Theoretical Calculations for Elastic and Thermodynamic Properties of NbN$_2$ under High Pressure

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(Received March 31, 2017; in final form July 29, 2017)

The structural and elastic properties of NbN$_2$ at high pressures were investigated through the first-principles calculation. Results indicate that NbN$_2$ is a potential hard material. NbN$_2$ meets mechanical stability criteria and possesses ductility within the pressure of 100 GPa. The elastic anisotropy under high pressure was achieved by the elastic anisotropy factors, which reduce with increasing pressure. Using the quasi-harmonic Debye model, we also investigated the thermodynamic properties of NbN$_2$.

1. Introduction

The transition metal nitrides (TMNs) become more and more important in various industrial applications owing to their outstanding and unique physical properties, such as chemical and thermal stabilities, high hardness and strength, high melting point, good thermal and electronic conductivity, and superconductivity [1–3]. Some noble metal nitrides with orthorhombic marcasite-type structure (space group of $Pnam$, No. 58) such as PtN$_2$ [4, 5], IrN$_2$ [5, 6], OsN$_2$ [6] and PdN$_2$ [7] with moderate synthesis conditions and very large bulk modulus (close to 400 GPa) are expected to be alternative materials to traditional superhard materials that are of synthesis expensive [8]. Among these, IrN$_2$ is the least compressible compound, with the highest bulk modulus (428 GPa) [6].

For Nb–N system, cubic $\delta$-NbN superconducting phase possesses high bulk modulus (348 GPa) and Vickers hardness (20 GPa) closing to sapphire [9]. Jiang et al. [10] first proposed that U$_2$S$_3$ type Nb$_2$N$_3$ may be stable at wide pressures, and is a potential candidate for hard material. Recently, the phase diagram and mechanical properties of Nb–N system were analyzed by Zhao et al. [11]. They successfully predicted high pressure phases NbN$_2$ with orthorhombic structure (space group of $Cmca$, No. 64), which is thermodynamically stable up to 100 GPa, and meet mechanical and dynamical stability at ambient condition. The elastic constants, elastic modulus and density of states of NbN$_2$ have already been studied at ambient pressure. So far, however, the elastic constants, elastic anisotropy and especially thermodynamic properties of NbN$_2$ at high pressure have not been investigated, which is significant for their synthesis and practical applications [12]. Based on the above reasons, in this article, we focus on the detailed investigation on these fundamental properties of NbN$_2$ at various pressures and temperatures, including elastic constants, elastic anisotropy, and thermodynamic properties. We expect that our calculations can have guidable significances to accelerate the synthesis of NbN$_2$.

2. Computational method

In this paper, all first-principles calculations were performed with the CASTEP code [13]. Non-local ultrasoft pseudopotential (USPP) introduced by Vanderbilt [14] or norm-conserving pseudopotential (NCPP) presented by Hamann et al. [15] were employed for all ion–electron interactions. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [16] and the local density approximation (LDA) proposed by Vosko et al. [17] were used to describe the exchange and correlation potentials. Pseudo-atomic calculations are performed for Nb: 4s$^2$4p$^6$4d$^{4}5s^1$ and N: 2s$^2$2p$^3$. The plane-wave basis set with energy cut-off of 550 eV, and $2 \times 6 \times 6$ Monkhorst–Pack grid for Brillouin zone sampling is used throughout. The structural optimizations were conducted using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization [18]. We found successfully the lowest energy structure, and the threshold of $5.0 \times 10^{-6}$ eV/atom is used to determine whether the self-consistent progress has been converged.

Single crystal elastic constants were calculated via a strain–stress approach, i.e., by applying a small strain to the equilibrium lattice of orthorhombic unit cell and fitting the dependence of the resulting change in stress on the strain [12]. The elastic constants of c-W$_3$N$_4$ [19], TaN [20] and RuN$_2$ [21] were successfully obtained by using this method. This method is made as follows by a brief description.

