First-principles calculations of electronic and thermodynamic properties of cubic structures of NdTe

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The electronic and thermodynamic properties are investigated in cubic crystal structures (B1, B2 and B3) of NdTe with first principle studies. Understanding of measured physical properties of NdTe compound is mostly studied. It is also important that thermodynamic and electronic band structure calculations are necessary to figure out many properties of compound. We have also predicted sound velocities, melting points and Debye temperatures for cubic structures of NdTe compound. The thermodynamical properties of the considered structures are obtained through the quasi-harmonic Debye model. In order to gain further information, the pressure and temperature- dependent behaviour of the volume, bulk modulus, thermal expansion coefficient, heat capacity, entropy, Debye temperature and Grüneisen parameter are also evaluated over a pressure range of 0 - 20 GPa and a wide temperature range of 0-2000 K for cubic structures of NdTe compound. The obtained results are compared with the other reported values.

1. Introduction

The observations relevant to the rare-earth compounds which show crucial and interesting physical properties are performed [1-5]. Structurally, compound of NdTe has been studied experimentally. Imamalieva *et al* [6] have measured the lattice constants of NdTe compounds using differential thermal analysis (DTA) and x-ray diffraction. Lin *et al.* [7] have obtained lattice constant for NdTe using XRD technique and determined all the intermediate phases which exist in NdTe system. Schobinger *et al.* [8] have refined structural parameter values from the neutron intensities of rare earth monochalcogenides in different temperatures using neutron diffraction method. We have also investigated structural and elastic properties of NdTe [9].

The aim here is to determine the electronic and thermodynamic properties of NdTe in NaCl(B1), CsCl(B2) and ZB(B3) structures using ab-initio method using with plane-wave pseudopotential.

2. Method of calculation

In this work, all calculations have been made using reliable ab initio techniques by Vienna Ab initio Simulation Package (VASP) based on density functional theory. The electron-ion interaction was taken into consideration in the form of the potential projector-augmented-wave (PAW) method [10-12].

The wave functions are expanded in the plane waves up to a kinetic energy cut-off 500 eV. This cut-off value was found to be convenient for the electronic band

structures and the thermodynamic properties. The 16x16x16 Monkhorst and Pack [14] grid of k-points have been used for integration in capable of being reduced part of the Brillouin zone. The quasi-harmonic Debye model is used for thermodynamic calculations [15-18]. The quasi-harmonic Debye model [15-18] has been carried out to calculate the thermodynamic properties of NdTe compounds. The non-equilibrium Gibbs function $G^*(V; P, T)$ can be written as follow [15]:

$$G^*(V;P,T) = E(V) + PV + A_{vib}[\Theta(V);T] \quad (1)$$

where $E(V)$ is the total energy for per unit cell of NdTe, PV is the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature and A_{vib} is the vibrational Helmholtz free energy which can be written as [19-22]

$$A_{vib}(\Theta,T) = nkT\left[\frac{9\Theta}{8T} + 3\ln\left(1 - e^{-\Theta/T}\right) - D(\Theta/T)\right] \quad (2)$$

where n is the number of atoms per formula unit, $D(\Theta/T)$ describes the Debye integral. The Debye temperature Θ is meant as [22]

$$\Theta = \frac{\hbar}{k}\left[6\pi^2 V^{1/2}n\right]^{1/3} f(\sigma)\sqrt{\frac{B_s}{M}} \quad (3)$$

where M is the molecular mass per unit cell and B_S is the adiabatic bulk modulus which is approximated given by the static compressibility [15]

$$B_s \approx B(V) = V\left(\frac{d^2 E(V)}{dV^2}\right), \qquad (4)$$

$f(\sigma)$ is given by [18, 19]

$$f(\sigma) = \left\{ 3\left[2\left(\frac{2}{3}\frac{1+\sigma}{1-2\sigma}\right)^{3/2} + \left(\frac{1}{3}\frac{1+\sigma}{1-\sigma}\right)^{3/2} \right]^{-1} \right\}^{1/3} \qquad (5)$$

where σ is Poisson ratio. Therefore, the non-equilibrium Gibbs function $G^*(V; P, T)$ as a function of $(V; P, T)$ can be minimized according to volume V as

$$\left[\frac{\partial G^*(V; P, T)}{\partial V}\right]_{P,T} = 0. \qquad (6)$$

The thermal equation-of-state (EOS) $V(P, T)$ can be obtained by solving the equation (6). The isothermal bulk modulus B_T is given by [15]

$$B_T(P, T) = V\left(\frac{\partial^2 G^*(V; P, T)}{\partial V^2}\right)_{P,T}. \qquad (7)$$

