Elastic and thermodynamic properties of Re₂N at high pressure and high temperature

Mei-guang ZHANG¹, Hai-yan YAN², Qun WEI³, Duo-hui HUANG⁴

1. Department of Physics and Information Technology, Baoji University of Arts and Sciences, Baoji 721016, China; 2. College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721013, China; 3. School of Physics and Optoelectronic Engineering, Xidian University, Xi’an 710071, China; 4. Computational Physics Key Laboratory of Sichuan Province, Yibin University, Yibin 644007, China

Received 24 September 2012; accepted 14 April 2013

Abstract: First principles calculations are performed to systematically investigate the elastic and thermodynamic properties of Re₂N at high pressure and high temperature. The Re₂N exhibits a clear elastic anisotropy and the elastic constants $C_{11}$ and $C_{33}$ vary rapidly in comparison with the variations in $C_{12}$, $C_{13}$ and $C_{44}$ at high pressure. In addition, bulk modulus $B$, elastic modulus $E$, and shear modulus $G$ as a function of crystal orientations for Re₂N are also investigated for the first time. The tensile directional dependences of the elastic modulus obey the following trend: $E_{[0001]} > E_{[12\bar{1}1]} > E_{[10\bar{1}0]} > E_{[10\bar{1}1]}$. The shear moduli of Re₂N within the (0001) basal plane are the smallest and greatly reduce the resistance of against large shear deformations. Based on the quasi-harmonic Debye model, the dependences of Debye temperature, Grüneisen parameter, heat capacity and thermal expansion coefficient on the temperature and pressure are explored in the whole pressure range from 0 to 50 GPa and temperature range from 0 to 1600 K.

Key words: Re₂N; transition metal nitrides; elastic properties; thermodynamic properties

1 Introduction

Transition metal nitrides are of great interest in both fundamental science and technological applications because of their unusual physical and chemical properties [1–3]. Traditional applications have taken advantage of the hard and refractory nature of many early transition metal nitrides, such as TiN, CrN and HfN. In contrast, not too much success has been achieved in exploring the late transition metal nitrides, especially for platinum group and noble metals nitrides. Until recently, a significant progress in synthesis of the dinitrides of Pt, Ir, Os, and Pd has been made at extreme conditions (approximately 50 GPa and 2000 K) [4–7]. These nitrides have been shown to possess ultrahigh bulk moduli (428 GPa for IrN₂) comparable with those of the traditional superhard materials, thus exhibiting interesting mechanical properties. Extensive studies [8–13] are therefore carried out in order to hunt for new potential superhard transition metal nitrides.

More recently, FRIEDRICH et al [14] have succeeded in synthesizing two novel rhenium nitrides (Re₄N and Re₅N) and characterized them using white beam Laue microdiffraction. Both hexagonal phases have very high bulk moduli (> 400 GPa); close to that of c-BN and higher than that of ReB₂. Between these two nitrides, the Re₂N adopts hexagonal structures with a space group $P6₃/mmc$, and the atomic positions are Re (1/3, 2/3, 0.106) and N (1/3, 2/3, 3/4). Following this exciting work, FRIEDRICH et al [15] and DELIGOZ et al [16] investigated the vibrational properties of the hexagonal Re₂N. ZHANG et al [17] later have studied the thermodynamic stability and mechanical properties as well as a bond deformation mechanism of Re₂N. The structural, electronic, and elastic properties of Re₂N have been also investigated at ambient conditions [18–21], and the Re₂N was found to be an ultra-incompressible
and hard material due to its high bulk modulus, originating from the strong Re–N covalent bonds. Very recently, SOTO et al. [22] have systematically investigated two classes of variable-composition rhenium nitride: 1) interstitial rhenium nitride as a solid solution and 2) rhenium nitride in lamellar structures. They pointed out that Re$_2$N phase belongs to the second class and possesses the higher stability compared to the interstitial phases. Up to now, the properties of hexagonal Re$_2$N under ambient pressure are basically clear, but those under high pressures have never been fully investigated.