In the elastic range, the orthorhombic crystal owns nine independent elastic coefficients $C_{11}$, $C_{22}$, $C_{33}$, $C_{44}$, $C_{66}$, $C_{12}$, $C_{13}$, $C_{23}$, and $C_{44}$. The elastic constants were calculated by fitting the dependence of the resulting change in stress on the strain [12].
$C_{55}, C_{66}, C_{12}, C_{13}, C_{23}$ because of the symmetry of the crystal. Elastic modulus values and the Poisson ratio can be obtained directly within these elastic constants based on the Voigt–Reuss–Hill method (VRH) [22], in which the Voigt and Reuss approximation is the theoretical maximum and minimum values. For the orthorhombic structure of NbN$_2$, the formulae as follows [23]:

$$B_V = \frac{[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})]}{9},$$

$$G_V = \frac{[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66})]}{9},$$

$$B_R = \Delta / [C_{11}(C_{22} + C_{33} - 2C_{23}) + C_{22}(C_{33} - 2C_{13}) - 2C_{33}C_{12} + C_{12}(2C_{23} - C_{13}) + C_{13}(2C_{12} - C_{13}) + C_{23}(C_{13} - C_{23})],$$

$$G_R = \frac{15}{4} \left( \frac{1}{[C_{11}(C_{22} + C_{33} + C_{21}) + 2C_{22}(C_{33} + C_{13}) + C_{33}C_{12} - C_{12}(C_{23} + C_{13}) - C_{13}(C_{12} + C_{13}) - C_{23}(C_{13} - C_{23})]} \right),$$

where

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

The Hill approximation represents the arithmetic mean values of the Voigt and Reuss approximation. The formulae as follows [22]:

$$B_H = \frac{1}{2}(B_V + B_R),$$

$$G_H = \frac{1}{2}(G_V + G_R).$$

Once $B$ and $G$ are determined, the Young modulus $E$ and the Poisson ratio $v$ by the following formulae:

$$E = \frac{9B_H G_H}{3B_H + G_H},$$

$$v = \frac{3B_H - 2G_H}{2(3B_H + G_H)}.$$

To investigate the thermodynamic properties, we here apply the quasi-harmonic Debye model [24]. In this model, the non-equilibrium Gibbs function $G^*(V; P, T)$ is as the following form:

$$G^*(V; P, T) = E(V) + PV + A_{\text{vib}}(\Theta_D(V); T)\quad(7)$$

in which $E(V)$ is the total energy per unit cell for NbN$_2$; $\Theta_D(V)$ is the Debye temperature; vibrational Helmholtz free energy $A_{\text{vib}}$ can be written as [25–27]:

$$A_{\text{vib}}(\Theta_D; T) = n k_B T \left( \frac{9}{8} \frac{\Theta_D}{T} + 3 \ln(1 - e^{-\Theta_D/T}) - D(\Theta_D/T) \right),$$

where $D(\Theta_D/T)$ represents the Debye integral, $n$ is the number of atoms per formula unit and $k_B$ is Boltzmann constant. Then the non-equilibrium Gibbs function $G^*(V; P, T)$, as a function of $(V; P, T)$, can be mini-

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

We could obtain the thermal equation of state (EOS) by solving Eq. (9). Thus the isothermal bulk modulus $B_T$, the heat capacity $C_V$ and the thermal expansion coefficient $\alpha$ are given by [28]:

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

$$C_V = 3n k_B \left( 4D(\Theta_D/T) - \frac{3\Theta_D/T}{e^{\Theta_D/T} - 1} \right),$$

$$\alpha = \frac{\gamma C_V}{B_T V},$$

$$\gamma = -\frac{\text{d} \ln \Theta_D(V)}{\text{d} \ln V},$$

where $\gamma$ is the Grüneisen parameter.