The thermodynamical quantities, e.g., heat capacities C_V at stable volume and C_P at stable pressure, and entropy S have been calculated by applying the following relations [15]:

$$C_V = 3nk\left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\theta/T} - 1}\right], \qquad (8)$$

$$C_P = C_V(1 + \alpha\gamma T), \qquad (9)$$

$$S = nk\left[4D(\Theta/T) - 3\ln(1 - e^{-\Theta/T})\right], \qquad (10)$$

where α is the thermal expansion coefficient and γ are the Grüneisen parameter which are given by following equations [15]:

$$\alpha = \frac{\gamma C_V}{B_T V}, \qquad (11)$$

Here is the thermal expansion coefficient is related with volume. It depends on the changes in the sizes of structure.

$$\gamma = -\frac{d \ln \Theta(V)}{d \ln V}. \qquad (12)$$

The Grüneisen parameter defines the volume changing with respect to vibrational properties.

3. Results and discussion

3.1. Electronic properties

Band structures have calculated for cubic structures of NdTe along the high symmetry directions in the first Brillouin zone from the calculated equilibrium lattice constants. Fig. 1, Fig. 2 and Fig. 3 show the band structures and corresponding electronic density of state (DOS) respectively. The position of the Fermi level is given at 0 eV for all cubic structures of NdTe.
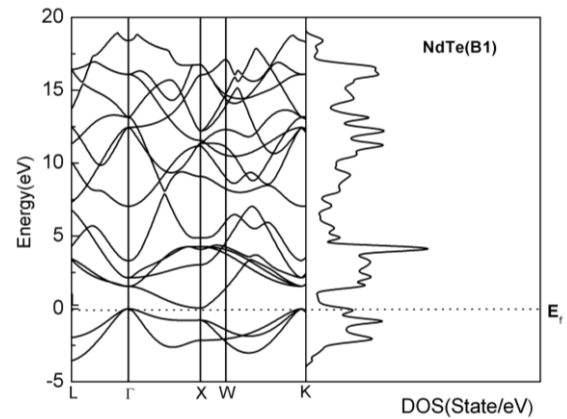

Fig. 1. Calculated energy band structure and DOS of NdTe(B1) versus the composition x.

It can be seen easily from Fig. 1 no band gap exists for NdTe(B1). NdTe(B1) has semi metallic characteristic. DOS are compatible with band structures.
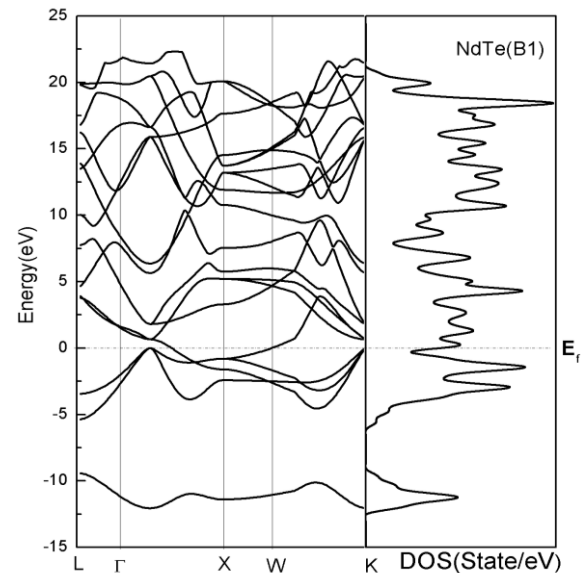

Fig. 2. Calculated energy band structure and DOS of NdTe(B1) at 50 GPa.

Fig. 2 shows that the metallic characteristic for NdTe(B1) at 50 GPa pressure value. Due to the fact that NdTe(B1) stable structure shows semi metallic property

but under pressure it has metallic property. It can be also seen that DOS is very compatible with electronic bands.
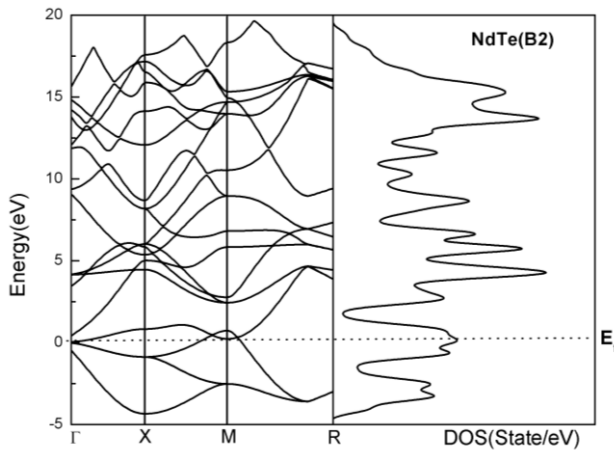

Fig. 3. Calculated energy band structure and DOS of NdTe(B2) versus the composition x.