In this work, the elastic and thermodynamic properties of hexagonal Re$_2$N under high pressure are investigated to provide some additional information to the existing data on the physical properties of Re$_2$N. In addition, the elastic anisotropy of crystals can exert great effects on the properties of physical mechanism, such as anisotropic plastic deformation, crack behavior and elastic instability. Compared to previous works, we extend the mechanical properties and present in detail the elastic moduli as a function of crystal orientation for Re$_2$N at ambient pressure and high pressure in order to further clarify mechanical properties of Re$_2$N. The calculated results indicate that the (0001) plane may be the cleavage plane of Re$_2$N which was attributed to the presence of soft metallic Re–Re layers.

2 Computational methods

All calculations are performed based on the plane-wave pseudopotential density function theory, as implemented in CASTEP package [23]. Vanderbilt ultrasoft pseudopotentials [24] are employed to describe the electron-ion interactions. The exchange correlation energy is described in the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional [25]. The structure is optimized with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [26] method. Pseudo-atomic calculations are performed for Re 5s$^2$5p$^6$6s$^2$5d$^5$ and N 2s$^2$2p$^3$. In the structure calculation, the electronic wave functions are expanded in plane-wave basis set with cutoff energy of 520 eV, and the special points sampling integration over the Brillouin zone was employed by the Monkhorst-Pack method [27] with a grid of 0.03 Å$^{-1}$. The self-consistent convergence of the total energy is $10^{-7}$ eV/atom and the maximum force on the atom is $10^{-3}$ eV/Å. Furthermore, the quasi-harmonic Debye model [28], which is constructed from the Helmholtz free energy at the temperature below the melting point in the quasi-harmonic approximation, is applied to obtaining thermodynamic properties of Re$_2$N.

3 Results and discussion

3.1 Structural parameters of Re$_2$N

The equilibrium structural parameters for Re$_2$N were obtained by full relaxations of both lattice constants and internal atomic coordinations without any restrictions at ambient pressure. The optimized lattice constants are $a_0=2.855$ Å and $c_0=9.849$ Å, which are in good agreement with the experimental values of $a=2.835$ Å and $c=9.881$ Å. The calculated $a_0$ and $c_0$ deviate from the corresponding experimental values are within 0.7% and 0.3%, respectively. In addition, these predicted lattice parameters also agree well with the previous theoretical values [16–21]. Therefore, the excellent agreements above support the reliability of the computational procedure employed in the present work. In order to provide some insights into the pressure behavior of Re$_2$N, the pressure acting on the system as a function of lattice parameters ($a/a_0$ and $c/c_0$) and unit cell volume ($V/V_0$) as well as $c$-BN are obtained and plotted in Fig. 1, where $a_0$, $c_0$ and $V_0$ are the equilibrium structural parameters at zero pressure. Firstly, the volume incompressibility of Re$_2$N exceeds that of c-BN at high pressure, indicating its ultra-incompressible nature. Secondly, by fitting these calculated data with the least squares method, the relationships at the temperature of 0 K are obtained as the following relationships:

$$a/a_0 = 0.9999 - 9.4392 \times 10^{-4} P + 3.6569 \times 10^{-6} P^2$$  (1)

$$c/c_0 = 0.9999 - 5.6005 \times 10^{-4} P + 2.0651 \times 10^{-6} P^2$$  (2)

$$V/V_0 = 0.9998 - 2.43 \times 10^{-3} P + 1.0331 \times 10^{-6} P^2$$  (3)

It can be seen that the incompressibility along the $c$-axis is larger than that along the $a$-axis, suggesting its clear elastic anisotropy.

