Indian Journal of Pure & Applied Physics
Vol. 60, March 2022, pp. 261-267

Thermal Properties of Solids Under Varying Conditions of Pressure and Temperature

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Received 26 November 2021; accepted 27 January 2022

A simple theoretical method is developed to study the properties of solids under varying conditions of pressure and temperature. We have considered different types of materials viz. metallic, hydrides, sulphides and coesites. Unit cell volume, coefficient of volume thermal expansion and bulk modulus have been investigated under varying conditions of pressures and temperatures. The results obtained are compared with the available experimental data. A good agreement between theory and experiment demonstrates the suitability of the model used. It is realized that due to simplicity and applicability, it may be used to a large number of materials and may be of current interest to the researchers working in the high pressure and temperature science.

Keywords: Equation of state, Pressure, Volume, Temperature

1 Introduction

High pressures are encounters from deep down the earth to the astrophysical objects. Shock compression data up to 290 GPa and volume thermal expansion data between 100 and 2000 K have been used to develop high temperature and high pressure equation of state (EOS). A concise report on the analysis with a graphical summary including most of the aspects of high pressure metrology in a single window manner has been provided by Rab *et al*[1]. The thermal pressures at high temperatures have been estimated using the Mie-Grunrisen relation with Debye thermal model. Compression versus pressure at ambient temperature has been measured[2] for Tantalum, Gold and Platinum upto 94 GPa. Pressure effect on structural stability, elastic properties and Debye temperature of face centered cubic Mg_7TMH_{16} (TM=Sc, Ti, V, Y, Zr and Nb) hydrides, have been investigated by first principle calculations based on density functional theory (DFT) with the generalized gradient approximation[3] (GGA).

Nickle sulfides are common in nature, which are found in mantle-related rocks and xenoliths. Their properties exhibit significant differences with silicates in density, conductivity, and elasticity, which may be responsible for the geophysical anomalies in the upper mantle. The thermodynamic properties of millerite (NiS), heazlewoodite (Ni_3S_2) and polydymite (Ni_3S_4) have been calculated using first principle methods[4]. Synchrotron powder X-ray diffraction has been used[5] to study thermal expansion of synthetic coesite in the temperature range of 100 to 1000 K. These authors determined the unit cell parameters of monoclinic coesite. It has been found that parameter a and b increases with increase of temperature while c decreases with decrease of temperature. These measurements provide thermal expansion coefficient of coesite with temperature. Phase transition boundary with zinc blende and rock salt structure in zinc selenide (ZnSe) has been determined using high pressure experiments combined with the synchrotron X ray diffraction technique. At high temperature significant hysteresis in phase transition was not observed[6]. EOS of synthetic garnet solid solutions with ternary grossular-almandine-pyrope compositions relevant to the Earth's mantle have been determined in order to examine whether garnet properties can be accurately interpolated from those of the end-members[7].

Lenard-Jones potential and the crystal Einstein model have been used to calculate the thermophysical properties and melting temperature as well as thermal EOS for Niobium[8]. With the use of in situ X-ray diffraction measurements thermal EOS has been determined[9]. X-ray diffraction has also been used to measure ambient temperature EOS of metals using diamond anvil cell[10, 11]. High pressure X-ray diffraction studies up to 10.4 GPa have been performed for the $Mn_{0.94}Ti_{0.06}CoGe$ alloy using

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*Corresponding author: (E-mail: sonisharma.physics@gmail.com) synchrotron radiation with diamond anvil cell[12]. High-pressure behavior of a very low density amorphous zircon model having Zr coordination of 5.6 is explained by simulation[13]. DFT has been used to study structural stability, electronic and optical properties of BeH_2 under high pressure[14]. Modified interaction potential model has been used to investigate the pressure induced phase transition and thermophysical properties of some materials[15].