Fig. 3 shows that no band gap exists for NdTe(B2). Valance and conductive bands are one within the other at Fermi level. Considering, energy band structure of NdTe(B2) shows metallic characteristic. DOS are also compatible with electronic band structure.
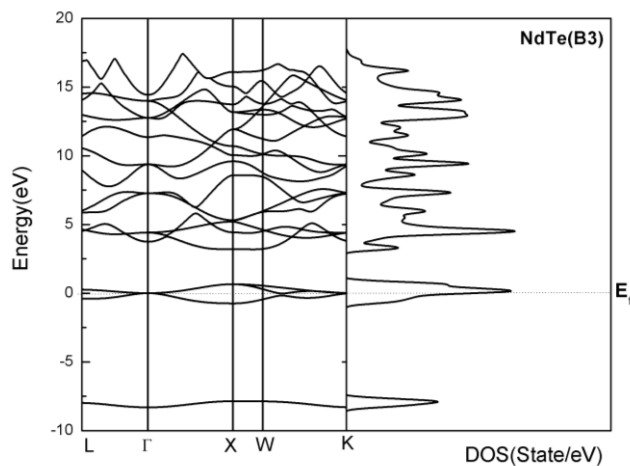

Fig. 4. Calculated energy band structure and DOS of NdTe(B3) versus the composition x.

Fig. 4 shows that the metallic characteristic for NdTe(B3). It can be seen that DOS is very compatible with electronic band structures.
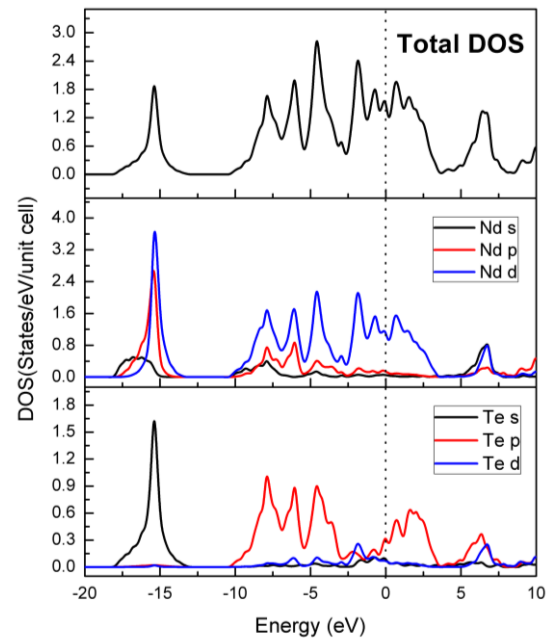

Fig. 5. Calculated DOS of NdTe(B1).

The total and partial density of states (DOS and PDOS) corresponding to the energy band structures shown in Fig. 5 along with the Fermi energy level where is at 0 eV. In this figure, the lowest valance bands occur between about -18 eV and -15 eV and are essentially dominated by Te s states. Especially, other valance bands are essentially dominated by Nd-p and Nd-d states the energy regions just above Fermi energy level are dominated by unoccupied Nd-d states. On the contrary, for conductivity Te-p states are contribute to valance band. The results indicate that there is a strong hybridization between the Nd states and Te states.
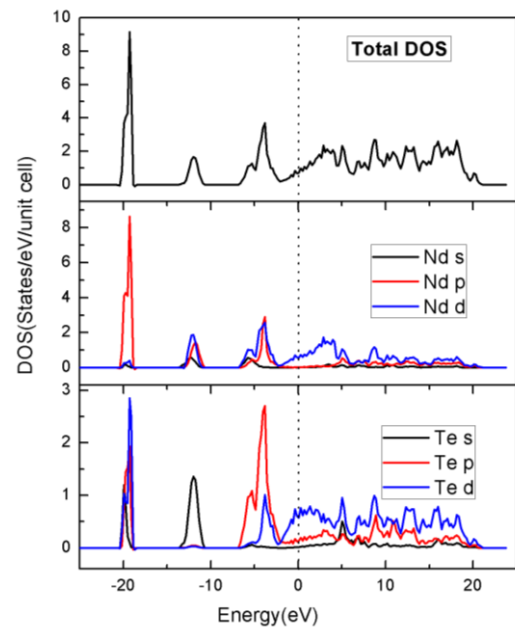

Fig. 6. Calculated DOS of NdTe(B1) at 50 GPa.