Fig. 1 Normalized parameters $a/a_0$, $c/c_0$, and $V/V_0$ as a function of pressure for Re$_2$N.
3.2 Elastic properties of Re$_2$N

The elastic constants of a material describe its response to applied stress and provide useful information about its bonding character. For the hexagonal Re$_2$N, the matrix of its elastic stiffness constants contains five independent elements $C_{ij}$ ($C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, and $C_{44}$). The elastic constants of Re$_2$N at zero pressure were calculated by the strain–stress method, meanwhile, the corresponding elastic compliance constants $s_{ij}$ can be obtained using the relations between elastic compliance constants and the elastic constants suggested by NYE [29]. The calculated values of $C_{ij}$ and $s_{ij}$ are collected in Table 1. Also the results obtained in previous theoretical works are included. For Re$_2$N, there are no available experimental data; however, taking account of the excellent agreements of our calculated results and the other theoretical values, our predicted values should be reliable. Furthermore, the key criterion for mechanical stability of a crystal is that strain energy must be positive, that is in a hexagonal crystal [30]: $C_{33}>0, C_{44}>0, C_{11}>C_{12}$, $(C_{11}+2C_{12})C_{33}>2C_{13}^2$. According to the above criteria, it is clear that Re$_2$N is mechanically stable at ambient condition. To further illustrate the effect of pressure on the elastic properties of Re$_2$N, the variations of elastic constants with pressure are shown in Fig. 2. As shown in Fig. 2, five independent elastic constants increase monotonically with pressure. Meanwhile, the predicted pressure derivatives of elastic constants, $\partial C_{ij}/\partial P$, $\partial C_{12}/\partial P$, $\partial C_{13}/\partial P$, $\partial C_{33}/\partial P$ and $\partial C_{44}/\partial P$ for Re$_2$N are found to be 5.65, 3.03, 4.25, 4.68 and 1.89, respectively. These results indicate that $C_{11}$ and $C_{33}$ vary rapidly under the effect of pressure in comparison with the variations in $C_{12}$, $C_{13}$ and $C_{44}$, which is the same as the case for Re$_2$N [31]. It indicates that $C_{11}$ and $C_{33}$ are sensitive to pressure compared with $C_{12}$, $C_{13}$ and $C_{44}$. Furthermore, the calculated elastic constants under pressure up to 50 GPa also satisfy the well-known Born stability criteria, indicating that Re$_2$N under pressure is also mechanically stable.

Like the elastic constants, the bulk modulus, shear modulus, and elastic modulus contain information regarding the hardness of a material with respect to various types of deformation. Bulk modulus $B$ measures the resistance of a material to volume changes and provides an estimate of its response to a hydrostatic pressure. Shear modulus $G$ describes the resistance of a material to shape change. Elastic modulus $E$ measures the resistance against uniaxial tensions. These are important parameters for defining the mechanical properties of a material. For engineering applications that make use of single crystals, it is necessary to know these elastic moduli as a function of crystal orientation. As outlined by PANDA and RAVI CHANDRAN [32] and HE et al [33], executing the appropriate coordinate system transformations for the compliances allows the determination of the variation of bulk modulus, elastic moduli, and shear modulus with crystallographic direction $[uvw]$ for a given crystallographic plane $(hkl)$ containing these directions (i.e., $B_{[uvw]}$, $E_{[uvw]}$, and $G_{[uvw]}$) are obtained. For the hexagonal Re$_2$N, the bulk modulus $B$ and elastic modulus $E$ can be expressed as follows:

$$B = (s_{11} + s_{12} + s_{13}) - (s_{11} + s_{12} - s_{13} - s_{33})\gamma^2$$

$$E = s_{11}(\alpha^4 + \beta^4) + s_{13}\gamma^2 + 2s_{12}\alpha^2\beta^2 + 2s_{13}(\beta^2\gamma^2 + \alpha^2\gamma^2) + s_{44}(\beta^2\gamma^2 + \alpha^2\gamma^2) + 6s_{66}\alpha^2\beta^2$$

where $\alpha$, $\beta$ and $\gamma$ are the direction cosines of $[uvw]$ direction. The shear modulus $G$ on the $(hkl)$ shear plane with shear stress applied along $[uvw]$ direction is given by