### 3. Results and discussion

#### 3.1. Equilibrium structure and elastic properties

Equilibrium lattice parameters, equilibrium volume and N–N bond length calculated by USPP GGA-PBE, GGA-PW91, LDA-CAPZ, NCPP GGA-PBE, together with the other calculated results of NbN$_2$, RuN$_2$, IrN$_2$ and Nb$_2$N$_3$ for comparison are listed in Table I. By USPP GGA-PBE the calculated lattice parameters $a$ (12.333 Å), $b$ (4.202 Å), $c$ (4.120 Å) and equilibrium volume $V$ (27.208 Å$^3$) for NbN$_2$ are in accordance with the theoretical data [11], and the differences between them are within about 1.31%, 0.51%, 0.52% and 2.32% for $a$, $b$, $c$ axes and volume $V$, respectively. Good agreement between our computation results and other theoretical data provides a good support to investigate the elastic, anisotropy, and thermodynamic properties of NbN$_2$ under high pressures.

|       | $a$   | $b$   | $c$   | $V$   | $d_N-N$ |
|-------|-------|-------|-------|-------|---------|
| NbN$_2$ | 12.333 | 4.202 | 4.120 | 27.208 | 1.366   |
| $^{b}$ | 12.291 | 4.213 | 4.209 | 27.243 | 1.374   |
| $^{c}$ | 12.075 | 4.152 | 4.151 | 26.010 | 1.367   |
| $^{d}$ | 12.565 | 4.270 | 4.263 | 28.585 | 1.348   |
| $^{e}$ | 12.406 | 4.224 | 4.222 | 27.854 | 1.325   |
| RuN$_2$ | 4.098 | 4.919 | 2.696 | 54.344 | 1.379$^g$ |
| $^{f}$ | 4.103 | 4.925 | 2.773 | 28.0   | 1.375   |
| IrN$_2$ | 8.20  | 8.31  | 3.02  | 1.32   |
| $^{g}$ | 8.20  | 8.31  | 3.02  | 1.32   |

$^a$ Ref. [11], PAW within GGA-PBE; $^b$ Ref. [21], USPP within GGA-PBE; $^c$ Ref. [29], USPP within GGA-PBE; $^{d}$ Ref. [23], GGA; $^{e}$ Ref. [10], PAW within GGA-PBE.

NbN$_2$ has not been synthesized in the laboratory, therefore, we list the elastic constants of several other transition metal nitrides hard materials RuN$_2$, IrN$_2$ and Nb$_2$N$_3$ for comparison in Table II.
Elastic coefficients $C_{ij}$ [GPa], bulk modulus $B$ [GPa], shear modulus $G$ [GPa], the Young modulus $E$ [GPa], $B/G$, the Poisson ratio $\nu$, and Vickers hardness $H_v$ of NbN$_2$ from 0 to 100 GPa (USPP GGA-PBE\textsuperscript{a}, GGA-PW91\textsuperscript{b}, LDA-CAPZ\textsuperscript{c}; NCPP GGA-PBE\textsuperscript{d} at 0 GPa).

|       | $P$ | $C_{11}$ | $C_{22}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | $C_{23}$ | $B$  | $E$  | $B/G$ | $\nu$ | $H_v$ |
|-------|-----|---------|---------|---------|---------|---------|---------|---------|---------|---------|-----|-----|-------|------|------|
| NbN$_2$ | 0  | 635     | 609     | 621     | 308     | 57      | 74      | 117     | 94      | 241     | 307 | 149 | 385   | 2.057 | 0.291 | 22.36 |
|       | 100|         |         |         |         |         |         |         |         |         |     |     |       |      |      |       |
| RuN$_2$ | 0  | 642     | 783     | 524     | 113     | 283     | 152     | 160     | 216     | 45      | 306 | 196 | 484   | 1.562 | 0.236 | 13.66 |
| IrN$_2$ | 0  | 739     | 883     | 554     | 124     | 297     | 190     | 156     | 277     | 82      | 345 | 217 | 538   | 0.240 | 17.92 |       |
| Nb$_2$N$_3$ | 0  | 426     | 549     | 582     | 152     | 169     | 96      | 237     | 188     | 168     | 303 | 143 | 370   | 0.297 |       |       |

$^a$Ref. [11], PAW within GGA-PBE, $^b$Ref. [21], USPP within GGA-PBE, $^c$Ref. [29], USPP within GGA-PBE, $^d$Ref. [23], GGA, $^e$Ref. [10], PAW within GGA-PBE.