Thus, a review of literature shows that a lot of work has been done to understand the properties of solids under varying conditions of pressures and temperatures. Moreover, a simple theoretical model for complicated solids is still awaited. Thus it is legitimate and may be useful to discuss a simple approach, which is the purpose of present paper. EOS is thermodynamic relation which describes how volume of the material changes with pressure, which can be effectively used to study the behavior of solids under different conditions of pressure and temperature. We will discuss behavior of materials under different conditions of pressures and temperatures using the knowledge of EOS. For this purpose we selected Platinum, Hydides, Sulfides and Coesite because of the fact that experimental data are available so that the model predictions can be compared.

2 Theory

To study the matter under extreme conditions of pressure and temperature, the theory of (EOS) may be regarded as a tool. Therefore, the EOS models have been proposed using the knowledge of interatomic potentials as well as based on thermodynamic analysis. A critical discussion on this subject has already been presented[16]. This shows that the thermodynamical models are better as compared with those based on the knowledge of potentials. For this purpose a simple thermodynamic theory has been proposed by Kumar[17], which can be used to study the properties of solids from atmospheric pressure upto structural transition pressure by varying the temperature from room temperature upto melting temperature. A comparative study demonstrates that the theory is better than the other formulations[18] reported in the literature and agree well with the experimental data available in the literature. The detailed analysis is available elsewhere[19] and mathematical form reads as follows:

$$\mathrm{P} = \frac{\mathrm{B_0}}{\mathrm{A}}\left[\mathrm{expA}\left(1 - \frac{\mathrm{V}}{\mathrm{V_0}}\right) - 1\right] + \alpha_0 \mathrm{B_0}(\mathrm{T} - \mathrm{T_0}) \qquad \ldots (1)$$

or

$$\frac{V}{V_0} = 1 - \frac{1}{A} ln\left[1 + \frac{A}{B_0}\{P - \alpha_0 B_0 (T - T_0)\}\right] \qquad \ldots (2)$$

Where, V/V_0 represents the relative change in the volume, parameter $A=\delta_T + 1$, B_0 is the value of bulk modulus, P is the pressure. The solids for which δ_T is not available, we can use the approximation $\delta_T \approx B_0'$, and T is the temperature. 0 refers to the initial value.

The coefficient of volume thermal expansion α is defined as;

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots (3)$$

Thus Eq. (2) gives the following relation

$$\frac{\alpha}{\alpha_0} = \left[1 - \frac{1}{A} ln\left\{1 + \frac{AP}{B_0} - A\alpha_0(T - T_0\right\}\right]^{-1}\left[1 + \frac{AP}{B_0} - A\alpha_0(T - T_0)\right]^{-1} \qquad \ldots (4)$$

The coefficient of volume thermal expansion can be studied with the help of equations (4) under variable conditions of pressure and temperatures. At P=0, Eq. (4) can be written as follows;

$$\frac{\alpha}{\alpha_0} = \left[1 - \frac{1}{A} ln\{1 - A\alpha_0(T - T_0\}\right]^{-1}[1 - A\alpha_0(T - T_0)]^{-1} \qquad \ldots (5)$$

Bulk modulus is defined as

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T \qquad \ldots (6)$$

Now, Eq. (1) and Eq. (6) give the following relation.

$$\frac{B}{B_0} = \left[1 - \frac{1}{A} ln\left\{1 + \frac{AP}{B_0} - A\alpha_0(T - T_0)\right\}\right]\left[1 + \frac{AP}{B_0} - A\alpha_0(T - T_0)\right] \qquad \ldots (7)$$

At P= 0 Eq. (7) gives

$$\frac{B}{B_0} = \left[1 - \frac{1}{A} ln\{1 - A\alpha_0(T - T_0)\}\right][1 - A\alpha_0(T - T_0)] \qquad \ldots (8)$$

Thus, there are simple theoretical formulations, which can be used to study the properties of solids under varying conditions of pressure and temperature. In the present paper, we use this theory to study different materials under varying conditions of pressure and temperature.

