A New Potential Superhard Phase of OsN₂

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A new phase of $C2/m$ OsN₂ is proposed in this paper. The crystal structure, elasticity and electronic properties of $C2/m$ OsN₂ were studied by first-principles calculations. The elastic constants, the elastic moduli (B , G , and E) and Poisson's ratio ν of OsN₂ have been investigated. From the first-principles calculations, we find that $C2/m$ OsN₂ is metallic and mechanically stable. The quasi-harmonic Debye model, using a set of total energy versus molar volume obtained from the first-principles calculations, is applied to the study of the thermal and vibrational effects. The dependence of structural parameters, thermal expansions, heat capacities, Grüneisen parameters and Debye temperatures on the temperature and pressure are obtained in the whole pressure range from 0 to 80 GPa and temperature range from 0 to 800 K as well as compared with available data.

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1. Introduction

Binary transition metal (TM) nitrides have increasing interest due to their absorbing properties, such as high thermal and chemical stability, electrical or thermal conductivity, catalytic activity, and superior hardness [1–5]. Recently, many types of transition metal compounds have been investigated because of the rapid development of theoretical and experimental methods in materials science. Here, we readdress structural and elastic properties of OsN₂ and find that a new metastable state with $C2/m$ phase is more stable than that of fluorite phase ($Fm-3m$).

The $Pnnm$ OsN₂ was firstly synthesized at high pressures and temperatures using laser-heated diamond-anvil cell techniques by Young et al. [6], whose theoretical calculations reflected that the metal and nitrogen stoichiometry was 1:2 in the compound. From then on, the theoretical researches on the structures and physical properties of OsN₂ have been employed. The pyrite and fluorite structures were firstly researched by Fan et al. [7] using the generalized gradient approximation (GGA) and local density approximation (LDA) based on density functional theory (DFT). They found that OsN₂ was metallic, and both pyrite and fluorite phases were stable. The $Pnnm$ OsN₂ were studied by Wang et al. [8] using DFT. They found that calculated elastic constants for marcasite OsN₂ satisfy the stability condition and the band structure shows that marcasite OsN₂ is metallic. Subsequently, Chen et al. [9] investigated the crystal structure, phonon stability, elasticity and electronic properties of four noble metal nitrides (PtN₂, IrN₂, OsN₂, and AuN₂)

with three structural types (pyrite, marcasite, and CoSb₂ structures) by first-principles calculations. They found that the most stable phase is $Pnnm$, and the structure for the lowest enthalpy is the marcasite structure for OsN₂. The structural properties and elastic constants of OsN₂ at high pressure were computed by the ultrasoft pseudopotential (USPP) [10] within the GGA in the frame of DFT, Peng et al. [11] found that when $P > 20$ GPa, the calculated values of the B/G (> 1.75) increase with pressures which indicate that pressure can improve ductility and the obtained Poisson ratio ν exhibit that the interatomic forces in the OsN₂ are central forces.

The structural and thermodynamic properties of OsN₂ were discovered using a plane-wave pseudopotential DFT method by Liu et al. [12]. They revealed the transition pressure of OsN₂ from $Pa-3$ to $Fm-3m$ at zero temperature is 67.2 GPa. Yu et al. [13] have solved the crystal structures of OsN₂ and IrN₂ and predicted those of RuN₂ and RhN₂. In their researches, a pressure induced displacive phase transition and semiconductor–metal transition are predicted for IrN₂, which also has an ultrahigh bulk modulus. Montoya et al. [14] found that the crystal structure of osmium nitride is isostructural to $Pnnm$ OsN₂, and in the $Pnnm$ OsN₂ single-bonded N₂ units occupy the interstitial sites of the Os close-packed lattice, giving rise to a metallic compound.

In this work, we will study the properties of $C2/m$ phase, by comparing the crystal structure, elastic properties, and electronic properties of $C2/m$ phase with $P2_1/c$, $Pnnm$ and $Fm-3m$ phases.