$$G^{-1} = 4s_{11}(\alpha^4 + \beta^4) + 4s_{13}\gamma^2 + 8s_{12}\alpha_1\alpha_2\beta_1\beta_2 + s_{46}(\alpha_1\beta_2 + \alpha_2\beta_1) + 8s_{13}(\beta_2\gamma_1\gamma_2 + \alpha_1\gamma_1\gamma_2) + s_{44}[(\beta_1\gamma_2^2 + \beta_2\gamma_1^2)^2 + (\alpha_1\gamma_1^2 + \alpha_2\gamma_2^2)]$$

where $\alpha_1$, $\beta_1$, $\gamma_1$, $\alpha_2$, $\beta_2$ and $\gamma_2$ are the direction cosines of the $[uvw]$ and $[HKL]$ directions in the coordinate systems, and the $[HKL]$ denotes the vector normal to the $(hkl)$ shear plane.

Figures 3(a) and (b) illustrate the directional dependence of the bulk modulus and elastic modulus of Re$_2$N using Eqs. (4) and (5). The plane projections of the directional dependence of the bulk modulus and elastic.

<table>
<thead>
<tr>
<th>Source</th>
<th>$C_{11}$/GPa</th>
<th>$C_{12}$/GPa</th>
<th>$C_{13}$/GPa</th>
<th>$C_{33}$/GPa</th>
<th>$C_{44}$/GPa</th>
<th>$s_{11}$/10$^{-3}$GPa$^{-1}$</th>
<th>$s_{12}$/10$^{-3}$GPa$^{-1}$</th>
<th>$s_{13}$/10$^{-3}$GPa$^{-1}$</th>
<th>$s_{33}$/10$^{-3}$GPa$^{-1}$</th>
<th>$s_{44}$/10$^{-3}$GPa$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>626</td>
<td>220</td>
<td>280</td>
<td>782</td>
<td>169</td>
<td>1.98</td>
<td>-0.29</td>
<td>-0.67</td>
<td>1.91</td>
<td>6.13</td>
</tr>
<tr>
<td>Ref. [17]</td>
<td>618</td>
<td>207</td>
<td>306</td>
<td>737</td>
<td>159</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ref. [18]</td>
<td>662</td>
<td>237</td>
<td>258</td>
<td>870</td>
<td>192</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ref. [19]</td>
<td>711</td>
<td>258</td>
<td>280</td>
<td>926</td>
<td>211</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ref. [20]</td>
<td>625</td>
<td>204</td>
<td>282</td>
<td>755</td>
<td>184</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ref. [21]</td>
<td>645</td>
<td>203</td>
<td>301</td>
<td>773</td>
<td>192</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
modulus are also shown in Figs. 3(c) and (d) for comparison. It can be seen that the nonspherical nature of Re$_2$N in Figs. 3(a) and (b) shows the clear anisotropy of the bulk modulus and elastic modulus. Moreover, while in-plane anisotropy in $ab$ plane is nonexistent, a significant in-plane elastic anisotropy in $ac$ plane is revealed in Figs. 3(c) and (d). This is consistent with the hexagonal symmetry of $ab$ plane where Re–Re and N–N bonds exist in ‘graphite-like’ layers alternatively stacked in the $c$-direction. The bulk modulus in the $c$-direction ($B_{[0001]}$) is significantly higher than in other two directions ($B_{[\bar{2}2\bar{T}0]}$ and $B_{[T2\bar{T}0]}$), which is in agreement with the calculated elastic constants in Table 1. In order to get a better understanding of the origin of the changes in elastic modulus along different directions, the orientation dependence of elastic modulus is calculated when the tensile axis is within specific planes, as shown in Fig. 4(a). For elastic modulus in the (0001) plane, let $\theta$ to be the angle between tensile stress and [10T0]. From Eq. (5), it obtains $E^{-1} = s_{11}^{-1}$. This indicates that elastic modulus on the basal plane is independent of tensile stress direction, which is a result of the isotropy of elasticity in the basal plane for hexagonal crystal. These results are also in agreement with the results shown in Fig. 3(d). For the orientation dependence of elastic modulus from [0001] ($\theta=0^\circ$) to [10T0] ($\theta=90^\circ$) on the prismatic plane (10T0), the Re$_2$N possess a maximum of $E_{[0001]}$ and a minimum of $E_{[T2\bar{T}0]}$. For the pyramidal plane (1012) in Fig. 4(a), it displays the variation of elastic modulus with $E_{\text{max}}$ along $[T2\bar{T}0]$. 