3 Results and discussions

The input data[2-5, 20-22] required for present work are given in Table 1. We selected different materials viz. metallic, hydrides, sulfides and coesites. We used Eq. (1) to compute the values of pressures at different V/V_0 for metallic (Platinum) at $T=T_0=300K$. The results obtained are reported in Fig. 1, along with the available experimental data[2]. It is observed that our computed values are in good agreement with the experimental results for the entire range of pressure. This encouraged us to extend the application of Eq. (1) for different types of solids under varying conditions of pressure. Variation of V/V_0 with temperature at different pressures is reported in Fig. 2. We concluded that V/V_0 increases with temperature and decreases by the application of pressure.

Recently, a lot of research has been focused towards hydrogen as clean and sustainable energy source. It may replace rich carbon energies in the short time. Thus, it may be interesting to study hydrides under variable physical conditions. In the present paper, we considered some hydrides viz. Mg_7ScH_{16}, Mg_7YH_{16}, Mg_7TiH_{16}, Mg_7NbH_{16}, to study the effect of pressure. We used Eq. (1) to study the effect of pressure. The results obtained are reported in Figs. 3-6. To judge on the model predictions, we have used the results as reported by Benyelloul *et al*[3]. These authors studied the effect of pressure on hydrides. They reported first principles calculations based on DFT with the generalized gradient approximation (GGA). These results are included in Figs. 3-6 for comparison purposes. A good agreement demonstrates the suitability of the model used in the present paper. It should be mentioned that present model is very simple and straight forward as compared with earlier studies[3]. To test the model

Table 1 — Input data required in the present work [2-5, 20-22]

Materials	B_0 (GPa)	B'_0	α_0 (10^{-5} K^{-1})
Pt	273	5.2	0.895
Mg_7ScH_{16}	63.94	3.66	
Mg_7YH_{16}	60.7	3.7	
Mg_7TiH_{16}	68.46	3.64	
Mg_7NbH_{16}	73.63	3.65	
NiS	111	5	1.63
Ni_3S_2	119.2	4.7	3.73
Ni_3S_4	109.14	4.64	
Coesites	96	4.1	6.1

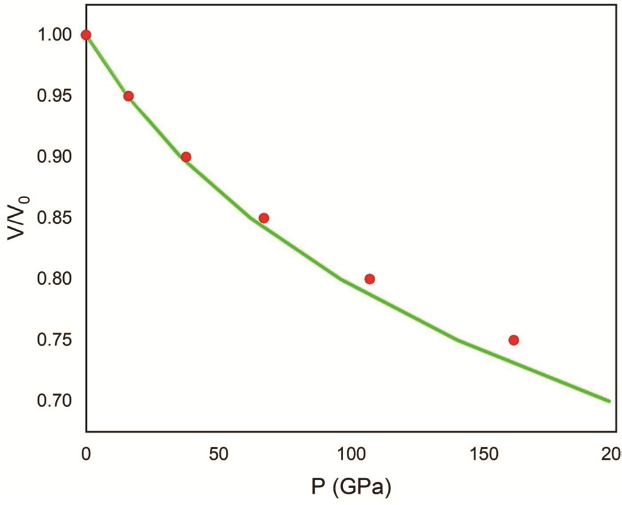

Fig. 1 — Pressure dependence of V/V_0 for Pt using Eq. (1). ▬ represents the results using Eq. (1) and ● represents experimental data[3].