2. Computational details

The first-principles calculations are performed based on the DFT packaged in Cambridge Serial Total Energy Package (CASTEP) [15]. Interactions between the ions and the electrons were described by using the Vanderbilt pseudopotential [10]. The electronic exchange-

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-correlation potentials were described within the LDA [16] and GGA parameterized by Perdew, Burke and Ernzerhof (PBE) [17]. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) [18] minimization scheme was used in geometry optimization. For *C2/m* phase, we used a plane-wave basis set with energy cut-off 500 (620) eV is used with GGA (LDA). For the Brillouin-zone sampling, the $10 \times 14 \times 7$ Monkhorst–Pack mesh [19] is adopted. The self-consistent convergence of the total energy is 5×10^{-6} eV/atom; the maximum force on the atom is 0.01 eV/Å; the maximum ionic displacement is within 5×10^{-4} Å. For *Pnnm*, *P2₁/c*, and *Fm-3m* phases, energy cut-off was used with 560 eV, 500 eV, and 520 eV, respectively. The *k*-points of $7 \times 6 \times 11$ for *marcasite Pnnm*, $7 \times 7 \times 7$ for *P2₁/c* and $9 \times 9 \times 9$ for *Fm-3m* are using the Monkhorst–Pack mesh scheme with GGA, respectively. The other parameters are set as the same as in *C2/m* phase.

In order to obtain the thermodynamic properties of OsN₂, the quasi-harmonic Debye model [20–23] is introduced, in which the non-equilibrium Gibbs function $G^*(V; P, T)$ takes the form of

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

where $E(V)$ is the total energy per unit cell for OsN₂, $\Theta(V)$ is the Debye temperature, and the vibrational Helmholtz free energy A_{vib} can be written by [24–28]:

$$A_{\text{vib}}(\Theta; T) =$$

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

where $D(\Theta/T)$ represents the Debye integral. Assume that y is equal to Θ/T , so

$$D(y) = \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx, \quad (3)$$

n is the number of atoms per formula unit, Θ is the Debye temperature, and Θ is expressed as [24]:

$$\Theta = \frac{h}{2\pi k} \left[6\pi^2 V^{1/2} n \right]^{1/3} f(\nu) \sqrt{\frac{B_s}{M}}, \quad (4)$$

where M is the molecular mass per formula unit. B_s is the adiabatic bulk modulus, the Poisson ratio ν is taken as 0.28 in our calculation, and $f(\nu)$ is given by [26, 27]:

$$f(\nu) = \sqrt[3]{\frac{3}{\left[2 \left(\frac{2}{3} \frac{1+\nu}{1-2\nu} \right)^{3/2} + \left(\frac{1}{3} \frac{1+\nu}{1-\nu} \right)^{3/2} \right]}}. \quad (5)$$

The isothermal bulk modulus and other thermal properties such as heat capacity at constant volume C_v , the heat capacity at constant pressure C_p , and thermal expansion α are respectively taken as [29]:

$$B_T = -x^{-2} B_0 e^{a(1-x)} f(x), \quad (6)$$

$$x = \left(\frac{V}{V_0} \right)^{1/3}, \quad (7)$$

$$f(x) = x - 2 - ax(1 - x), \quad (8)$$

where $V_0 = V(0, T)$ is the zero-pressure equilibrium volume, B_0 is the zero-pressure bulk modulus, and a through

the relation

$$a = 3(B'_0 - 1)/2, \quad (9)$$

where B'_0 is first pressure derivative. In addition, B_0 , B'_0 , and a are the fitting parameters. And

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

$$C_p = C_V(1 + \alpha\gamma T), \quad (11)$$

$$\alpha = \frac{\gamma C_V}{B_T V}, \quad (12)$$

where C_V is the heat capacity and γ represents the Grüneisen parameter and it is expressed as

$$\gamma = -(\text{d} \ln \Theta(V) / \text{d} \ln V). \quad (13)$$

3. Results and discussion

3.1. Structural properties

In this work, we consider monoclinic, orthorhombic, tetragonal and cubic phases, including this initial structure of ReN₂ in *C2/m* phase [30].

