

# First-principles investigations of structural and electronic properties of niobium nitrides under pressures

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**Abstract.** The ground structure, elastic and electronic properties of several phases of NbN are determined based on *ab initio* total-energy calculations within the framework of density functional theory. Among the five crystallographic structures that have been investigated, the hexagonal phases have been found to be more stable than the cubic ones. The calculated equilibrium structural parameters are in good agreement with the available experimental results. The elastic constants of five structures in NbN are calculated, which are in consistent with the obtained theoretical and experimental data. The corresponding Debye temperature and elastic anisotropies are also obtained. The Debye temperature of NbN in various structures consistent with available experimental and theoretical data, in which the Debye temperature of  $\delta$ -NbN is highest. The anisotropies of ZB-NbN, NaCl-NbN, CsCl-NbN gradually increases. For hexagonal structure, the anisotropies of  $\epsilon$ -NbN are stronger than that of  $\delta$ -NbN. The electronic structures of NbN under pressure are investigated. It is found that NbN have metallization and the hybridizations of atoms in NbN under pressure become stronger.

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**Key words:** phase transition, elastic constants, electronic structure, NbN

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## 1 Introduction

The transition-metal nitrides are refractory compounds and put forward a technologically important series of materials. The compounds have a lot of interesting properties, such as high melting point [1], high hardness [2], superconductivity [3], magnetism [4] and so on. Because of these properties, they become the focus of view of fundamental studies. It is

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found that the superconducting temperature of solid solutions of NbN with rock salt structure reaches a maximum value of 17.8 K [5], which is comparable to that of Nb<sub>3</sub>Sn and V<sub>3</sub>Si [6].

Due to a great deal of attentions on NbN, several research groups have studied the physical properties of NbN theoretically and experimentally. Chen *et al.* [7] conducted the experiments on the high-pressure phonon spectra of transition-metal nitrides HfN, ZrN, and NbN by Raman-scattering measurements. Later using Raman scattering and x-ray diffraction Chen *et al.* [8] reported a quantitative study of pressure effects on the superconducting transition temperature  $T_c$  and the electronic stiffness of NbN, and they found that superconducting temperature  $T_c$  increases initially with pressure and then saturates up to 42 GPa. The equation of states, elastic properties and hardness of TMN (TM=Zr, Nb, Hf) [5] are investigated by angle-dispersive synchrotron powder x-ray diffractometry with a diamond anvil cell. It is found that NbN crystallized cubic structure and also have hexagonal structure experimentally [9]. The electronic structure of hex-NbN and NaCl-NbN are measured by X-ray photoemission spectroscopy and ellipsometric measurements [10]. Theoretically, the phase transition (NaCl→CsCl) and elastic properties of the selected transition metal nitrides are studied by two-body interionic potential theory [11]. The thermophysical properties of transition metal carbides and nitrides with NaCl structure were calculated using the Debye-Grüneisen model combined with *ab initio* calculations [12]. The elastic constants and electronic structure of transition metal nitrides and carbides are calculated using *ab initio* density functional perturbation theory [13]. The electronic structure and bonding mechanism of NbN and NbC are studied by means of the accurate first-principles total energy calculations using the full-potential linearized augmented plane wave method (FP-LAPW) [14]. The elastic constants of NbN (NaCl structure) are investigated under pressure up to 50 GPa within the framework of the density functional theory [5]. The mechanical properties of NbN in NaCl and NiAs structures have been reported by first-principles [15]. Wang *et al.* has calculated the structural phase transition in WC and NaCl structures and the hardness of NbN [16].

However, to our knowledge, the researches of fundamental physical properties of NbN focus on cubic structure, there are few reports on other hexagonal structures theoretically under pressure. In the present paper, we investigate the structure and fundamental physical properties of niobium nitrides for all possible cubic and hexagonal structures by the plane-wave pseudopotential density functional theory method through the Cambridge Serial Total Energy Package (CASTEP) program [17]. In this work, the mechanical properties and electronic structures of the five different structures of NbN are studied: NaCl structure (Fm-3m); CsCl structure (Pm-3m); ZB structure (F4-3m); hexagonal structure ( $\delta$ ) (P63/mmc) and tungsten-carbide-like structure ( $\epsilon$ ) (P-6m2).

