Structural and thermodynamic properties of OsN_2 from first-principles calculations*

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We investigate the structural and thermodynamic properties of OsN_2 by a plane-wave pseudopotential density functional theory method. The obtained lattice constant, bulk modulus and cell volume per unit formula are consistent with the available theoretical data. Moreover, the pressure-induced phase transition of OsN_2 from pyrite structure to fluorite structure has been obtained. It is found that the transition pressure of OsN_2 at zero temperature is 67.2 GPa. The bulk modulus B as well as other thermodynamic quantities of fluorite OsN_2 (including the Grüneisen constant γ and thermal expansion α) on temperatures and pressures have also been obtained.

Keywords: transition phase, thermodynamic properties, density functional theory, OsN_2

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1. Introduction

Recently, many types of transition metal compounds have been investigated because of the theoretical and experimental developments in materials science.[1−10] However, the 4d and 5d series of the noble transition metals (Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au)[1] have been rarely considered with regard to their compounds, such as nitrides and oxides, since the theory about the electronic correlation of 4d or 5d electrons is still imperfect.

The marcasite structure of OsN_2 was firstly synthesized at high pressures and temperatures using laser-heated diamond-anvil cell techniques by Young *et al.*,[2] whose theoretical calculations reflected that the metal and nitrogen stoichiometry was 1:2 in the compound. From then on began the theoretical research on the structures and properties of OsN_2. The pyrite and fluorite structures were firstly researched by Fan *et al.*[3] using the generalized gradient approximation (GGA) and the local-density approximation (LDA) based on density functional theory. They thought that OsN_2 was metallic and both pyrite and fluorite phases were stable from their elastic constants, electron density and density of state.

Theoretical research of the marcasite structure was conducted by comparing this with the pyrite and fluorite structures.[4−6] From the study of bulk modulus, band structure, elastic constants and density of states, we found that the marcasite structure was more stable than the other two structures, though the fluorite[4] and pyrite[3,5] structures were mechanically stable. From calculations of lattice parameters and band structures of marcasite and arsenopyrite phases, Hernandez *et al.* revealed that, with respect to the marcasite structure, the arsenopyrite structure was found to be unstable.[7]

By comparing the OsB, OsB_2, OsC, OsO_2, OsN, and OsN_2 electronic structures and phase stabilities, Zhang *et al.*[8] illustrated that OsN_2 in fluorite structure was more stable than OsN. Aberg *et al.*[9] considered the platinum–metal (PM) nitrides. They found that the structures of these compounds were thermodynamically stable at pressures above 50 GPa, and two kinds of simple tetragonal structures were obtained for the first time by VASP code. By first-principles investigation of the electron–phonon interaction in OsN_2, Hernández *et al.* predicted that OsN_2 compound was a superconductor.[10]

Based on the above investigations, the mechanical properties were researched extensively, but to the

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best of our knowledge, the thermodynamic properties of OsN_2 were not well considered. In this paper, we will focus on investigating the high pressure phase transition of OsN_2 in fluorite (space group $Fm\bar{3}m$) and pyrite structures (space group $Pa\bar{3}$), as well as the thermodynamic properties of fluorite OsN_2 over the range of 0–450 GPa by the plane-wave pseudopotential density functional theory method through the Cambridge Serial Total Energy Package (CASTEP) program,[11,12] the equation of state (EOS) program[13,14] and the quasi-harmonic Debye model.[15] In Section 2, we will illuminate the theoretical method. The results and some discussion are presented in Section 3. A conclusion is drawn in the last section.

