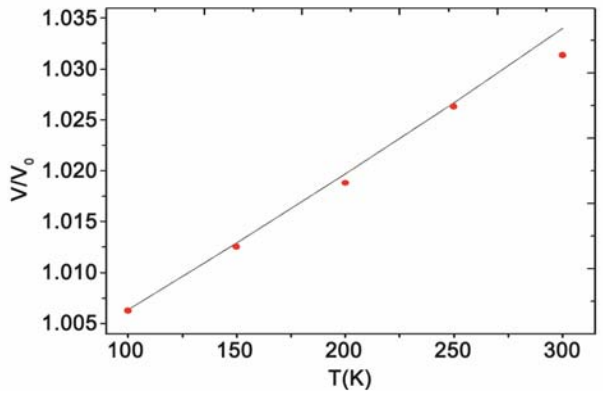

Fig. 12 — Temperature dependence of V/V_0 for Se (13 nm) [• represents experimental data[5]]

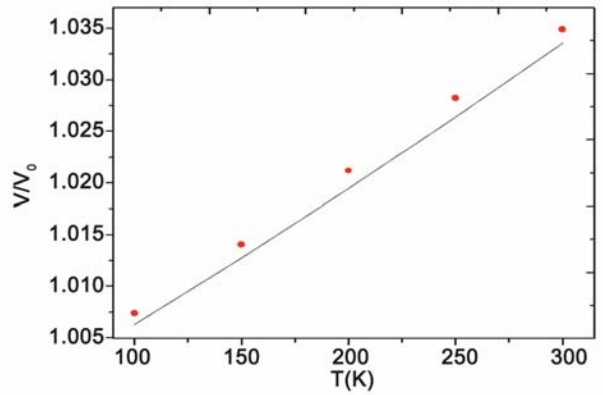

Fig. 13 — Temperature dependence of V/V_0 for Se (19 nm) [• represents experimental data[5]]

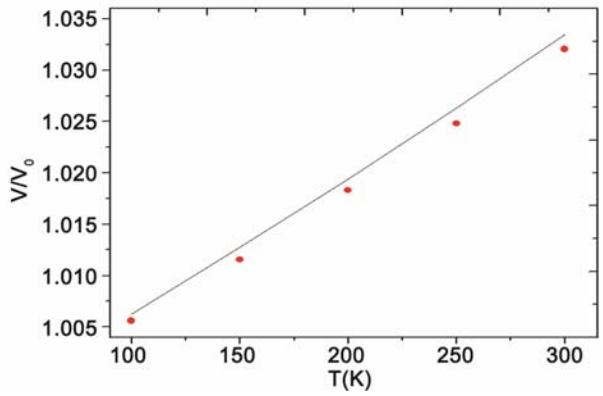

Fig. 14 — Temperature dependence of V/V_0 for Se (21 nm) [• represents experimental data[5]]

A comparative study of the temperature dependence of V/V_0 for different sizes, viz., 13 nm and 80 nm is presented in Fig. 17. The present computed values show similar trend of variation as reported by Zhao and Lu[5] on experimental basis. Thus, the present model predictions are justified as far as experimental information is concerned. To verify the model

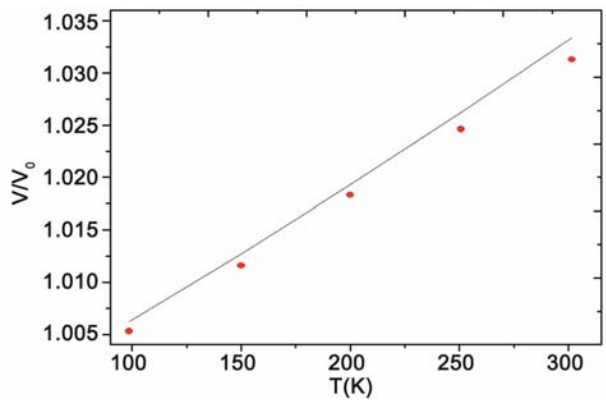

Fig. 15 — Temperature dependence of V/V_0 for Se (24 nm) [• represents experimental data[5]]

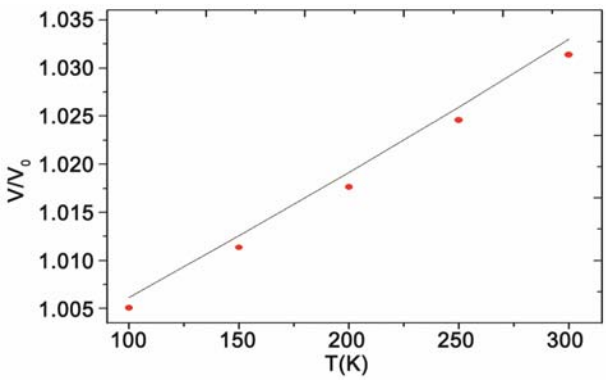

Fig. 16 — Temperature dependence of V/V_0 for Se (46 nm) [• represents experimental data[5]]