The calculated lattice parameters for four structures of OsN₂, together with previously obtained experimental results for *Fm-3m*, *P2₁/c* and *Pnnm* phases are presented in Table I. It can be observed that the lattice parameters are reasonably well reproduced for *Pnnm*, *Fm-3m* and *P2₁/c* OsN₂ with a maximum error of 2.9%. For *C2/m* phase, we calculated lattice volume is slightly smaller than *Pnnm*, *Fm-3m*, and *P2₁/c* phases. For *P2₁/c* phase, the calculated lattice parameters are in good agreement with the reported calculated results of other theoretical results [9, 31], while larger deviations from Ref. [9] lattice parameters are found in both a and c directions 0.29% and 1.09%, respectively, but smaller deviations are found in b directions 0.20%, and larger deviations from Ref. [31] lattice parameters are found in both a , b , and c directions 0.43%, 0.47%, and 0.51%, respectively. For *Pnnm* phase, the calculated lattice parameters are in good agreement with the reported experimental and theoretical values [8, 9, 31, 32], and larger deviations from the experimental lattice parameters are found in both a (0.82%) and b (0.58%) directions, respectively, but smaller deviation from the experimental lattice parameters is found in c (0.71%) direction. For *Fm-3m* phase, the calculated lattice parameters are also in good agreement with the reported calculated results [7, 12, 33, 34].

The lattice parameters volume V/V_0 as a function of applied pressure is plotted in Fig. 1, where V_0 is the values at $P = 0$ GPa. It can be easily seen that the compression of *Pnnm* OsN₂ is the most difficult. With pressure increases, atoms in the interlayers become closer, and their interactions become stronger.

In addition, we have also calculated the enthalpy of each structure for OsN₂. The calculated enthalpy of OsN₂ as a function of pressure for the *Pnnm*, *Fm-3m*, *P2₁/c*, and *C2/m* phases are given in Fig. 2. One can see that the structures for the lowest enthalpy are *Pnnm* and *P2₁/c* phase, and *Fm-3m* phase has the highest enthalpy. The enthalpies of OsN₂ with *Pnnm* and *P2₁/c*

Fig. 1. Lattice parameter volume V/V_0 with applied pressure of $C2/m$, $P2_1/c$, $Pnnm$, and $Fm-3m$ OsN_2 .

TABLE I

Lattice constants a , b , and c ($\text{\AA}$), β (deg), cell volume per formula unit V_0 ($\text{\AA}^3$).

		a	b	c	β	V_0
$C2/m$	GGA	3.6524	3.6524	9.4838	142.6937	27.706
	LDA	3.6305	3.6305	9.1508	136.4025	27.517
$P2_1/c$	GGA	4.9241	4.9061	4.9681	112.0376	30.005
	GGA ^a	4.9030	4.8830	4.9430		29.585
	GGA ^b	4.9100	4.9160	4.9140		29.653
$Pnnm$	GGA	4.1361	4.9385	2.6950		27.523
	GGA ^a	4.1190	4.9150	2.6830		27.158
	GGA ^b	4.1160	4.9150	2.6860		27.169
	GGA ^c	4.1470	4.9550	2.6690		27.422
	LDA ^c	4.1010	4.8890	2.6540		26.606
	LDA ^d	4.0770	4.8442	2.6212		25.884
	Exp. ^c	4.1020	4.9100	2.7140		27.331
$Fm-3m$	GGA	4.8557	4.8557	4.8557		28.622
	GGA ^e	4.8280	4.8280	4.8280		28.135
	GGA ^f	4.8560	4.8560	4.8560		28.627
	GGA ^g	4.8340	4.8340	4.8340		28.240
	GGA ^h	4.8760	4.8760	4.8760		28.982

^a Ref. [31]; ^b Ref. [9]; ^c Ref. [8]; ^d Ref. [32]; ^e Ref. [12];

^f Ref. [7]; ^g Ref. [34]; ^h Ref. [33]

phases are very close, but the $Pnnm$ OsN_2 has a slightly lower value. Our results suggest that $C2/m$ phase is a metastable state for OsN_2 and the $Fm-3m$ phase is relatively difficult to be directly synthesized.