Fig. 2 Pressure dependences of $C_{ij}$ for Re$_2$N

Fig. 3 Illustrations of directional dependence of bulk modulus (a) and elastic modulus (b) for Re$_2$N, projections in different planes of directional dependent bulk modulus (c) and elastic modulus (d) for Re$_2$N
directions and $E_{\text{min}}$ along $[10\bar{1}0]$ directions. For the pyramidal ($\bar{1}2\bar{1}2$) plane elastic moduli $E$ behave again very similar for the directions between $[10\bar{1}0]$ and $[\bar{T}2\bar{T}1]$ with a minimum of $E_{[10\bar{1}0]}$ and a maximum of $E_{[\bar{T}2\bar{T}1]}$. Therefore, the ordering of elastic modulus as a function of the principal crystal tensile $[uvw]$ for Re$_2$N is: $E_{[0001]} > E_{[\bar{T}2\bar{T}1]} > E_{[10\bar{1}0]} > E_{[10\bar{1}0]}$.

To understand plastic deformation in Re$_2$N on a fundamental level, the shear moduli on the ($hkl$) shear planes with shear stress applied along $[uvw]$ directions are plotted in Fig. 4(b). Firstly, the shear modulus of Re$_2$N is independent of the shear directions from $[10\bar{1}0]$ to $[\bar{T}2\bar{T}0]$ directions within (0001) basal plane. More importantly, the shear modulus within the (0001) basal plane for Re$_2$N is the smallest, where the corresponding shear deformation involves a shear displacement between pure Re-Re metallic bonding layers in this plane. This result demonstrates that the (0001) plane may be the cleavage plane of Re$_2$N and is also in agreement with the ideal shear strengths calculation performed by ZHANG et al [17]. Secondly, the shear modulus within prismatic shear plane ($10\bar{1}0$) increases with the shear stress direction rotating from [0001] to $[\bar{T}2\bar{T}0]$ directions, while on the contrary it decreases with the shear stress direction rotating from $[10\bar{1}0]$ to $[\bar{T}2\bar{T}1]$ directions within pyramidal plane ($\bar{1}2\bar{1}2$). Thirdly, the shear modulus of Re$_2$N remains nearly invariant within pyramidal plane ($\bar{1}0\bar{1}2$) with the shear stress direction rotating from $[\bar{T}2\bar{T}0]$ to $[10\bar{1}0]$ directions. This suggests that the shape change in the ($\bar{1}0\bar{1}2$) plane with any shear stress directions is very small.