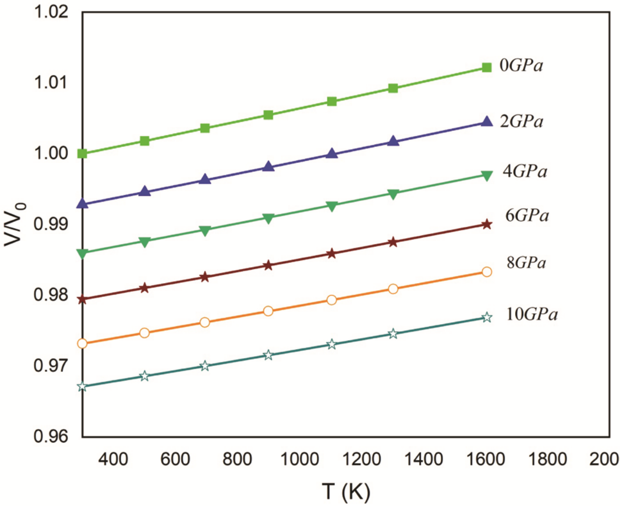

Fig. 2 — Temperature dependence of V/V_0 for Pt using Eq. (2) at different pressure.

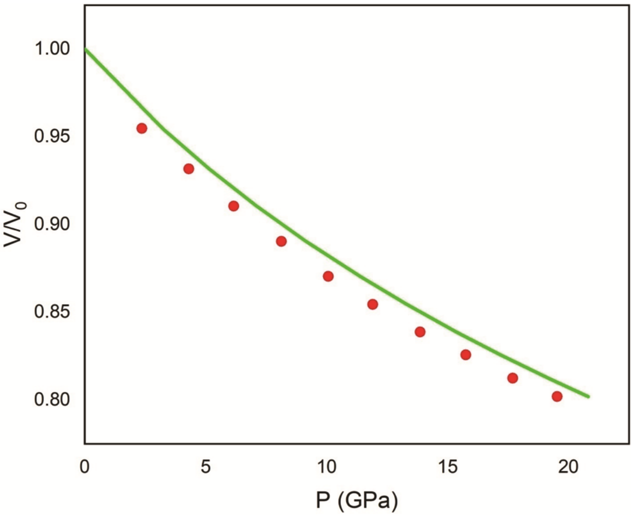

Fig. 3 — Pressure dependence of V/V_0 for Mg_7ScH_{16} using Eq. (1). ▬ represents the result using Eq. (1) and ● GGA[3].

predictions further, we extended this to other solids of geophysical interest. Nickle sulfides are common in nature, which have been found in mantle-related rocks with difference in properties as compared with silicates. We used Eq. (1) to study the effect of pressure on NiS. The variation of V/V_0 with pressure is reported in Fig. 7 along with the results reported by Tian *et al*[4] based on first principles and experimental data[20]. It is found that our results are in good agreement with the earlier investigations. The temperature dependence of V/V_0 using Eq. (2) at different pressures is reported in Fig. 8. It is found that V/V_0 increases with increasing the temperature and affected by pressure. A similar trend of variation is observed for α during the results computed using Eq. (4) as reported in Fig. 9. Variation of bulk modulus with the temperature using Eq. (7) is reported in Fig. 10. It is concluded that bulk modulus decreases with increase of temperature and affected by pressure.

It is observed that behavior of α and B is reverse to each other under varying conditions of pressure and temperature. Ni_3S_2 and Ni_3S_4 are also some important materials. We have also considered these materials in the present work. The compression behavior of Ni_3S_2 using Eq. (1) is reported in Fig. 11 along with the results reported by Tian *et al* [4] and the experimental data[21]. Our calculated results are in good agreement with experimental data. This demonstrates the

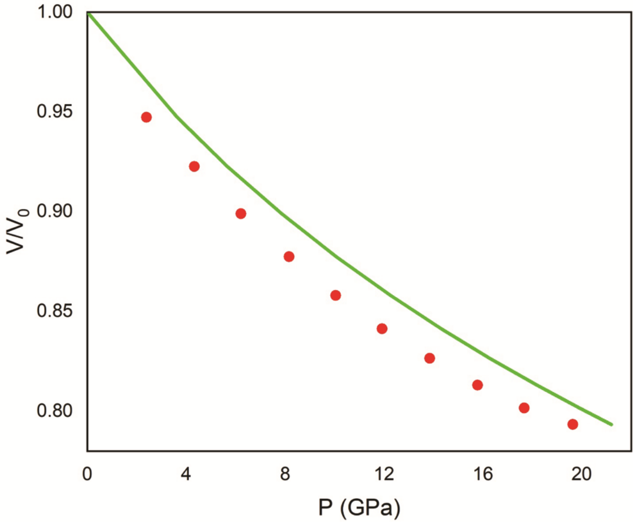

Fig. 4 — Pressure dependence of V/V_0 for Mg_7YH_{16} using Eq. (1). ▬ represents the result using Eq. (1) and ● GGA[3].