3.2. Elastic properties

The elastic properties of a solid are important. They are not only closely related to various fundamental solid-state phenomena such as interatomic bonding, equations of state, and phonon spectra, but also linked thermody-

Fig. 2. Enthalpy difference per formula unit as function of pressure. $C2/m$ phase is taken as a reference.

namically with specific heat, thermal expansion, Debye temperature, and Grüneisen parameter. Most important, knowledge of the elastic constants is essential for many practical applications related to the mechanical properties of a solid. In the following section, we will introduce the formulae of elastic moduli and mechanical stability criteria for the considered crystal systems. The mechanical stability criteria of monoclinic phase are given by [35, 36]:

$$C_{ii} > 0, \quad i = 1 \dots 6, \quad (14)$$

$$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, \quad (15)$$

$$(C_{33}C_{55} - C_{35}^2) > 0, \quad (16)$$

$$(C_{44}C_{66} - C_{46}^2) > 0, \quad (17)$$

$$(C_{22} + C_{33} - 2C_{23}) > 0, \quad (18)$$

$$[C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{55} - C_{25}^2C_{33}] > 0, \quad (19)$$

$$2[C_{15}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{12}C_{23}) + C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})] - [C_{15}^2(C_{22}C_{33} - C_{23}^2) + C_{25}^2(C_{11}C_{33} - C_{13}^2) + C_{35}^2(C_{11}C_{22} - C_{12}^2)] + C_{55}g > 0, \quad (20)$$

$$g = C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 + 2C_{12}C_{13}C_{23}. \quad (21)$$

The criteria for mechanical stability of orthorhombic phase are given by

$$C_{ii} > 0, \quad i = 1 \dots 6, \quad (22)$$

$$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, \quad (23)$$

$$(C_{11} + C_{22} - 2C_{12}) > 0, \quad (24)$$

$$(C_{11} + C_{33} - 2C_{12}) > 0, \quad (25)$$

$$(C_{22} + C_{33} - 2C_{23}) > 0. \quad (26)$$

The criteria for mechanical stability of cubic phase are given by

$$C_{11} > 0, \quad C_{44} > 0, \quad (27)$$

$$C_{11} > |C_{12}|, \quad (28)$$

$$(C_{11} + 2C_{12}) > 0. \quad (29)$$

The criteria for mechanical stability of tetragonal phase are given by

$$C_{ii} > 0, \quad i = 1, 3, 4, 6, \quad (30)$$

$$(C_{11} - C_{12}) > 0, \quad (31)$$

$$(C_{11} + C_{33} - 2C_{13}) > 0, \quad (32)$$

$$[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0. \quad (33)$$

Calculated single crystal elastic constants C_{ij} , bulk modulus B , shear modulus G for $C2/m$, $P2_1/c$, $Pnnm$ and $Fm-3m$ phases of OsN_2 are shown in Table II. From Table II, we found that our calculation results of $C2/m$ phase are in excellent agreement with the criteria for mechanical stability which indicates that it is elastically stable. In the same manner, from our calculation results in Table II, we can find that OsN_2 with $P2_1/c$, $Pnnm$, and

Fm-3m phases are also mechanically stable because their elastic constants fit well in the above formulae. It is interesting to note that there is a slightly larger C_{33} value

in the *P2₁/c* phase, implying the higher incompressibility along the *c* axis. This fact is caused by the strong covalent N=N and Os–N bonds along the *c* axis.

TABLE II

Calculated single crystal elastic constants C_{ij} (GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa) and Poisson's ratio ν for *C2/m*, *P2₁/c*, *Pnnm* and *Fm-3m* structures of OsN₂.