In Fig. 6 the total and partial density of states corresponding to the energy band structures for different pressure value which is at 50 GPa. Fermi energy level is at 0 eV. In this graph the lowest valance bands occur at -20 eV. Dominantly, Nd-p and Te-d electronic states are additive for conductivity.

3.2. Thermodynamic properties

Debye temperature, melting point, average, transverse and longitudinal sound velocities have been calculated for NdTe system using following equations. Debye temperature is given in equation 13 [23]:

$$\theta_D = \frac{\hbar}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} v_m \qquad (13)$$

where $\hbar$ is Planck's constant, k is Boltzmann's constant, N_A is Avogadro's number, n is the number of atoms per formula unit, ρ is the density.

Average sound velocity (v_m), transverse (v_t) and longitudinal (v_l) velocities are given respectively [24, 25]:

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{1/3} \qquad (14)$$

Sound velocities are related with elastic properties of solid systems. To determine the sound velocity it is necessary to calculate elastic constants and their some elastic modules like bulk modulus. In Equation 14, average sound velocity explains that how it depends the other velocities.

$$v_t = \sqrt{\frac{G}{\rho}} \qquad (15)$$

In Equation 15, transverse sound velocity is calculated using shear modules and density.

$$v_l = \sqrt{\frac{3B+4G}{3\rho}} \qquad (16)$$

In Equation 16, longitudinal sound velocity is found from the bulk and shear modules with density.

The melting temperature (T_m) has been calculated completely empirical relation [20].

$$T_m = 553 + (591/Bar)C_{11} \pm 300K \qquad (17)$$

All these calculated values are represented in Table 1.

Table 1. The longitudinal, transverse, average elastic wave velocity, Debye temperature and melting temperature for cubic NdTe.

Material	Structure	v_l [m/s]	v_t [m/s]	v_m [m/s]	θ_D [K]	T_m [K]
NdTe	B1	3541.2	1795.1	2012.1	495.442	1483±300
NdTe	B2	1815.2	1036.4	1151.7	375.764	1250±300
NdTe	B3	2813.9	1428.5	1601.1	136.110	809 ±300

Elastic constants are used upper equations and structural parameters (*a, B, B′*) are taken from Ref. [9]. The melting point value is 1483±300K for NdTe in NaCl(B1). This value is bigger than that for constituent atom Nd (1294K) and for constituent atom Te (722.66K).

Some physical properties such as bulk modulus, linear thermal expansion coefficient and heat capacity have investigated under different pressure and temperature values by using quasi-harmonic Debye approximations for B1 structure of NdTe.
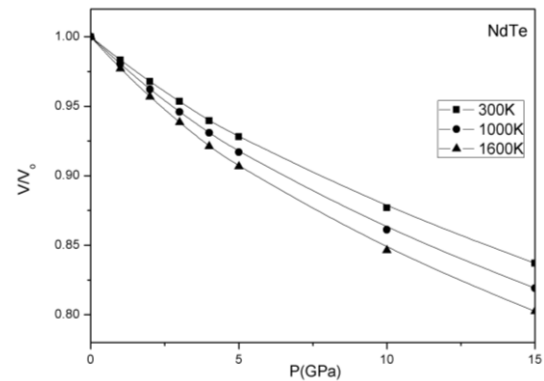

Fig. 7. The normalized volume-pressure diagram of the cubic structures for NdTe at 300K, 1000K and 1600K.