## 2 Theoretical method

### 2.1 Total energy calculations

In the electronic structure calculations, the ultrasoft pseudopotentials introduced by Vanderbilt [18] have been employed for all the ion-electron interaction. The generalized gradi-

ent approximation of Perdew Burke Ernzerhof [19] (GGA-PBE) are employed for the influence of exchange-correlation potentials. A plane wave basis set with energy cut-off energy 800.0 eV is used. As for the Brillouin-zone sampling, we use the  $12 \times 12 \times 12$ ,  $12 \times 12 \times 12$ ,  $12 \times 12 \times 12$ ,  $8 \times 8 \times 8$ ,  $8 \times 8 \times 8$  k-points Monkhorst-Pack mesh [20] for the ZB-, NaCl-, CsCl-, hcp( $\delta$ )- and hcp( $\epsilon$ )-NbN, respectively. The self-consistent convergence of the total energy is at  $10^{-7}$  eV/atom.

## 2.2 Elastic properties

For the system with respect to a small strain  $\delta$  of the lattice primitive cell volume  $V$ , elastic constants are determined by a Taylor expansion of the total energy,  $E(V, \delta)$ . The energy of a strained system is expressed as follows [21]

$$E(V, \delta) = E(V_0, 0) + V_0 \left( \sum_i \tau_i \xi_i \delta_i + \frac{1}{2} \sum_{ij} C_{ij} \delta_i \xi_i \delta_j \right), \quad (1)$$

where  $E(V_0, 0)$  is the energy of the unstrained system with equilibrium volume  $V_0$ ,  $\tau_i$  is an element in the stress tensor, and  $\xi_i$  is a factor to take care of Voigt index. It is known, there are three independent components of the elastic tensor for cubic structure NbN, i.e.,  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$  and five independent components for hcp-NbN, i.e.,  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ ,  $C_{44}$ .

The Debye temperature may be estimated from the average sound velocity  $V_m$  [22]

$$\Theta = \frac{\hbar}{k} \left( \frac{3n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right)^{\frac{1}{3}} V_m, \quad (2)$$

where  $\hbar$  is Planck's constants,  $k$  is Boltzmann's constant,  $N_A$  is Avogadro's number,  $n$  is the number of atoms per formula unit,  $M$  is the molecular mass per formula unit,  $\rho$  ( $=M/V$ ) is the density, and  $V_m$  is obtained from [22]

$$V_m = \left( \frac{1}{3} \left( \frac{2}{V_S^3} + \frac{1}{V_L^3} \right) \right)^{-\frac{1}{3}}, \quad (3)$$

where  $V_S$  and  $V_L$  are the shear and longitudinal sound velocities, respectively. They are determined from Navier equation [23, 24]

$$v_s = \sqrt{\frac{(B + \frac{4}{3}G)}{\rho}}, \quad v_L = \sqrt{\frac{G}{\rho}}, \quad (4)$$

where  $B$  and  $G$  represent bulk and shearing modulus, respectively.

For hexagonal structure, the bulk modulus are defined

$$B = \frac{C_{33}(C_{11} + C_{12}) - 2C_{13}^2}{C_{11} + C_{12} - 4C_{13} + 2C_{33}}. \quad (5)$$

For cubic structure, the zero-pressure bulk modulus is

$$B = \frac{1}{3}(C_{11} + 2C_{12}). \quad (6)$$

It is known that the acoustic velocities are obtained from elastic constants by Christoffel equation [25]. For the hexagonal phase, by solving the Christoffel equation, we obtained the anisotropy of compressional wave from

$$\Delta_p = \frac{C_{33}}{C_{11}}. \quad (7)$$

The anisotropies of the wave polarized perpendicular to the basal plane ( $S_1$ ) and the polarized basal plane ( $S_2$ ) are calculated

$$\Delta_{S_1} = \frac{C_{11} + C_{33} - 2C_{13}}{4C_{44}}, \quad \Delta_{S_2} = \frac{2C_{44}}{C_{11} - C_{12}}. \quad (8)$$