2. Theoretical method

2.1. Total energy electronic structure calculations

In our calculations, we adopt a non-local ultrasoft pseudopotential introduced by Vanderbilt[16] together with two types of functional forms for the exchange–correlation potential among electrons, i.e., the local density approximation (LDA) proposed by Vosko *et al.*[17] and the generalized gradient approximation (GGA) proposed by Perdew *et al.*[18] Before starting with calculations, a set of convergence tests have been carried out in order to choose correctly the grid of special k points and the cut-off for the plane wave kinetic energy. We here use a plane wave kinetic energy cut-off of 550.00 eV and the Brillouin zone integration is confined to a 9×9×9 Monkhorst–Pack mesh,[19] where the self-consistent convergence of the total energy is at 10^{-6} eV/atom. Pseudo atomic calculations are performed for N $2s^2 2p^3$ and Os $5s^2 5p^6 5d^6 6s^2$. All of the total energy electronic structure calculations are implemented through the CASTEP code.[11,12]

2.2. Quasi-harmonic Debye model

To investigate the phase transition of OsN_2, the EOS program[13,14] was used, with which we have studied the transition phase of GaN.[20] For thermodynamic properties of OsN_2, we apply the quasi-harmonic Debye model,[15] in which the phonon effect is considered. In the quasi-harmonic Debye model, the non-equilibrium Gibbs function $G^*(V;P,T)$ is given as

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

where $E(V)$ is the total energy, PV corresponds to the constant hydrostatic pressure condition, and $A_{\rm Vib}$ is the vibrational Helmholtz free energy. Considering the quasi-harmonic approximation[21] and using the Debye model of phonon density of states, one can write $A_{\rm Vib}$ as[22,23]

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

where Θ is the Debye temperature, $D(\Theta/T)$ represents the Debye integral, and n is the number of atoms per unit formula. The standard thermodynamic relations that depend on temperature and pressure are used to derive other macroscopic properties, and with the isotropic approximation, Θ is expressed as[22]

$$\Theta_{\rm D} = \frac{\hbar}{k_{\rm B}}\left[6\pi^2 V^{1/2} n\right]^{1/3} f(\sigma)\sqrt{\frac{B_{\rm S}}{M}}, \quad (3)$$

where V, M, n, $B_{\rm S}$, $f(\sigma)$, and $k_{\rm B}$ are the molar volume, the molar mass, the number of atoms per formula unit, the adiabatic bulk modulus, a scaling function that depends on the Poisson's ratio of the isotropic solid, and the Boltzmann constant, respectively. In addition, the heat capacity C_V is taken as

$$C_{\rm V} = 3nk_{\rm B}\left[4D\left(\frac{\Theta}{T}\right) - \frac{3\Theta/T}{e^{\Theta/T}-1}\right]. \quad (4)$$

Applying this theoretical method, we have investigated some materials, such as GaN,[20] SrS,[24] AlN,[25] and BC_2N.[26]

3. Results and discussion

First of all, we calculate the equilibrium properties of both the fluorite and pyrite structures of OsN_2 (the structures are shown in Fig. 1) for the sake of judging whether the computational methodology is reliable and effective. To calculate the total energy E and the corresponding volume V, we take a series of different lattice parameters a. The lattice constant a_0 and equilibrium volume per unit formula of the fluorite and pyrite structure of OsN_2 we obtained are nearly the same as other theoretical results.[3,6,8] In our calculation, our LDA results seem to be in better agreement with other theoretical data than our GGA results. So, the LDA functional forms are applied in the following calculation.

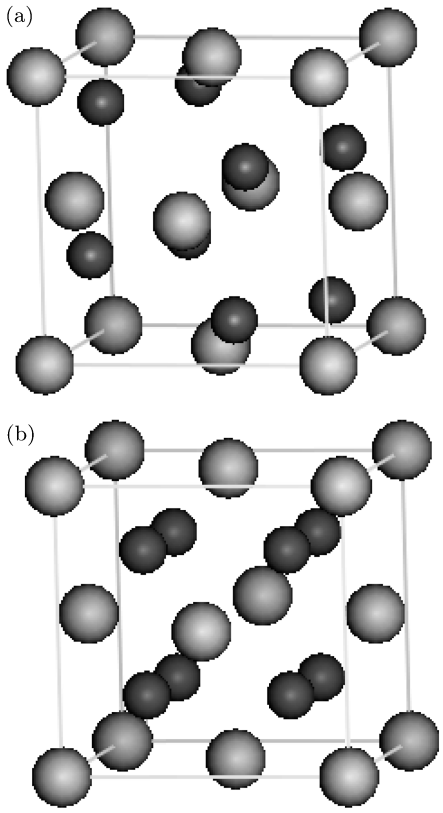


Fig. 1. The crystal structures of OsN_2: (a) pyrite; (b) fluorite.