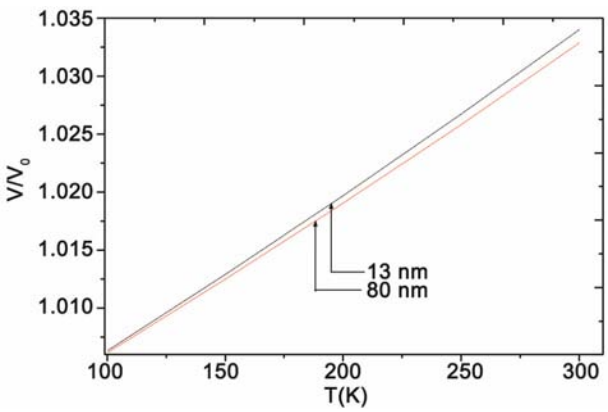

Fig. 17 — Temperature dependence of V/V_0 for Se at different size

predictions, the computational work is repeated for Zr. The results obtained are reported in Figs 18-22. A similar trend of variation is in good agreement with the available experimental data[6] and hence, supports the validity of the model proposed.

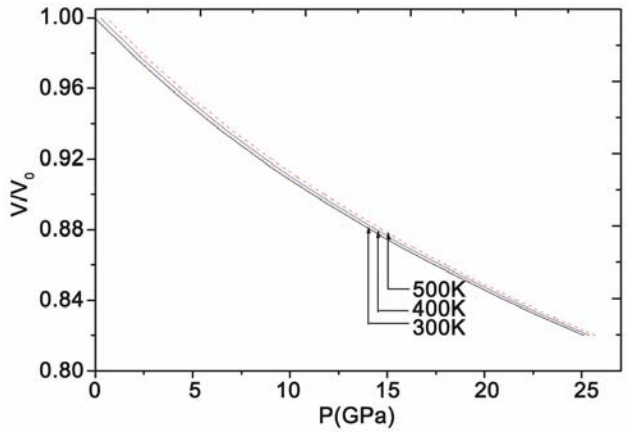

Fig. 18 — Pressure dependence of V/V_0 for Zr (10 nm) at different temperatures

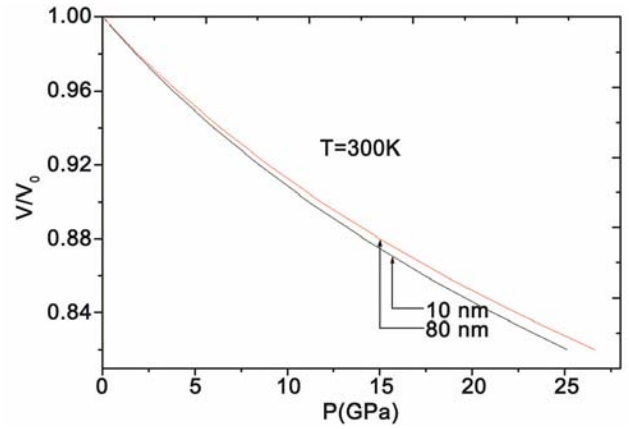

Fig. 19 — Pressure dependence of V/V_0 for different size of Zr

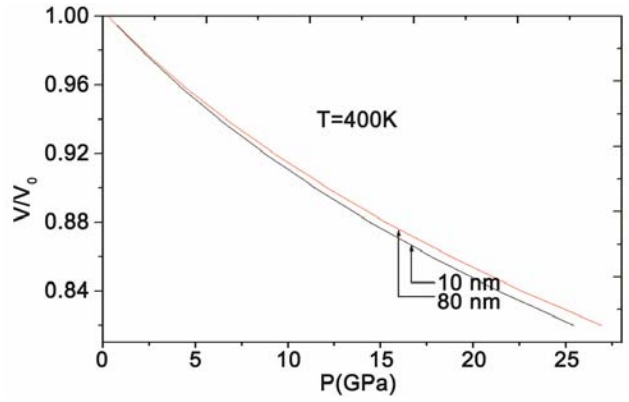

Fig. 20 — Pressure dependence of V/V_0 for different size of Zr

Basically, there are many proposed EOSs available in the literature for bulk materials[15,16] but the present study is confined to some of those more commonly adopted for nanomaterials[17]. A critical analysis of such EOSs models have been presented[17] in the light of experimental data. It has been concluded that in most of the nanomaterials, Eq. (5) or its low pressure form (Murnaghan) perform well, which are also very convenient for application. It has also been recognized for bulk materials[8] that Eq. (5) gives better agreement in high pressure range as far as experimental data are concerned and theoretically reproduces many other EOSs models[8-10]. Equation (5) has also been found to be applicable for different classes of solids in a way better than other EOSs models[8]. In the present paper, Eq. (5) is derived in a simple way and used it as a tool. The effect of size and temperature is incorporated to get the final formulation. While performing the present