For the cubic phase,

$$\Delta_{S_1} = \frac{1}{\Delta_{S_2}} = \frac{C_{11} - C_{12}}{2C_{44}}. \quad (9)$$

### 3 Results and discussion

The equilibrium structural parameters at  $P=0$  and  $T=0$  are listed in Table 1 for ZB-, NaCl-, CsCl-, hcp( $\delta$ )- and hcp( $\epsilon$ )-NbN. The equilibrium lattice parameters, bulk modulus  $B_0$  and its pressure derivative bulk modulus  $B'_0$  are obtained by fitting  $E-V$  data to the Birch-Murnaghan equation of state (Table 1) [26]. The obtained structure parameters, bulk modulus and its pressure derivative bulk modulus  $B'_0$  of NaCl-NbN,  $\delta$ -NbN and  $\epsilon$ -NbN are in good agreement with available experimental data [27–29]. It is noticed that the bulk modulus of  $\epsilon$ -NbN is highest among all the structures, which is similar to that observed in MoN [30]. From Fig. 1, it is obvious that the lowest energies of the cubic structures of NbN are higher than those of the hexagonal ones. Thus it is concluded that the hexagonal phases are possibly more stable

Table 1: The calculated equilibrium parameter  $a$  (Å),  $c$  (Å), ratio  $c/a$ , bulk modulus  $B_0$ (GPa) and pressure derivative bulk modulus  $B'_0$  with available experimental data (in bracket).

	ZB-NbN	NaCl-NbN	CsCl-NbN	$\delta$ -NbN	$\epsilon$ -NbN
$a$	3.348	3.114 (3.107 <sup>a</sup> )	2.721	2.959 (2.958 <sup>c</sup> )	2.942 (2.968 <sup>d</sup> )
$c$				2.784 (2.779 <sup>c</sup> )	5.507 (5.549 <sup>d</sup> )
$c/a$				0.9408 (0.9395 <sup>c</sup> )	1.8718 (1.8696 <sup>d</sup> )
$B_0$	251.8	349.5 (320 <sup>b</sup> )	332.7	367.9	372.9
$B'_0$	3.99	4.18	3.66	3.55	3.56

<sup>a</sup> Ref. [5], <sup>b</sup> Ref. [27], <sup>c</sup> Ref. [28], <sup>d</sup> Ref. [29].

than the cubic phases. In order to further determine the most stable structure at zero pressure and temperature, Gibbs free energy of different structures of NbN at zero are obtained by Debye model. It is found that at zero pressure the Gibbs free energies of hexagonal structures are about 0.33 eV lower than those of the cubic phases. The Gibbs free energy of the  $\epsilon$ -NbN is about 0.112 eV higher than that of  $\delta$ -NbN. If Gibbs free energy is lower, the structure is more stable. Therefore,  $\delta$ -NbN should be more stable at zero pressure and temperature. The obtained result is different from the observed cubic phase in Ref. [7], as is possibly due to our not taking into account the phononic effects. Finding the real reason is our main goal in the future research.

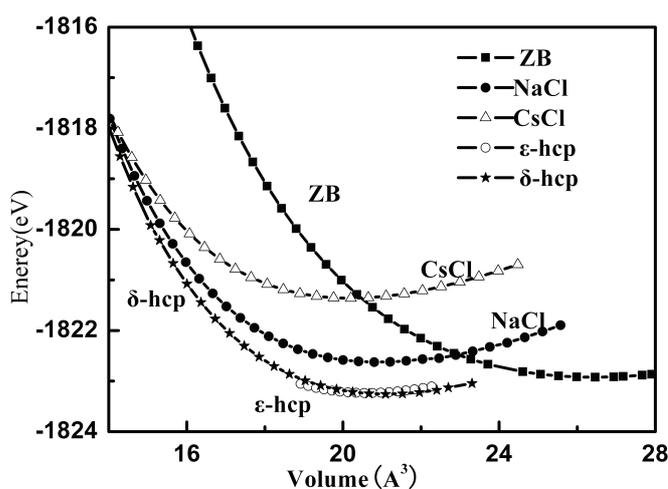


Figure 1: Total energy versus the unit cell volume (in  $\text{\AA}^3$ ) for five possible structures of NbN.