The calculated energies as a function of the volume per formula unit for OsN_2 are shown in Fig. 2, together with the information concerning the static equations of state (EOS) and the phase stability data. Here, we fit the calculated E–V points to the Murnaghan EOS[13] and the natural strain EOS.[14] The obtained lattice constant a_0, bulk modulus B_0 and pressure derivative of the bulk modulus B_0' for the fluorite and pyrite structures of OsN_2 at zero pressure are also shown in Table 1.

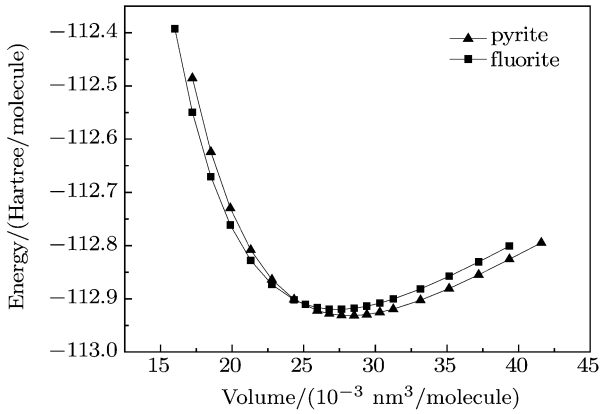


Fig. 2. Energy as a function of volume per formula unit for OsN_2.

Table 1. Lattice constant a (Å), bulk modulus B_0 (GPa), its pressure derivative B' and the volume per formula unit V (Å^3) of OsN_2 at 0 GPa and 0 K, 1 Å=0.1 nm.

	present	others
$Fm-3m$ (225)		
a/Å	4.780 (LDA)	4.781[a], 4.781[b], 4.805[c] (LDA)
	4.828 (GGA)	4.856[a], 4.834[b], 4.876[c] (GGA)
	4.804 (Ave)	4.819[a], 4.807[b] (Ave)
	4.796[d], 4.777[e]	
V/Å^3	27.3 (LDA)	
	28.1 (GGA)	
	27.7 (Ave)	
	27.581[d], 27.254[e]	
B_0/GPa	357.06[d], 410.36[e]	388.0[a], 386[b], 388.0[c] (LDA)
		333.3[a], 341[b], 332.9[c] (GGA)
		360.7[a], 363[b] (Ave)
B_0'	3.915[d], 4.476[e]	
$Pa\bar{3}$ (205)		
a/Å	4.828 (LDA)	4.831 [b] (LDA)
	4.899 (GGA)	4.925[a] , 4.884[b] (GGA)
	4.8635 (Ave)	4.857[b] (Ave)
	4.842[d], 4.829[e]	
V/Å^3	28.1 (LDA)	28.2[b] (LDA)
	29.4 (GGA)	29.1[b] (GGA)
	28.7 (Ave)	28.6[b] (Ave)
	28.374[d], 28.230[e]	
B_0/GPa	353.20 [d], 409.52[e]	352[b] (LDA)
		316[a], 320[b] (GGA)
		336[b] (Ave)
B_0'	4.087[d], 4.407[e]	

[a]From Ref. [3]; [b]From Ref. [6]; [c]From Ref. [8]; [d]From the Murnaghan EOS;[13] [e]From the natural strain 3rd-order EOS.[15]

Clearly, the lattice constant a_0 and equilibrium volume per formula unit V calculated from Murnaghan EOS are in better agreement with other theoretical values,[3,6,8] and our bulk modulus B_0, 357.06 GPa and 353.20 GPa for fluorite structure and pyrite structure are also consistent with other theoretical values (360.7 GPa, 363 GPa for fluorite structure and 336 GPa for pyrite structure).[3,6] Unfortunately, the experimental values or other theoretical results for the pressure derivative B_0' are not yet available for comparison.