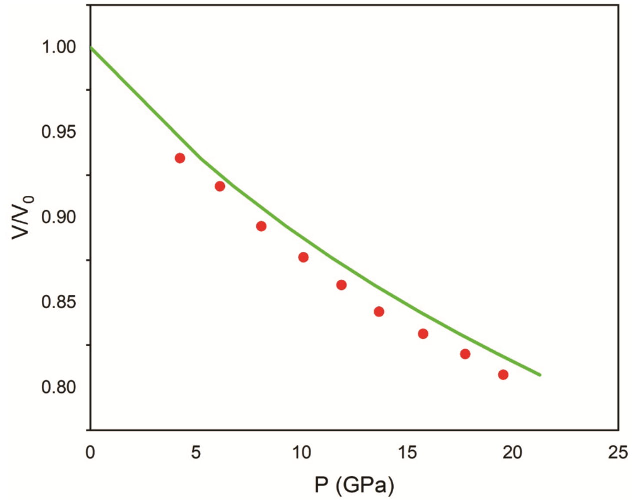

Fig. 5 — Pressure dependence of V/V_0 for Mg_7TiH_{16} using Eq. (1). ▬ represents the results using Eq. (1) and ● GGA[3].

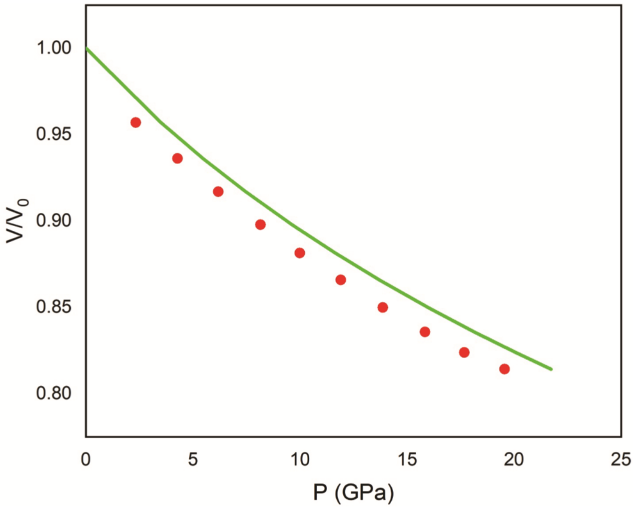

Fig. 6 — Pressure dependence of V/V_0 for Mg_7NbH_{16} using Eq. (1). ▬ represents the results using Eq. (1). ● GGA[3].

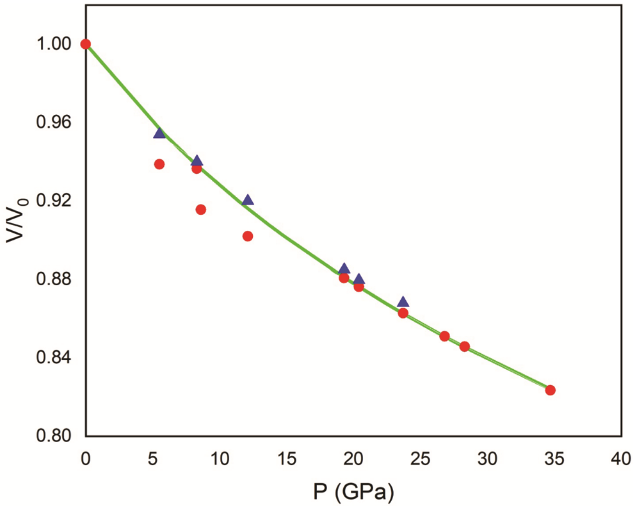

Fig. 7 — Pressure dependence of V/V_0 for NiS. ▬ represents results using Eq. (1), ● shows experimental data[20] and ▲shows the results by Tian *et al*[4].