Moreover, from Fig. 1 it can be seen that the  $E$ - $V$  curve of NaCl-NbN crosses that of CsCl-NbN, which indicates the structure phase transforming from NaCl to CsCl structure. In order to investigate the phase transition of NbN, we determined the transition pressure according to the equality of Gibbs free energy of two phases. And it is found that NaCl structure transforms to CsCl at 290 GPa (Fig. 2). In other transition metal nitrides, similar transition from NaCl to CsCl structure have been found experimentally [31] and theoretically [32–35].

To investigate the mechanical stability of NbN, a set of zero-temperature-pressure elastic constants of all possible structures of NbN are obtained from first-principles calculations. The obtained elastic constants, bulk modulus, elastic anisotropies and Debye temperature are shown in Table 2 according to Eqs. (1)–(9). The calculated elastic constants and Debye temperature of NaCl-NbN compare well with the available experimental and theoretical data. Unfortunately, for other structures, there are no other experimental and theoretical data to compare each other. The agreements between our results and other available theoretical and experimental data are good, indicating that our calculations are valid and believable. The anisotropies of ZB-NbN, NaCl-NbN, CsCl-NbN gradually increases. For hexagonal structure, the anisotropies of  $\epsilon$ -NbN are stronger than that of  $\delta$ -NbN.

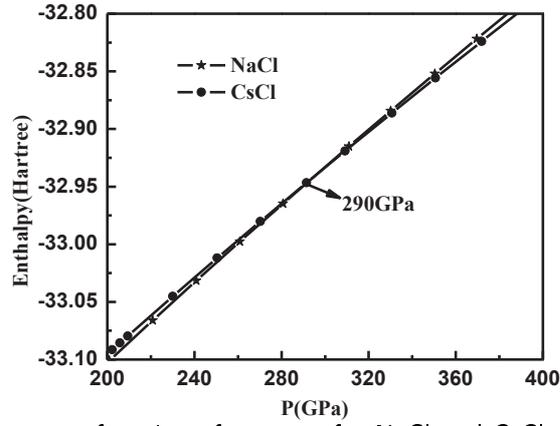


Figure 2: Gibbs free energy as a function of pressure for NaCl and CsCl structures of NbN at 0 K.

Table 2: Elastic constants  $C_{ij}$  (GPa), the bulk modulus  $B$  (GPa), elastic anisotropies  $\Delta_{S1}$ ,  $\Delta_{S2}$ ,  $\Delta_P$  and Debye temperature  $\Theta_D$  (K) at 0 GPa and 0 K.

	ZB	NaCl	CsCl	$\delta$	$\epsilon$
$C_{11}$	287.8	718.0 (739 <sup>a</sup> , 608 <sup>b</sup> )	915.6	640.9	576.1
$C_{12}$	217.2	122.9 (161 <sup>a</sup> , 134 <sup>b</sup> )	16.4	252.2	253.1
$C_{13}$				192.2	163.8
$C_{33}$				694.5	891.2
$C_{44}$	23.9	101.8 (76 <sup>a</sup> , 117 <sup>b</sup> )	86.4	223.9	241.4
$B$	240.75	311.3 (354 <sup>a</sup> , 292 <sup>b</sup> )	316.1	361.1	350.3
$\Delta_{S1}$	1.477	2.923	5.204	1.062	1.180
$\Delta_{S2}$				1.152	1.495
$\Delta_P$				1.084	1.547
$\Theta_D$	231	521 (514 <sup>c</sup> )	516	736	573

<sup>a</sup> Ref. [5] (theory), <sup>b</sup> Ref. [5] (experiment),

<sup>c</sup> Ref. [5] (the results are determined from experimental data).