Our results described above suggest that the plane-wave pseudopotential density functional theory method through the CASTEP program and the EOS program are suitable and effective for investigating the properties of OsN_2. An estimate of the zero-temperature transition pressure between the fluorite and the pyrite structures of OsN_2 may be obtained from the usual condition of equal enthalpies, i.e. the pressure P, at which the enthalpy $H = E + PV$ of both phases is the same. Figure 3 shows the enthalpy as a function of the pressure from the Murnaghan EOS. It is found that the transition pressure from the pyrite to the fluorite structure is about 67.2 GPa. We also calculated the transition pressure with the natural strain 3rd-order EOS, 65 GPa, which also agrees well with the result from the Murnaghan EOS. OsN_2 has been studied in recent years, but there is no experimental or theoretical value available on the transition pressure. We hope our study could provide useful guidance for future research.

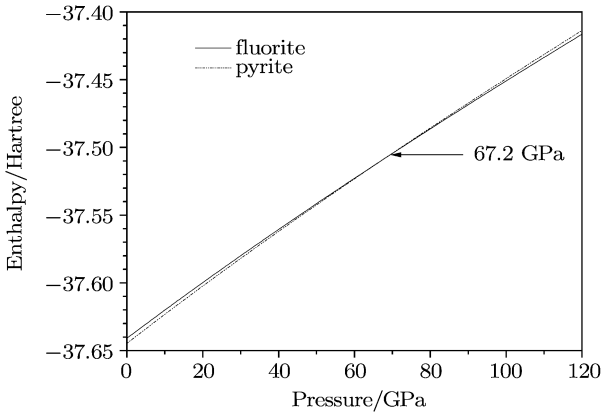


Fig. 3. Enthalpy as a function of pressure for OsN_2.

It is known that the fluorite structure is more stable than the pyrite structure of OsN_2 at high pressure. Here we focus our attention on the thermodynamic properties of fluorite OsN_2 at high pressure and high temperature through the quasi-harmonic Debye model.[15] In Figs. 4 and 5, we illustrate the relations of the bulk modulus B as a function of temperature T up to 3000 K at different pressures P = 100, 250, and 400 GPa, and as a function of pressure P up to 450 GPa at different temperatures T = 0, 300, 1500, and 3000 K. It is shown fin Fig. 4 that when $T < 300$ K, the bulk modulus B nearly keeps constant; when $T > 300$ K, as temperature T increases, B decreases dramatically. The linear coefficient of thermal expansion of OsN_2 as a function of temperature at various pressures is calculated from the volumes.

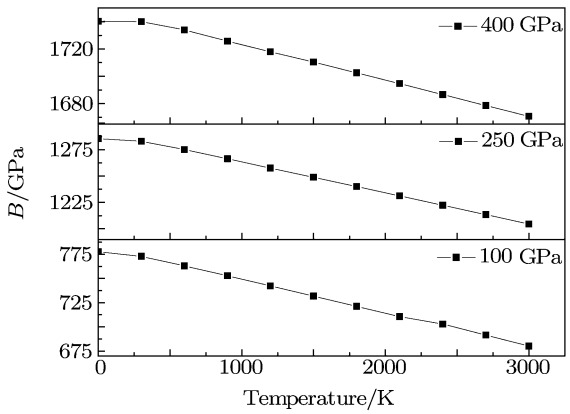


Fig. 4. The bulk modulus B as a function of temperature T up to 3000 K at various pressures.