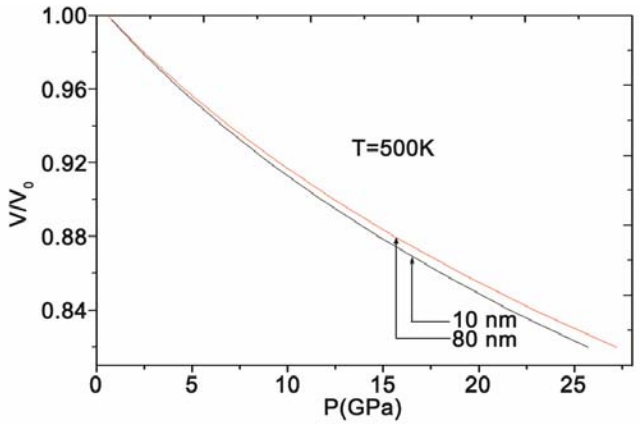

Fig. 21 — Pressure dependence of V/V_0 for different size of Zr

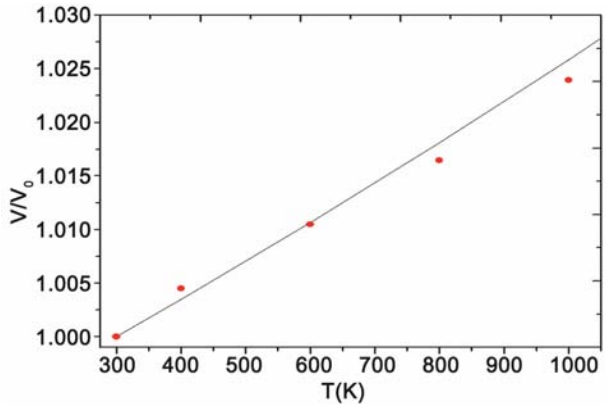

Fig. 22 — Temperature dependence of V/V_0 for Zr (8 nm) [• represents experimental data[6]]

computational work, other EOSs models[17] are also used but no improvement in the results have been found. It is felt that present model is very convenient and useful for nanomaterials and change of EOS model (Eq. 5) does not improve the results.

4 Conclusions

In the present paper, a combination of new freedom of size with the freedom of temperature and pressure is reported. This would vastly simplify the space of exploration in Condensed Matter Physics and Chemistry. It is pertinent to mention here that in the present paper, few materials, viz., ε-Fe, Ni, Se and Zr are selected as examples following the inverse Hall-Petch effect (IHPE). It is observed that the model predictions are in good agreement with the available experimental data. Due to the simplicity and applicability of the model, it may be extended to the materials having IHPE, viz. TiO_2, SnO_2, γ-Fe_2O_3 and γ-Al_2O_3. Moreover, there are materials which do not follow IHPE, e.g., CuO, ZnO, Ag and Pb. For such materials, the model may be considered as an approximate case and may be used at particular size with the available experimental values of B_{0n} as already demonstrated by Bhatt *et al.*[17]

Acknowledgment

The authors are thankful to the University for providing the financial support in the form of research project (Code No 21A).

References

1 Abril R J, *J Mater Sci*, 46 (2011) 7247.
2 Chen B, Penwell D & Kruger M B, *J Appl Phys*, 89 (2001) 4794.
3 Grant C D, *J Appl Phys*, 105 (2009) 084311.
4 Sharma U D & Kumar M, *Physica B*, 405 (2010) 2820.
5 Zhao Y H & Lu K, *Phys Rev B*, 56 (1997) 14330.
6 Bhagwat M & Ramaswamy V, *Mater Res Bull*, 39 (2004) 1627.
7 Sun C Q, *Prog Solid State Chem*, 35 (2007) 1.
8 Kumar M, *Physica B*, 212 (1995) 391.
9 Kumar M, *J Phys Chem Solids*, 65 (2004) 1177.
10 Kumar M, *Physica B*, 365 (2005) 1.
11 Qi W H, *Physica B*, 46 (2005) 368.
12 Kumar R & Kumar M, *Int J Nanosci*, 9 (2010) 537.
13 Born M & Huang K, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford), 1954.
14 Lu K, Wang J T & Wei W D, *J Phys D: Appl Phys*, 25 (1992) 808.
15 Poirier J P, *Introduction to Physics to the Earth's Interior* (Cambridge University Press), 1991.
16 Anderson O L & Isaak D G, *Am Miner*, 85 (2000) 376.
17 Bhatt Archana, Sharma Geeta & Kumar M, *Indian J Pure Appl Phys*, 51 (2013) 642.