suitability of the model used in the present work. Variation of α with pressure at different temperatures for Ni_3S_2 is reported in Fig. 12 and temperature dependence of bulk modulus at different pressures is reported in Fig. 13. It is further observed that bulk modulus decreases with temperature and affected by the pressure. The compression behavior of Ni_3S_4 studied using Eq. (1) is reported in Fig. 14, along with the results reported by Tian *et al*[4]. There is a very good agreement between computed and experimental data, which demonstrates the suitability of the model used.

For further test of the model, we considered one more material coesite, which is a high- pressure polymorph of silicon dioxide that crystallizes into the monoclinic crystal system[5]. Quartz is the

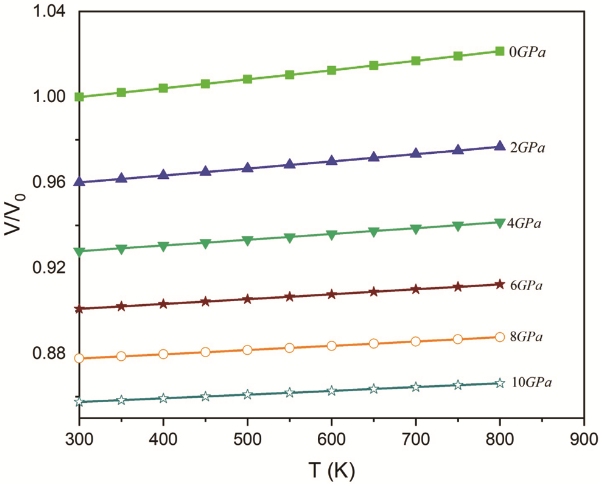

Fig. 8 — Temperature dependence of V/V_0 for NiS using Eq. (2) at different pressures.

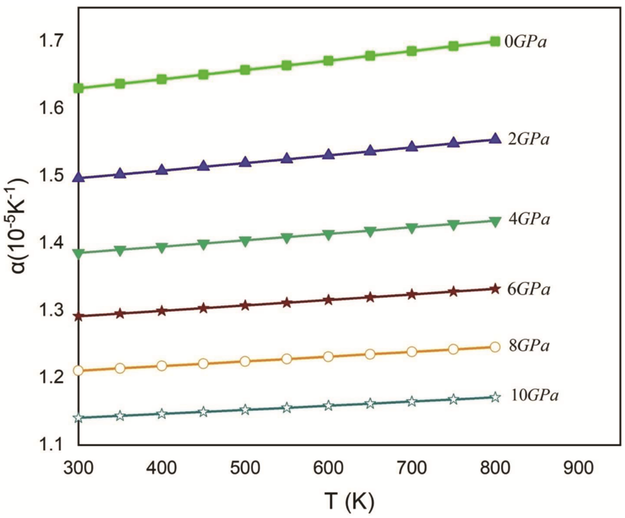

Fig. 9 — Temperature dependence of α for NiS using Eq. (4) at different pressures.