The LDA method to some extent overestimates the elastic constants [30]. It can be seen from the table that the LDA-calculated elastic coefficients are significantly larger than the other theoretical value. Correspondingly, the shear modulus $G$ is also distinct greater than the other theoretical value. On the other hand, the results of GGA-PBE and GGA-PW91 are in good agreement with the values in Ref. [11]. As is known to all, the requirement of mechanical stability in an orthorhombic crystal leads to the following restrictions on the elastic constants [21]:

$$C_{11} > 0, \quad C_{22} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{55} > 0, \quad C_{66} > 0, \quad C_{11} + C_{22} - 2C_{12} > 0,$$

$$C_{11} + C_{33} - 2C_{13} > 0, \quad C_{22} + C_{33} - 2C_{23} > 0.$$

$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0.$  (14)

The elastic constants $C_{ij}$ of NbN$_2$ as a function of pressure are plotted in Fig. 1. In the range of less than 100 GPa, all elastic coefficients $C_{ij}$ are in line with the stability criteria, which indicates that NbN$_2$ is mechanically stable under high pressure. Then all elastic coefficients increase linearly with the increase of pressure. Moreover, $C_{11}$, $C_{22}$, $C_{33}$ reflect the bond strength in the (001), (010), (100) direction. In Fig. 1, the elastic constants $C_{11}$, $C_{22}$, $C_{33}$ are distinctly larger than others and tend to be almost equal at high pressure.

Furthermore, it is also found that elastic constants of NbN$_2$ are almost comparable with them of RuN$_2$, IrN$_2$, and Nb$_2$N$_3$ i.e., elastic properties of NbN$_2$ is comparable to other potential (super)hard materials, which indicate that NbN$_2$ is a potential incompressible and hard material. In general, the shear modulus is a better indicator of hardness in the design of novel hard/superhard materials, which indicate that NbN$_2$ is a potential incompressible and hard material. In general, the shear modulus is a better indicator of hardness in the design of novel hard/superhard materials, which indicate that NbN$_2$ is a potential incompressible and hard material. In general, the shear modulus is a better indicator of hardness in the design of novel hard/superhard materials, which indicate that NbN$_2$ is a potential incompressible and hard material.

**Fig. 1.** Pressure dependence of the elastic coefficients ($C_{ij}$) of NbN$_2$.  

TABLE II
pressure. The calculated elastic moduli, especially shear moduli (149 GPa) of NbN₂ are comparable to those of RuN₂ (196 GPa), IrN₂ (217 GPa) and Nb₂N₃ (143 GPa). Further to check our conjecture, the hardness calculation seems to be of interest and necessary. The intrinsic hardness of NbN₂ compounds were calculated by the formula of Gao [33]. The intrinsic hardness of ReN₂, WN₂ [34], PtN₂ [35] and IrN₂, RuN₂ [29] were successfully obtained by applying this method. The calculated hardness values of orthorhombic NbN₂ are 22.36 GPa, which is larger that of RuN₂ (13.66 GPa) and IrN₂ (17.92 GPa). The fact further suggests NbN₂ is a candidate for hard material.

\( B/G \) and the Poisson ratio \( \nu \), listed in Table II are used to judge ductility of materials. According to the Pugh criterion [36] if \( B/G > 1.75 \), the material behaves in a ductile manner otherwise, the material behaves in a brittle manner. It can be clearly seen in Table II that the NbN₂ is strongly prone to ductile under high pressure, which is consistent with the result judged by the Poisson ratio \( \nu \) that can be judged of ductility and brittleness, for a brittle material \( \nu < 0.26 \), while for a ductile material \( \nu > 0.26 \) [37].