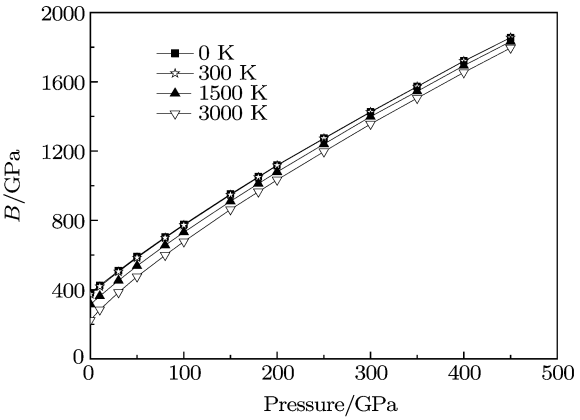


Fig. 5. The bulk modulus B versus pressure P at temperatures T = 0, 300, 1500 and 3000 K.

It can be seen clearly in Fig. 6. The linear coefficient of thermal expansion was obtained using $(a - a_0)/a_0$, where a_0 is the lattice constant at T = 300 K. At a given pressure, we find that the lattice parameter a nearly keeps constant when temperature $T < 300$ K, and this results in very little change in volume V. However, once the temperature $T > 300$ K, the lattice parameter a increases rapidly as the temperature

T increases. The volume V will be changed dramatically. The dramatic volume variation leads to the rapid decrease in the bulk modulus B_0. In addition, for a given temperature, the linear coefficient of thermal expansion $(a - a_0)/a_0$ decreases with increasing pressure.

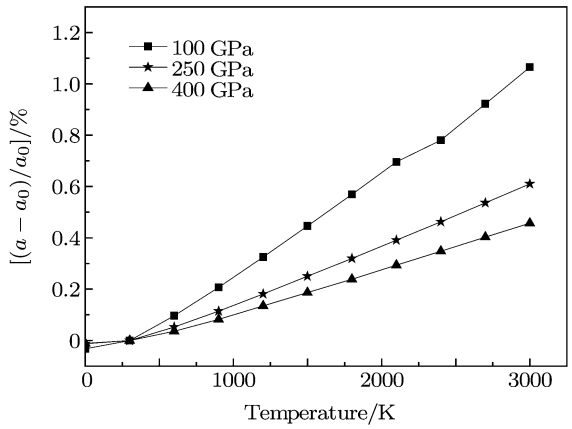


Fig. 6. Linear coefficient of thermal expansion versus temperature T at various pressures.

Moreover, we calculated the linear thermal expansion coefficient α_a. At room temperature, we obtained $\alpha_a = 2.46 \times 10^{-6}$ K^{-1} for the fluorite structure. No experimental value is available to compare with our result. Since the borides, carbides, oxides, and nitrides of Os are expected to be good candidates for superhard material, here we apply the linear thermal expansion coefficient of diamond for our comparison. At room temperature, the linear thermal expansion coefficient of diamond is 2.796×10^{-6} K^{-1} (theoretical data).[27] Our results are approximate on the order of magnitude.

On the other hand, it is noted from Fig. 5 that the relationships between bulk modulus B and pressure P are all nearly linear at $T = 0$, 300, 1500, and 3000 K. The bulk modulus increases with pressure at a given temperature and decreases with temperature at a given pressure. It is shown that increasing pressure has exactly the opposite effect on the bulk modulus of materials as does increasing temperature, as can be understood from the above quasi-harmonic Debye model. Grüneisen constant γ, which describes the anharmonic effects in the vibrating lattice, can correctly predict the anharmonic properties of a material, such as the thermal expansion coefficient and the temperature dependence of phonon frequencies and linewidths. In Fig. 7, we present the obtained Grüneisen constant γ at 0 K. It is noted that the Grüneisen constant γ decreases with increasing pressure at zero temperature.