As is known that, for hexagonal structure, the mechanical stability can be judged from Born-Huang criteria [36]

$$C_{12} > 0, \quad C_{33} > 0, \quad C_{66} = (C_{11} - C_{12}) > 0, \quad C_{44} > 0, \quad (C_{11} + C_{12})(C_{33}^2 - 2C_{13}^2) > 0.$$

For a cubic structure, the elastic constants should satisfy Born criteria

$$C_{12} > 0, \quad C_{11} > |C_{12}|, \quad C_{11} + 2C_{12} > 0.$$

From Table 2, we can see that the elastic constants of hcp-NbN, cubic NbN satisfy Born-Huang and Born criteria respectively. It indicated that the cubic and hexagonal structures are mechanically stable. The results are different from that observed in MoN [30].

Electronic properties are very important to understand the mechanical stability of different structures. To obtain a deeper insight into the shift in different structures, the total (TDOS) and local density of states (LDOS) and electronic structures of NbN are presented. The density of states (DOS) of various structures of NbN are shown in Fig. 3. From origin of the electronic structures of cubic and hexagonal NbN compounds, it is considered that two main factors determine the electronic structures of NbN under pressures which are the changes in nearest neighbor distances and variation in symmetry.

Fig. 3(a) exhibits the TDOS and LDOS of NaCl-NbN at zero pressure. The LDOS are decomposed into four energy regions: the lowest energy area are due to N 2s electrons; the area at -10 eV are stemming mainly from N 2p and Nb 4d electrons; the area below Fermi level is mainly to Nb 4d electrons mixed with N 2p electrons; the last one above  $E_F$  are dominated by Nb 4d states and a smaller contribution from other electrons. It can be concluded that the Nb 4d states hybridize strongly with the N 2p states. When compressing the NaCl phase of NbN (Fig. 3(b)), it is observed that the band broaden and the values of TDOS decreases, which suggests the stronger hybridization between Nb and N atom. As the phase transition from NaCl→CsCl of NbN, the Nb 4d electrons are broadened (Fig. 3(c)). It can be observed that the difference regions in the DOS of cubic structures in NbN are wider under pressures, indicating stronger interactions of atoms. Moreover, the CsCl structure of NbN are metallic, which are seen not only from the equilibrium volume, but also at high pressure. The DOS of hexagonal structures of NbN are showed in Figs.3 (e) and (f). The shapes of hexagonal electronic structures are found to have some similarities. It is also observed that the N 2p electrons hybridize strongly with Nb 4d electrons. For comparison, Figs. 3(e) and (f) show that the TODS of hexagonal NbN around the Fermi level  $E_F$  lie in a dip whereas the density of states varies monotonously at  $E_F$  in cubic structure. It confirms the total energy calculations: the hexagonal phases are more stable than the cubic ones.

Fig. 4 displayed the band structures of cubic and hexagonal NbN. They can provide more useful information about the electronic properties. Fig. 4(a) displays the band structure of NbN in the NaCl structure at zero pressure. It shows that a indirect energy gap is 1.35 eV. The band structure of rocksalt NbN before phase transition are plotted in Fig. 4(b). In the total dos graph, there is a broadening of the upper Nb 4d and N 2p band with some intermixing between them, which results in the metallization of NbN. In the CsCl structure after phase transition (Fig. 4(c)), Nb 4d and N 2p states are completely hybridized and can not be disentangled. So it also have metallic behavior. Similar result (Fig. 4(d)) appears in the CsCl structure at zero pressure. Although at zero pressure it has metallic behavior, the band becomes narrow at pressure. It is due to the weaker interaction and the larger distance between Nb and N atoms. In Figs. 4(e) and (f) shows the band structures of NbN in hexagonal structures at equilibrium volume. These behaviors are analogous to those of YN [31], ZrN [34].