As a fundamental parameter of a solid, the Debye temperature \( \Theta_D \) correlates with many physical properties of solid materials, such as vibrational internal energy and temperature \( \Theta \).

\[
\Theta_D = \frac{h}{k_B} \left( \frac{3n N A \rho}{4 \pi M} \right)^{\frac{1}{3}} \nu_m,
\]

which gives explicit information about the lattice vibrations [39]. The calculated shear wave velocity, longitudinal wave velocity, average sound velocity and the Debye temperature of NbN₂ compounds at zero, high pressure and zero temperature are presented in Table III, presenting a trend of increase with pressure. The calculated Debye temperature of NbN₂ at 0 K and 0 GPa is 715 GPa, which is larger than that of Nb₂N₃ (666 K) [10].

### TABLE III

| \( P \) | \( \rho \) | \( \nu_l \) | \( \nu_t \) | \( \nu_m \) | \( \Theta_D \) |
|---|---|---|---|---|---|
| 0 | 7.38 | 8277 | 4495 | 5015 | 715.77 |
| 10 | 7.60 | 8793 | 4817 | 5370 | 774.18 |
| 20 | 7.81 | 9231 | 5071 | 5653 | 822.13 |
| 30 | 8.00 | 9603 | 5277 | 5882 | 862.21 |
| 40 | 8.17 | 9927 | 5449 | 6074 | 896.85 |
| 50 | 8.33 | 10221 | 5617 | 6261 | 930.57 |
| 60 | 8.49 | 10467 | 5732 | 6391 | 955.85 |
| 70 | 8.64 | 10698 | 5836 | 6509 | 979.06 |
| 80 | 8.78 | 10911 | 5932 | 6618 | 1000.88 |
| 90 | 8.92 | 11111 | 6022 | 6719 | 1021.39 |
| 100 | 9.05 | 11304 | 6108 | 6817 | 1041.23 |

#### 3.2. Elastic anisotropy

Elastic anisotropy analysis is of great significance in understanding the mechanisms of materials micro-cracks, phase transformations, elastic instability and durability [40]. Hence, a proper description of such an anisotropic behavior is important in engineering science as well as in crystal physics. The universal elastic anisotropy index \( A^U \), the shear anisotropy factors \( (A_G, A_1, A_2, A_3) \) and the bulk modulus anisotropy factors \( B_a, B_b, B_c \) are appropriate measures to quantify the extent of anisotropy [41].

Firstly, the universal elastic anisotropy index \( A^U \), which can provide theoretical basis for the degree of anisotropy, is defined by Ranganathan and Ostoja-Starzewski from the bulk modulus \( B \) and shear modulus \( G \) by Voight and Reuss approaches [41], as

\[
A^U = \frac{5G_V}{G_R} + \frac{B_V}{B_R} - 6.
\]

Secondly, the percent shear and compressibility modulus factors in polycrystalline materials which can be defined as [42]:

\[
A_G = \frac{G_V - G_R}{G_V + G_R}, \quad A_B = \frac{B_V - B_R}{B_V + B_R}
\]

In addition, for orthorhombic crystals, the shear anisotropic factor for the \( (010) \) shear planes between the \( (011) \) and \( (001) \) directions is [41]:

\[
A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}},
\]

for the \( (010) \) shear planes between \( (101) \) and \( (001) \) directions is

\[
A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}},
\]

for the \( (001) \) shear planes between \( (110) \) and \( (010) \) directions is

\[
A_3 = \frac{4C_{66}}{C_{11} + C_{22} + C_{33}}.
\]

Meanwhile, the directional bulk modulus along different crystallographic axis can be defined as [42]:

\[
B_i = \left( \frac{dP}{dx} \right) (i = a, b, \text{and } c).
\]

The anisotropy of the bulk modulus along the a-axis and c-axis with respect to b-axis can be defined by:

\[
A_{B_a} = \frac{B_a}{B_b}, \quad A_{B_c} = \frac{B_c}{B_b}.
\]

Based on the formulae mentioned above, the calculated values of \( A^U, A_G \), and \( A_B \) are plotted in Fig. 2. For these three expressions, a value of zero represents elastic isotropy and a value of 1 (100%) is largest possible anisotropy. At 0 GPa, \( A^U = 2.852 \), it indicates that NbN₂ is anisotropic materials. In general, \( A^U, A_G \) and \( A_B \) decreases with increase of pressure and that is to say extent of anisotropy of NbN₂ will be decreased with increase of pressure. \( A_B \) is almost equal to 0 at high pressure which suggests NbN₂ is slightly isotropic in compressibility. Namely, bulk modulus anisotropy is evidently smaller than that of shear modulus anisotropy.