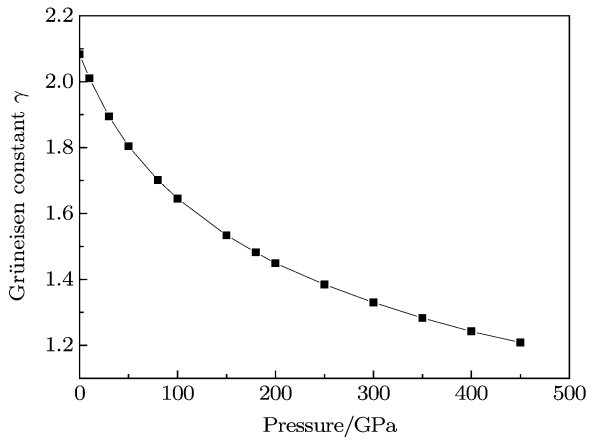


Fig. 7. Grüneisen constant γ versus pressure at zero temperature.

In Fig. 8, we present the variations in the thermal expansion α with temperature and pressure.

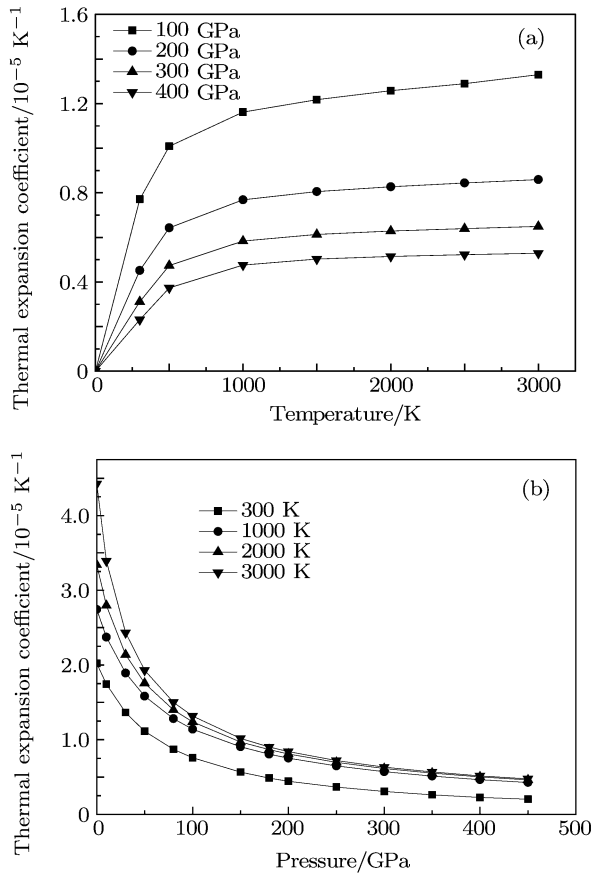


Fig. 8. The thermal expansion coefficient versus temperature (a) and pressure (b).

It is noted that at a given pressure, α increases exponentially with T at low temperatures and gradually approaches a linear increase at high temperatures. As

the pressure increases, the increase in α with temperature becomes smaller, especially at high temperatures. At a given temperature, α decreases drastically with an increase in pressure. When the pressure is above 200 GPa, the thermal expansion α of 2000 K is nearly the same as that of 3000 K and just a little larger than that of 1000 K, which means that the temperature dependence of α is very small at high temperature and higher pressure.