		C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}	B	G	E	ν
<i>C2/m</i>	LDA	743	159	177	402	353	679	263	205	159	341	178	455	0.28
	GGA	665	176	199	415	313	736	247	198	145	342	179	457	0.28
<i>P2₁/c</i>	GGA	713	136	156	887	159	736	153	171	124	351	197	498	0.26
	GGA ^a	716	142	163	881	154	753	149	166	123	355	194	493	0.27
<i>Pnnm</i>	GGA	739	194	265	948	84	598	140	341	179	369	231	573	0.24
	GGA ^b	750	181	278	931	73	602	141	346	174	362			
	GGA ^c	744	178	277	913	88	581	134	340	175	359	258	624	0.21
	GGA ^d	761	176	277	930	84	594	135	351	173	362	220	549	0.25
	GGA ^e	757	178	276	939	68	612	142	348	212	368	242	596	0.23
<i>Fm-3m</i>	GGA	497	250	250	497	250	497	93	93	93	332	104	283	0.36
	GGA ^e	433	295	295	433	295	433	96	96	96	341	84	233	0.38
	GGA ^f	465	267	267	465	267	465	80	80	80	333	89	246	0.38

^a Ref. [31]; ^b Ref. [9]; ^c Ref. [8]; ^d Ref. [38]; ^e Ref. [34]; ^f Ref. [7]

To discuss elasticity in detail, bulk modulus B , shear modulus G , Young's modulus E , and Poisson's ratio ν were calculated from elastic constants, using the Voigt–Reuss–Hill approximation [37], as presented in Table II. It is revealed in this table that *Pnnm* OsN₂ has the highest bulk modulus of 369 GPa in our calculations, this value of *Pnnm* phase is much higher than *C2/m* phase (341 GPa) and it is in good agreement with previous calculation (359 GPa [8], 362 GPa [9, 38]). It should be noted that the bulk moduli of osmium compounds are all very large to be in the range of 332–369 GPa for GGA. However, most of them are smaller than that (395–460 GPa) of Os compounds with the B, C, or O atoms [39]. The G of *C2/m* OsN₂ is calculated to be 179 GPa (178 GPa) with GGA (LDA), which is much lower than *Pnnm* phase, and much higher than *Fm-3m* phase. The Young modulus E and Poisson's ratio ν are obtained by the following formulae [37]:

$$E = \frac{9BG}{3B + G}, \quad (34)$$

$$\nu = \frac{3B - 2G}{2(3B + G)}. \quad (35)$$

The Young modulus E and Poisson's ratio ν are important for technological and engineering applications. The first one is defined as the ratio between stress and strain, and is used to provide a measure of the stiffness of solid, i.e., the larger the value of E , the stiffer is the material. The Young modulus of *C2/m* phase is 457 GPa, which is much lower than *Pnnm* phase (573 GPa) and higher than *Fm-3m* phase (283 GPa). The Poisson ratio ν provides more information about the characteristics of the bond-

ing forces than any of the other elastic constants. The Poisson ratio ν of *C2/m* is 0.28 (0.28) with GGA (LDA), much larger than diamond (0.08) [7], slightly greater than *P2₁/c* phase (0.26) and *Pnnm* phase (0.24), but smaller than *Fm-3m* phase (0.36).

3.3. Electronic properties

To investigate the electronic properties of OsN₂, the total and partial density of states (DOS) with respect to the Fermi level is shown in Fig. 3. These four phases showed metallic behavior because of finite $N(E_F)$ at the Fermi level. As can be seen from Fig. 3, there are finite DOS at the Fermi level $N(E_F)$ of 1.2265, 1.8033, 2.2954, and 0.9290 states/eV of *C2/m*, *Fm-3m*, *P2₁/c*, and *Pnnm* phases, respectively. Additionally, the values at Fermi level per atom follows a sequence: *Pnnm* OsN₂ (0.3097) < *C2/m* OsN₂ (0.4088) < *Fm-3m* OsN₂ (0.6011) < *P2₁/c* OsN₂ (0.7651). Near the Fermi level, the DOS is mainly contributed by the Os *d* orbital and N *p* orbital in *C2/m* OsN₂ (Fig. 3a) and *Fm-3m* OsN₂ (Fig. 3b), while in *P2₁/c* OsN₂ (Fig. 3c) and *Pnnm* OsN₂ (Fig. 3d), there are equal contributions from Os *d* orbital and other orbitals. The *Pnnm* OsN₂ has the lowest density of states at the Fermi level. This may help to enhance the stability of the polymorph, so the *Pnnm* phase OsN₂ is the most stable [9]. From Fig. 3b and d, we also see a deep valley near the Fermi level in *Fm-3m* and *Pnnm* OsN₂, which is termed as pseudogap. This suggests that not all the bonding states are filled and some extra electrons are required to reach maximum stability in this compound or it is caused by strong hybridization of Os *d* orbital and N *p* orbital and indicates the covalent bonding in OsN₂. It also reveals that the bonding states are