The values of \( A_1, A_2, A_3 \) and \( A_{B_a}, A_{B_c} \) equal to 1.0 mean that the crystal is isotropic and the degree of the
elastic anisotropy can be reflected by the deviation from one. Then these parameters are plotted as a function of pressure in Fig. 3a. When pressure is increased from 0 to 100 GPa, the shear anisotropy factors $A_1$ decrease by 17.2% and $A_2$, $A_3$ increase by 79.3% and 59.5%, respectively. This change is mainly caused by the change of the elastic constants, especially for $A_1$ the $C_{44}$ only increases by 17.2%, but for $A_2$ the $C_{55}$ and $A_3$ the $C_{66}$ increase by 284% and 197%, respectively. The anisotropy of the linear bulk modulus $A_{Bb}$ and $A_{Bc}$ increases by 13.3% and 3.9%, respectively. Meanwhile, in Fig. 3b, it is interesting to note that the directional bulk modulus $B_b$ along the $b$ axis is largest when compared to the $B_a$ and $B_c$ at 0 GPa, and $B_c$ is close to $B_b$ along with pressure increase.

To characterize the degree of anisotropy of the Young modulus, drawing a three-dimensional (3D) graph for NbN$_2$ compounds is necessary. The three-dimensional formulas for the Young modulus $E$ in the orthorhombic system [42] are expressed as follows:

$$E^{-1} = s_{11}l_1^4 + s_{22}l_2^4 + s_{33}l_3^4 + 2s_{12}l_1^2l_2^2 + 2s_{23}l_2^2l_3^2 + 2s_{13}l_1^2l_3^2 + s_{44}l_2^4 + s_{55}l_1^4 + s_{66}l_3^4,$$

(23)

where $s_{ij}$ is the usual elastic compliance constants and $l_i$ is the direction cosines in any arbitrary direction. The 3D graph of the Young modulus at three pressures is shown in Fig. 4. From Fig. 4, the Young modulus anisotropy of NbN$_2$ is described in detail and the degree of anisotropy will decrease when pressure increases. At 50, 100 GPa, the values of the Young modulus in $\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$ direction is almost equal and greater than that of other direction. Because a larger Young modulus often stands for more covalent feature of a material [43, 44], the facts indicate that the strength of chemical bonds in...
(100), (010) and (001) direction is stronger than other directions at high pressure, which is consistent with the results of analysis of elastic constants. Furthermore, the direction dependence of $E$ in (001) plane and in (110) plane at 0, 50, and 100 GPa also are shown in Fig. 5.

### 3.3. Thermodynamic properties

We calculated energy–volume points at 0 K and 0 GPa by compressive and tensile lattice constants under the same proportion. Then, thermodynamic quantities of NbN$_2$ at different temperatures (0, 500, 1000, 1500, 2000, and 2500 K) and pressures were obtained through the quasi-harmonic Debye model.

As one of the most important thermodynamic parameters, the special heat capacity $C_V$ of a substance not only provides essential information about its vibrational properties but also is fundamental to many applications [45]. The heat capacity $C_V$ of NbN$_2$ at different temperatures and pressure are presented in Fig. 6. It shows the heat capacity $C_V$ increases with the increase of temperature, while decreases as pressure increases. At low temperature ($\approx$ 500 K), the heat capacity $C_V$ is dependent on both temperature and pressure, which is owing to the anharmonic approximations of the Debye model [24]. At high temperatures, $C_V$ of all solid will nearly approach to the Dulong–Petit limit $3nN_Ak_B$ ($n$ represents the numbers of atoms in the molecule). As temperature increases, the heat capacity $C_V$ is close to the Dulong–Petit limit $3nN_Ak_B$ ($\approx$ 299.32 J mol$^{-1}$ K$^{-1}$), where $n = 12$ for NbN$_2$ in unit cell.