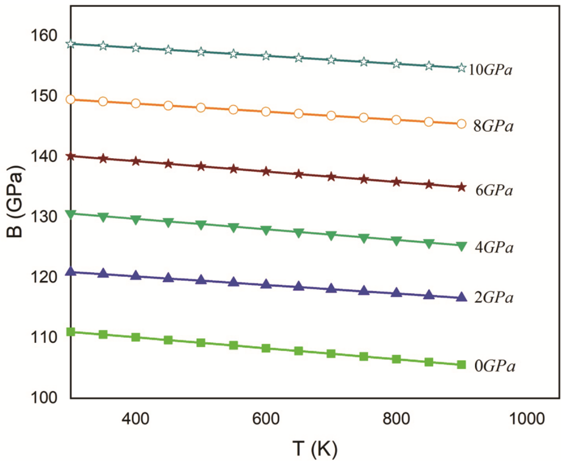

Fig. 10 — Temperature dependence of bulk modulus of NiS using Eq. (7) at different pressures.

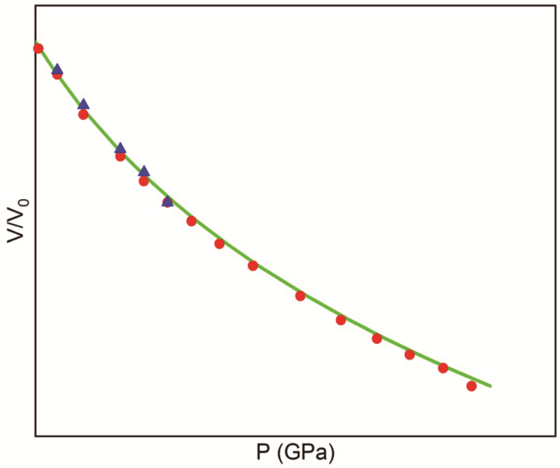

Fig. 11 — Pressure dependence of V/V_0 for Ni_3S_2 using Eq. (1). ● represents experimental data[21] and ▲ shows the results by Tian *et al*[4].

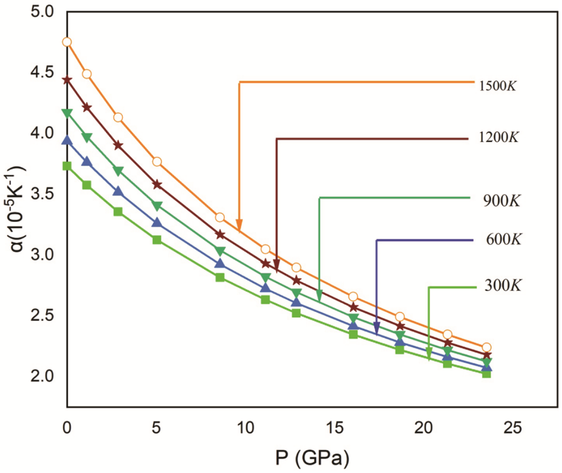

Fig. 12 — Pressure dependent thermal expansion coefficient for Ni_3S_2 using Eq. (4) at different temperatures.

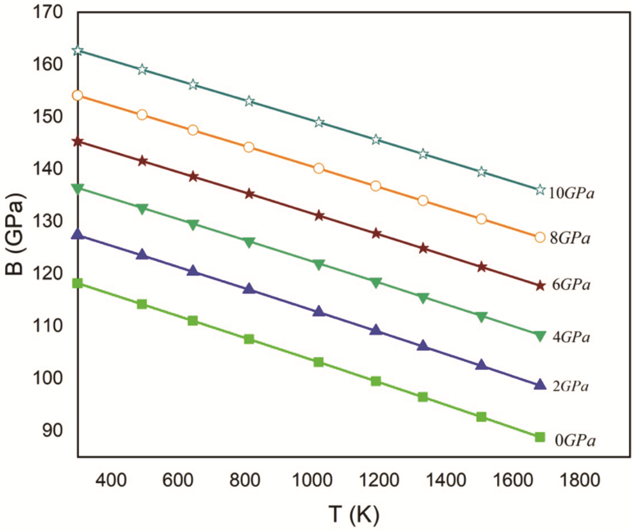

Fig. 13 — Temperature dependent of bulk modulus at 300 K for Ni_3S_2 using Eq. (7) at different pressures.