primarily composed of nitrogen $2p$ orbital and osmium $5d$ orbital.

Fig. 3. Calculated total and partial densities of states of (a) $C2/m$ OsN_2 , (b) $Fm-3m$ OsN_2 , (c) $P2_1/c$ OsN_2 , (d) $Pnnm$ OsN_2 . The Fermi levels are located at 0 eV.

3.4. Thermodynamic property

The relationship between bulk modulus B and temperature T at different pressures $P = 0, 40$, and 80 GPa are shown in Fig. 4a, and Fig. 4b presents the relations of the isothermal bulk modulus as a function of pressure P up to 80 GPa at $T = 0, 400$, and 800 K. One can obviously see that when $T < 200$ K, B keeps nearly constant; when $T > 200$ K, B decreases dramatically as T increases. The primitive cell volume of $C2/m$ OsN_2 as a function of pressure P at $T = 0, 200, 400, 600$, and 800 K are shown in Fig. 5. Correspondingly, in Fig. 5, when $T < 200$ K, the primitive cell volume of OsN_2 has a little change; when $T > 200$ K, the cell volume changes rapidly as temperature increases. It is the rapid volume variation that makes the bulk modulus B to decrease rapidly. These results indicate that B increases with P at a given temperature and decreases with temperature at certain pressure. From Fig. 4, we can find that the effect of the temperature on the isothermal bulk modulus is less important than that of pressure on it, and from Fig. 5, it is found that the effect of temperature on the volume is not as significant as that of pressure in our calculated pressure and temperature ranges.

The calculated heat capacity at constant pressure C_p and heat capacity at constant volume C_v with the temperature T at different pressure p are shown in Fig. 6. The difference between C_p and C_v is very small at low temperatures. However, at high temperatures, the C_v approaches a constant value, C_p increases monotonously with increments of the temperature. From Fig. 6, one

can also see that the heat capacity (C_p and C_v) increases

Fig. 4. Temperature (a) and pressure (b) dependence of the isothermal bulk modulus for $C2/m$ OsN_2 .

Fig. 5. The primitive cell volume of $C2/m$ OsN_2 as a function of pressure at $T = 0, 200, 400, 600$, and 800 K.

with the temperature at the same pressure and decreases with the pressure at the same temperature, the influences of the temperature on the heat capacity are much more significant than that of the pressure on it. It is also shown that when $T < 500$ K, the heat capacity C_v is sensitive to both temperature and pressure. This is because of the anharmonicity approximations of the Debye model. However, at higher temperatures, the anharmonic effect on C_v is suppressed, and C_v is very close to the Dulong-Petit limit.

Fig. 6. Temperature dependence of the heat capacity for $C2/m$ OsN_2 .

TABLE III

The calculated Debye temperature (Θ [K]) and Grüneisen parameter γ of the $C2/m$ -structure OsN₂ under pressures at different temperatures.