![Fig. 6.](image)

The heat capacity $C_V$ of NbN$_2$ as functions of temperature and pressure.

| $T$ [K] | $\Theta_D$ [K] | $\Theta_D$ [K] | $\Theta_D$ [K] | $\Theta_D$ [K] | $\Theta_D$ [K] | $\Theta_D$ [K] |
|---------|----------------|----------------|----------------|----------------|----------------|----------------|
| $P$ [GPa] | 0.0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
| 0 | 802 | 851 | 896 | 937 | 975 | 1011 | 1045 | 1077 | 1108 | 1137 | 1165 |
| 200 | 779 | 69.3 | 62.3 | 56.6 | 51.9 | 47.8 | 44.3 | 41.3 | 38.6 | 36.2 | 34.1 |
| 500 | 712 | 280.2 | 264.0 | 250.1 | 238.2 | 227.8 | 218.6 | 210.2 | 202.8 | 195.9 | 189.7 | 183.9 |
| 1500 | 681 | 740 | 795 | 845 | 891 | 933 | 972 | 1009 | 1043 | 1076 | 1107 | 1136 |
| 2500 | 788.7 | 762.2 | 741.0 | 723.1 | 707.5 | 694.0 | 682.0 | 671.1 | 661.1 | 652.1 | 643.6 |

| $\gamma$ | 2.044 | 1.985 | 1.936 | 1.893 | 1.854 | 1.819 | 1.786 | 1.756 | 1.728 | 1.702 | 1.677 |
| $\gamma$ | 2.043 | 1.986 | 1.937 | 1.894 | 1.855 | 1.818 | 1.787 | 1.757 | 1.729 | 1.703 | 1.675 |
| $\gamma$ | 2.056 | 1.997 | 1.946 | 1.902 | 1.862 | 1.826 | 1.793 | 1.762 | 1.733 | 1.707 | 1.687 |

The Debye temperature $\Theta_D$, entropy $S$ and Grüneisen parameter $\gamma$ of NbN$_2$ at different temperatures.

Thermal expansion coefficient $\alpha$ as functions of pressure (temperature) are shown in Fig. 7. In Fig. 7a, it is noted that the $\alpha$ increases quickly with temperature at low pressure and temperatures and the trend of increase will become slow at high temperatures. Specifically, temperature increases from 0 to 600 K at 20 GPa, $\alpha$ increases from 0 to 2.14 $\times$ 10$^{-5}$ K$^{-1}$. But $\alpha$ only increases 0.78 $\times$ 10$^{-5}$ K$^{-1}$ when temperature rises from 600 K to 2500 K. It is clearly seen that the curves at high temperature is very close in Fig. 7b. Additionally, the Debye temperature $\Theta_D$, entropy $S$ and Grüneisen parameter $\gamma$ of NbN$_2$ along with the change of pressure and temperature were also calculated, which were listed in Table IV. It is obvious that $\Theta_D$ rises with the increase of pressure and reduces with increase of temperature conversely. Meanwhile, pressure has a more evident influence on $\Theta_D$ than temperature.
temperature \( \Theta \) and pressure, dependences of Debye temperature and pressure have also been analyzed. Through the quasi-harmonic Debye model, special heat capacity \( C_V \) and thermal expansion \( \alpha \) as functions of pressure and temperature, dependences of Debye temperature \( \Theta_D \), entropy \( S \) and Grüneisen parameter \( \gamma \) on pressure and temperature have also been analyzed.

Acknowledgments

This work is supported by the international cooperation projects Foundation of SiChuan Provincial Science and Technology Department (Grant No. 2014HH0014) and the Scientific Research Fund of SiChuan Provincial Education Department (Grant No. 15ZA0033), and the Project funded by China Postdoctoral Science Foundation (Grant No. 2016M602666).

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