The Debye temperature is an important fundamental parameter and closely related to many physical properties of solids, such as the specific heat and melting temperature. Below the Debye temperature, quantum mechanical effects are very important in understanding the thermodynamic properties, while above the Debye temperature, quantum effects can be neglected. In Fig. 9, we show the $C_{\rm V}$ and the Debye temperature Θ as functions of pressure P at temperatures of 300 K and 2000 K for the fluorite structure OsN_2. It is shown that when the temperature is constant, the Debye temperature Θ increases almost linearly with applied pressure. However, the $C_{\rm V}$ decreases with applied pressure, which is due to the effect of increasing pressure on OsN_2 being the same as decreasing the temperature of OsN_2. On the other hand, the specific heat for 100, 200, 300, and 400 GPa of the fluorite structure OsN_2 is plotted in Fig. 10. It is readily seen that when $T < 1500$ K, the $C_{\rm V}$ is dependent on the temperature and pressure. When the applied pressure ranges from 100 GPa to 400 GPa, the heat capacity $C_{\rm V}$ decreases by 31.59%, 4.28%, 1.12%, 0.51% at 300, 1000, 2000, and 3000 K, respectively. This is due to the anharmonic approximations

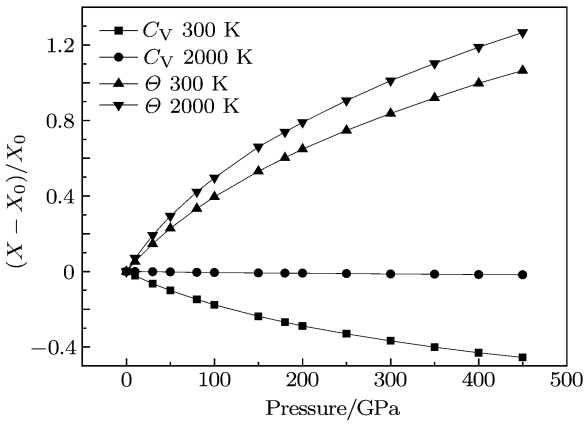


Fig. 9. Variations in thermodynamic parameters X (X: Debye temperature or specific heat) with pressure P. They are normalized by $(X - X_0)/X_0$, where X and X_0 are the Debye temperature or heat capacity under any pressure P and zero pressure P_0 at the temperatures of 300 K and 2000 K.

of the Debye model used here. At higher pressures and higher temperatures, the anharmonic effect on $C_{\rm V}$ is suppressed, and $C_{\rm V}$ is very close to the Dulong–Petit limit ($\approx$ 75 J·mol^{-1}·K^{-1}). The heat capacity $C_{\rm V}$ of the fluorite structure OsN_2 is 52.2 J·mol^{-1}·K^{-1} at transition pressure 67.2 GPa and ambient temperature.

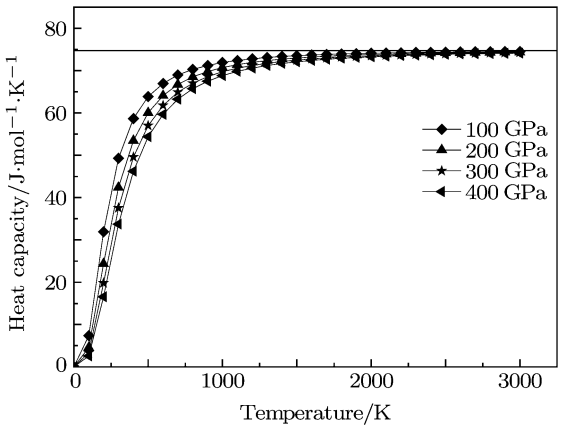


Fig. 10. The heat capacity at various pressures and temperatures.

4. Summary

In summary, we have investigated the lattice parameters and thermodynamic properties of OsN_2 in pyrite and fluorite structures by using first-principles calculations. The pressure induced phase transition of OsN_2 from pyrite structure to fluorite structure has also been investigated by the EOS program. It is found that the transition pressure of OsN_2 at zero temperature is 67.2 GPa. Moreover, we have obtained the pressure or temperature dependence of the bulk modulus B, linear coefficient of thermal expansion, Grüneisen constant γ, thermal expansion α, Debye temperature Θ, and specific heat $C_{\rm V}$ for fluorite OsN_2. Unfortunately, for these properties, there are no previous calculations and experimental values for our comparison. However, we believe that more experimental and theoretical work is required on all aspects of OsN_2 .

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