### 3.3 Thermodynamic properties of Re$_2$N

The investigation on the thermodynamic properties of solid at high pressure and high temperature is an interesting topic in the condensed matter physics. Compared to PtN$_2$ [34], PtN [35] and Re$_3$N [31], there are very limited theoretical works on the thermodynamic properties for Re$_2$N at high pressure and high temperature. The thermal properties of Re$_2$N are determined in the temperature range from 0 to 1600 K, where the quasi-harmonic model remains fully valid. The pressure effect is investigated in the range of 0 to 50 GPa. In the quasi-harmonic Debye model, the Debye temperature $\Theta$ and the Grüneisen parameter $\gamma$ are two key quantities. The Debye temperature closely relates to many physical properties of solids, such as specific heat, dynamic properties, and melting temperature. The Grüneisen parameter describes the anharmonic effects in the vibrating lattice, and it has been widely used to characterize and extrapolate the thermodynamic behavior of a material at high pressure and high temperature. The Debye temperature and the Grüneisen parameter at various temperatures (0, 300, 600, 900 and 1500 K) and different pressures (0, 10, 20, 30, 40 and 50 GPa) are listed in Table 2. It should be noted that our calculated Debye temperature at $T=0$ K and $P=0$ GPa is 462.6 J/(mol·K$^{-1}$) which is close to 474.8 J/(mol·K$^{-1}$) calculated by elastic constants, confirming the validity of quasi-harmonic model applied here. From Table 2, it can be found that when the applied pressure changes from 0 to 50 GPa, the Debye temperature increases by 19.6%, 24.2%, 25.1%, 26.1%, and 28.2%, and the Grüneisen parameter decreases by 14.2%, 14.5%, 15.1%, 15.6%, and 16.9% at temperatures of 0, 300, 600, 900, and 1500 K, respectively. It indicates that, when the temperature is kept constant, the Grüneisen parameter decreases with increasing applied pressure, in virtue of the fact that the effect of increasing pressure on the material is the same as decreasing temperature of the material. On the other hand, the Debye temperature decreases almost linearly with temperature at certain pressure.

Heat capacity belongs to one of the most important thermodynamic properties of solids. It is intimately related to the temperature dependence of fundamental thermodynamic functions, and it is of key importance for
Table 2 Calculated Debye temperature $\Theta$ (in K) and Grüneisen parameter $\gamma$ of Re$_2$N at different pressures and different temperatures

<table>
<thead>
<tr>
<th>T/K</th>
<th>Parameter</th>
<th>$p$/GPa</th>
<th>$T$/K</th>
<th>$\Theta$ (K)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$\Theta$</td>
<td>0</td>
<td>10</td>
<td>462.6</td>
<td>2.227</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>0</td>
<td>20</td>
<td>484.8</td>
<td>2.138</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>511.8</td>
<td>2.066</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>533.3</td>
<td>2.006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>553.4</td>
<td>1.955</td>
</tr>
<tr>
<td>300</td>
<td>$\Theta$</td>
<td>0</td>
<td>10</td>
<td>459.1</td>
<td>2.241</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>0</td>
<td>20</td>
<td>485.4</td>
<td>2.148</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>509.2</td>
<td>2.073</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>531.0</td>
<td>2.012</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>551.3</td>
<td>1.960</td>
</tr>
<tr>
<td>600</td>
<td>$\Theta$</td>
<td>0</td>
<td>10</td>
<td>452.9</td>
<td>2.265</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>0</td>
<td>20</td>
<td>479.9</td>
<td>2.166</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>504.3</td>
<td>2.088</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>526.6</td>
<td>2.024</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>547.2</td>
<td>1.970</td>
</tr>
<tr>
<td>900</td>
<td>$\Theta$</td>
<td>0</td>
<td>10</td>
<td>446.1</td>
<td>2.292</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>0</td>
<td>20</td>
<td>474.0</td>
<td>2.187</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>499.0</td>
<td>2.104</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>521.8</td>
<td>2.037</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>542.8</td>
<td>1.981</td>
</tr>
<tr>
<td>1500</td>
<td>$\Theta$</td>
<td>0</td>
<td>10</td>
<td>431.5</td>
<td>2.353</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>0</td>
<td>20</td>
<td>461.3</td>
<td>2.232</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>487.8</td>
<td>2.140</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>511.7</td>
<td>2.066</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>533.6</td>
<td>2.005</td>
</tr>
</tbody>
</table>