The normalized volume and pressure relation is shown in Fig. 7 for cubic NdTe. It can be seen that when the pressure increases from 0 GPa to 15 GPa, the volume variation decreases. The reason for this changing can be attributed to the atoms in the interlayer that become closer and that their interactions become stronger.
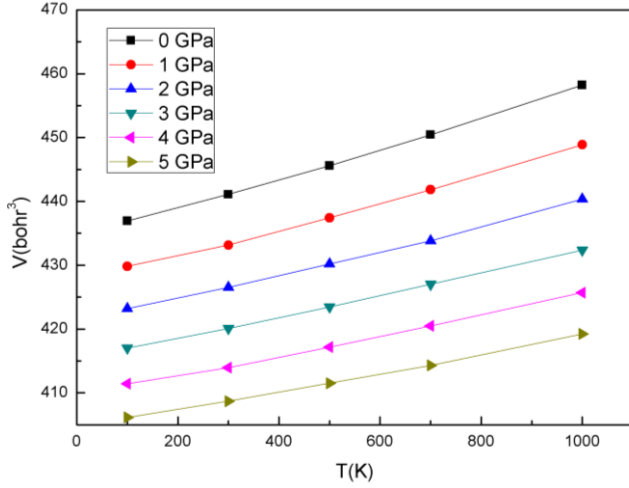

Fig. 8. Volume versus temperature in different pressures for NdTe(B1).

Volume values are plotted in spite of temperature values in different pressures for B1 structure of NdTe in Fig. 8. For B1 structure of NdTe compound the volume increases with increasing temperature, but the rate of increase is moderate.
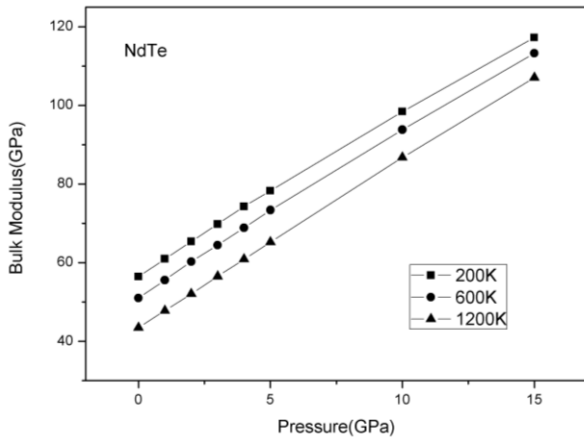

Fig. 9. The bulk modulus-pressure diagram of NdTe.

The relationship between bulk modulus and pressure at different temperatures (200, 600, and 1200K) is shown in Fig. 9. It can be seen easily that as the bulk modulus increases the pressure increases and as the temperature increases, the bulk modulus decreases.
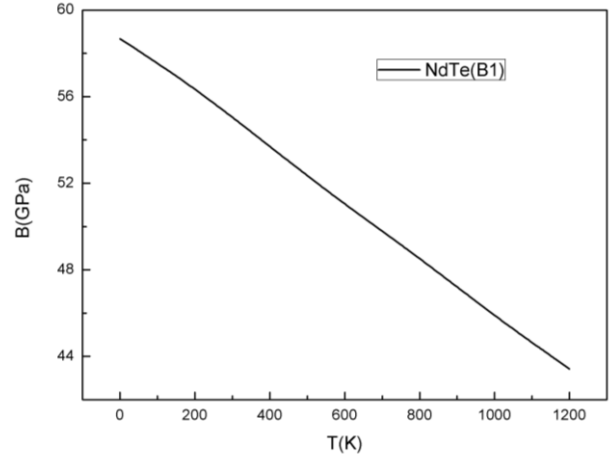

Fig. 10. The variation of bulk modulus(B) with temperatures(T) at 0 GPa.

The variation of bulk modulus (B) with temperatures (T) at 0 GPa is shown in Fig. 10 B1 structure of NdTe. It can be seen that bulk modulus decreases with the temperature at a given pressure. The temperature effects on the bulk modulus are shown at zero pressure. One can obviously see that when $T<150$ K, bulk modulus nearly remains constant; when $T>150$ K, B decreases dramatically as T increases. Correspondingly, when $T<150$K, the primitive cell volume of both compounds has a little change; when $T>150$ K, the cell volume changes rapidly as T increases. Rapid volume variation makes the B rapidly decreases. It is obviously seen that the bulk modulus rapidly increases- almost linearly- with pressure, and effect of the temperature T on the isothermal bulk modulus is very small.

The bulk modulus has also fitted data for the temperature-dependent behavior of bulk modulus to a third order polynomial fit:

$$B(T)=80.78272-0.01187T-1.44879T^2+4.5479T^3 \quad (18)$$

Table 2. Calculated Debye temperature θ(K) and Grüneisen parameter γ(K) for NdTe.