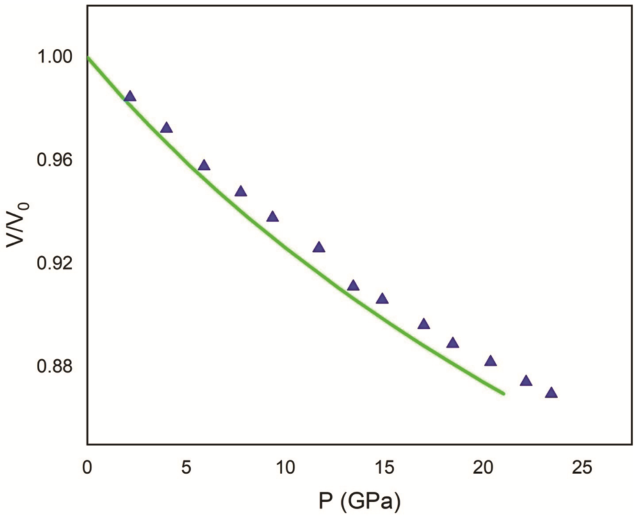

Fig. 14 — Pressure dependent of V/V_0 for Ni_3S_4. Where ▬ shows calculated results and ▲shows results by Tian *et al*[4].

thermodynamically stable phase at ambient conditions and it transforms into coesite at pressures about 3 GPa[5]. It further transforms to stishovite at pressures of about 9 GPa. Kulik *et al*[5] studied the thermal expansion of synthetic coesite with synchrotron power X ray diffraction upto 1000 K. These authors reported the unit cell parameters of monoclinic coesite at different temperatures. It has been found that a and b parameters increases with increasing temperature, while c decreases. The unit cell volume expands by only 0.7 % into this temperature range. In the present paper we used Eq. (2) to predict temperature dependence of unit cell volume at different pressures. The results obtained are reported in Fig. 15. It is found that V/V_0 increases as temperature increases but this increase becomes very slow as pressure increases. At zero pressure, experimental data are available as reported by Kulik[5]. We used these results for comparision purposes. There is a good agreement between theory and experiment. This demonstrates the suitability of the model used in the present work. Thus, a simple theory seems to be quite good to study the properties of different types of solids under varying conditions of pressures and temperatures.

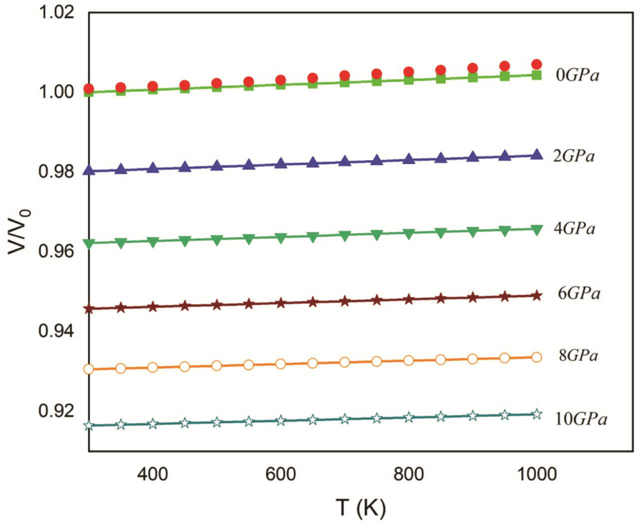

Fig. 15 —Temperature dependence of V/V_0 for Coesites using Eq. (2) at different pressures. ● shows experimental data[5].

4 Conclusions

We have thus presented a simple method to study the properties of solids under varying conditions of pressures and temperatures. Our computed results are in good agreement with the available experimental data. This demonstrates the suitability of the model used. Due to the simplicity and applicability of the model, it may be useful to study the trends of properties under high pressures and high temperatures of complicated solids for which it comes tedious to use potential models.

Acknowledgements

We are thankful to both the referees for their valuable comments, which have been found very useful to revise the manuscript.

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