T [K]	P [GPa]	0	10	20	30	40	50	60	70	80
200 K	Θ	547.13	594.37	632.16	663.91	691.51	716.15	738.46	758.87	777.72
	γ	2.876	2.467	2.203	2.015	1.871	1.757	1.663	1.584	1.516
400 K	Θ	534.58	588.61	626.47	659.41	687.82	712.97	735.65	756.40	775.57
	γ	3.002	2.527	2.240	2.040	1.890	1.771	1.674	1.593	1.524
600 K	Θ	517.46	576.72	619.38	653.77	683.12	708.96	732.20	753.44	773.07
	γ	3.191	2.608	2.287	2.072	1.913	1.789	1.689	1.604	1.533
800 K	Θ	493.45	565.16	611.41	647.56	677.96	704.61	728.44	750.24	770.40
	γ	3.488	2.708	2.342	2.108	1.940	1.809	1.704	1.617	1.542

In the quasi-harmonic Debye model, the Grüneisen parameter γ , and the Debye temperature Θ , are two key parameters. The Debye temperature and the Grüneisen parameter at a variety of temperatures and different pressures are listed in Table III. The 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. 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. From Table III, one can find: when the applied pressure changes from 0 GPa to 80 GPa, the Debye temperature increases by 45.35%, 48.42%, 52.93% and 59.94%, and the Grüneisen parameter decreases by 49.30%, 51.23%, 53.93% and 56.51% at temperatures of 200, 400, 600, and 800 K, respectively. It reveals that, when the temperature is kept constant, the Grüneisen parameter γ decreases with increasing applied pressure, in virtue of the fact that the effect of increased pressure on the material is the same as decreased temperature of the material. On the other hand, the Debye temperature Θ increases almost linearly with applied pressures.

Figure 7 shows the variations of the thermal expansion coefficient α with pressures and temperatures. From Fig. 7a, as the pressure increases, the thermal expansion coefficient α decreases almost exponentially, and the higher the temperature is, the faster the thermal expansion coefficient α decreases. This shows that the effect of temperature is much greater than that of pressure on the thermal expansion coefficient α . When the pressure is 80 GPa, the thermal expansion α at 800 K is just a little larger than that at 600 K, which means that the temperature dependence of α is very small at high temperature and high pressure. However, from Fig. 4b, the thermal expansion coefficient α increases with T^3 at low temperatures (0 ÷ 100 K) and gradually approaches a linear increase

Fig. 7. Pressure (a) and temperature (b) dependence of the thermal expansion coefficient α for $C2/m$ OsN₂.

at higher temperatures (100 ÷ 300 K) and then the increasing trend becomes gentler. The effects of pressure on the thermal expansion coefficient α are very small at low temperatures; the effects are increasingly obvious as the temperature increases. As pressure increases, the thermal expansion coefficient α decreases rapidly and the effects of temperature become less and less pronounced, resulting in linear high-temperature behavior. It can be found that the thermal expansion coefficient α converges to a constant value at high temperatures and pressures.

4. Conclusions

A new phase OsN₂ ($C2/m$) is proposed in the present work. The crystal structure, stability, elastic constants and electronic properties of $C2/m$ OsN₂ as well as other three phases ($P2_1/c$, $Fm-3m$, and $Pnnm$) were studied by first-principles calculations. From the calculations, we found that $C2/m$ OsN₂ are mechanically stable. The dependence of the elastic constants and the aggregate elastic moduli (B , G , and E) and Poisson's ratio ν of OsN₂ at 0 GPa are also calculated and OsN₂ in $Pnnm$ phase has the largest bulk modulus 369 GPa and shear modulus 231 GPa, it is slightly larger than that of $C2/m$ OsN₂. The electronic structures indicate that $C2/m$ OsN₂ is metallic and metastable. The structural determination

and the discussion of the elastic and electronic properties may be used in the synthesis and high pressure study of OsN₂. Finally, using the quasi-harmonic Debye model, the dependence of volume on pressure, and the dependences of thermodynamic properties, including special heat capacity, Debye temperature, thermal expansion α and Grüneisen parameter γ , on pressure and temperature have also been obtained successfully. It is found that the effect of temperature on volume is not as significant as that of pressure in our calculated pressure and temperature ranges. High temperatures lead to a smaller bulk modulus, a smaller Debye temperature, a larger Grüneisen parameter, a larger heat capacity, and a larger thermal expansion coefficient at constant pressure. For $C2/m$ OsN₂, there are no previous calculations and experimental values for comparison. More experimental and theoretical work are supposed to be carried out soon on all aspects of OsN₂.

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