T(K)		P(GPa)		
		0	2	4
100	θ	188.46	201.42	213.05
300	θ	184.68	198.25	210.52
500	θ	180.64	194.77	207.32
700	θ	176.39	191.36	204.06
1000	θ	169.72	185.33	199.02
100	γ	2.131	2.034	1.949
300	γ	2.16	2.057	1.967
500	γ	2.19	2.084	1.99
700	γ	2.222	2.109	2.014
1000	γ	2.27	2.155	2.052

Table 2 shows Debye temperatures and Grüneisen parameters at different temperatures andpressures. In the quasi-harmonic Debye model, the Grüneisen parameter, $\gamma(T)$, and the Debye temperature, $\theta(T)$, are two key quantities. These quantities at various temperatures (100, 300, 500, 700, 1000 K) and different pressures (0, 2, 4 GPa) are calculated and the results are shown in Table 2 for B1 structure of NdTe compound. It is clear from Table 2 that as temperature increases, the Grüneisen parameter decreases and the Debye temperature increases.
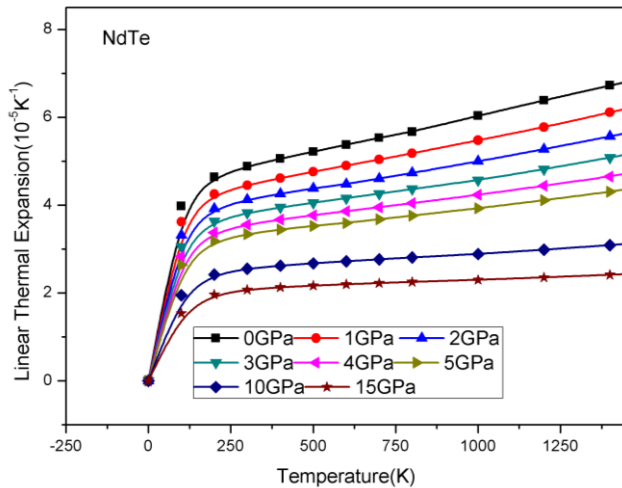

Fig. 11. The linear thermal expansion versus temperature.

The variations of the linear thermal expansion (α) with temperature and different pressures are shown in Fig. 11. α values decrease as the pressure increases, at high temperatures. At low temperatures the thermal expansion coefficient increases while pressure decreases.
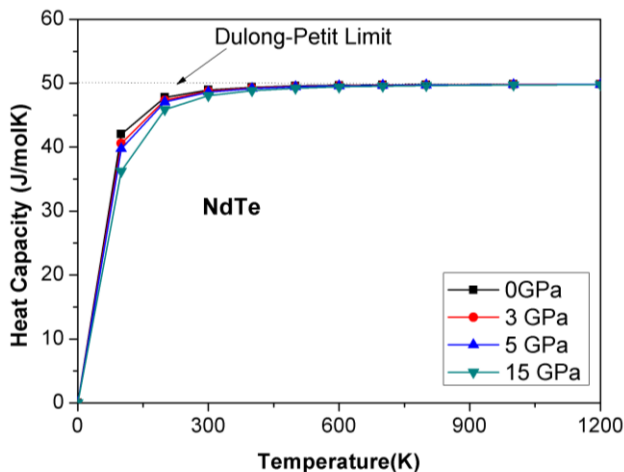

Fig. 12. Temperature dependence of heat capacity for NdTe in B1 structure.

The heat capacity (C_v) versus different temperature values are given in Figure 12. It is seen from this figure that when $T < 300$ K, C_v increases very rapidly with temperature; when $T > 400$ K, C_v increases slowly with temperature and it almost approaches a constant called as

Dulong-Petit limit ($C_v(T) \sim 3R$ for mono atomic solids) at higher temperatures for NdTe compounds.

4. Conclusions

In this study, the ab-initio pseudopotential calculations have been performed on the NdTe using the plane-wave pseudopotential approach to the density-functional theory (DFT) within PAW GGA approximation. Our present key results are on the thermodynamic and electronic properties for cubic structures of NdTe. The electronic band structures with density of states are presented. NdTe in B1(NaCl) structure is more preferable because of the stability. The calculated thermodynamic parameters are also given in this text. There are some theroretical and experimental work for NdTe(B1) [26, 27]. There is no experimental or theoretical work on NdTe(B2). The lattice parameters are compared of NdTe(B1). Ref. {26] is a theoretical study in which lattice constant is 6.278 Å and Ref. [27] is experimental study in which lattice constant is 6.262 Å. Our calculated lattice constant is 6.367 Å. It could be seen that lattice constants are very compatible.

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