linking thermodynamics with microscopic structure and dynamics. The calculated heat capacity at constant pressure $C_p$ and heat capacity at constant volume $C_V$ with the temperature and pressure are shown in Fig. 5. The difference between $C_p$ and $C_V$ is very small at low temperatures ($T<$300 K). However, at high temperatures, the $C_V$ approaches a constant value, while $C_p$ increases monotonously with increments of the temperature. It is also interesting to note that the values of $C_V$ follow the Debye model at low temperature due to the anharmonic approximations. However, the anharmonic effect on $C_V$ is suppressed and the $C_V$ is close to a constant at sufficient high temperatures, obeying Dulong and Petit’s rule. In a word, it can be seen that the heat capacity increases with the temperature at the same pressure and decreases with the pressure at the same temperature. The effects of the temperature on the heat capacity are much more significant than that of the pressure on it. The thermal expansion coefficient $\alpha$ dependendent on temperature and pressure is also shown in Fig. 6. Figure 6 shows that the thermal expansion coefficient $\alpha$ increases quickly with the temperature at $T<$ 300 K under different pressures. As pressure increases, the thermal expansion coefficient decreases rapidly and the effects of temperature become less and less pronounced, resulting in linear high-temperature behavior. At constant temperature, for instance $T=600$ K, it changes linearly with pressure following a gently decreasing trend.

4 Conclusions

1) The calculated lattice parameters by GGA method are in excellent agreement with the experimental data and previous theoretical values for Re$_2$N. The incompressibility of Re$_2$N along the $c$-axis is larger than that along the $a$-axis under high pressure.

2) The Re$_2$N is found to be mechanically stable up to 50 GPa and the elastic constants $C_{11}$ and $C_{33}$ vary rapidly under the effect of pressure in comparison with the variations in $C_{12}$, $C_{13}$ and $C_{44}$.

3) The tensile directional dependences of the elastic modulus $E$ have been investigated for the first time, and the results show $E_{[0001]} > E_{[\bar{1}2\bar{1}0]} > E_{[10\bar{1}0]} > E_{[1\bar{1}0\bar{1}]}$ for these principal crystal directions. The shear modulus of Re$_2$N within the (0001) basal plane is the smallest, where
the corresponding shear deformation involves a shear displacement between pure Re layers in this plane.

4) Using quasi-harmonic Debye model, the thermodynamic properties including the Debye temperature, Grüneisen parameter, heat capacity, and thermal expansion coefficient of Re2N are predicted under high pressure and high temperature.

References


高压高温下 Re$_2$N 的弹性和热力学性能

张美光 1, 闫海燕 2, 魏 群 3, 黄多辉 4

1. 宝鸡文理学院 物理与信息技术系, 宝鸡 721016;
2. 宝鸡文理学院 化学化工学院, 宝鸡 721013;
3. 西安电子科技大学 物理与光电工程学院, 西安 710071;
4. 宜宾学院 四川省计算物理重点实验室, 宜宾 644007

摘 要: 采用基于密度泛函理论的第一性原理计算方法, 系统研究高压高温下 Re$_2$N 的晶体参数、力学性能和热力学性能。结果表明: 在高压下 Re$_2$N 具有明显的弹性各向异性, 与弹性常数 $C_{12}$、$C_{13}$、$C_{44}$ 相比, $C_{11}$ 和 $C_{33}$ 的变化随着压力的变化非常明显。此外, 首次计算 Re$_2$N 的体弹模量 $B$、弹性模量 $E$ 和剪切模量 $G$ 沿不同晶轴的分布。弹性模量在一些主要晶轴方向上的大小分布趋势如下: $E_{[0001]} > E_{[1211]} > E_{[1010]} > E_{[1011]}$。计算结果还表明: 在(0001)晶面, Re$_2$N 的抗剪切能力是最低的, 从而极大地减小对大剪切变形的阻力。基于准简谐德拜模型, 在 0~50 GPa 压力和 0~1600 K 温度下得到德拜温度、格林艾森参数、热传导以及热扩散系数的变化行为。

关键词: Re$_2$N; 过渡金属氮化物; 弹性性能; 热力学性能

(Edited by Chao WANG)