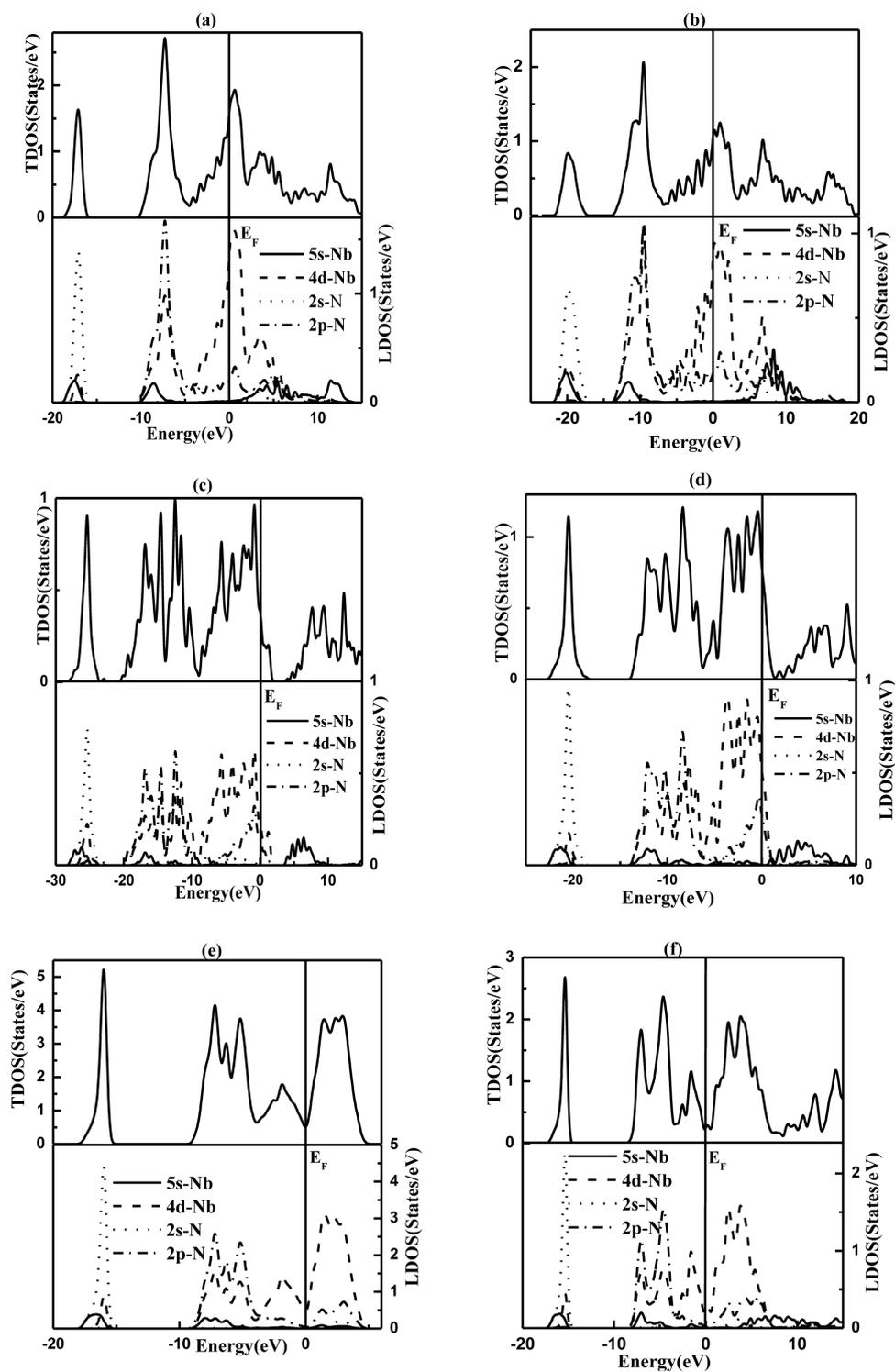


Figure 3: Total and local DOS for NbN in (a) the NaCl structure at  $P = 0$ , (b) the NaCl structure before the transition, (c) the CsCl structure after the transition, (d) the CsCl structure at  $P = 0$ , (e) the  $\delta$ -NbN at  $P = 0$ , and (f) the  $\epsilon$ -NbN at  $P = 0$ .

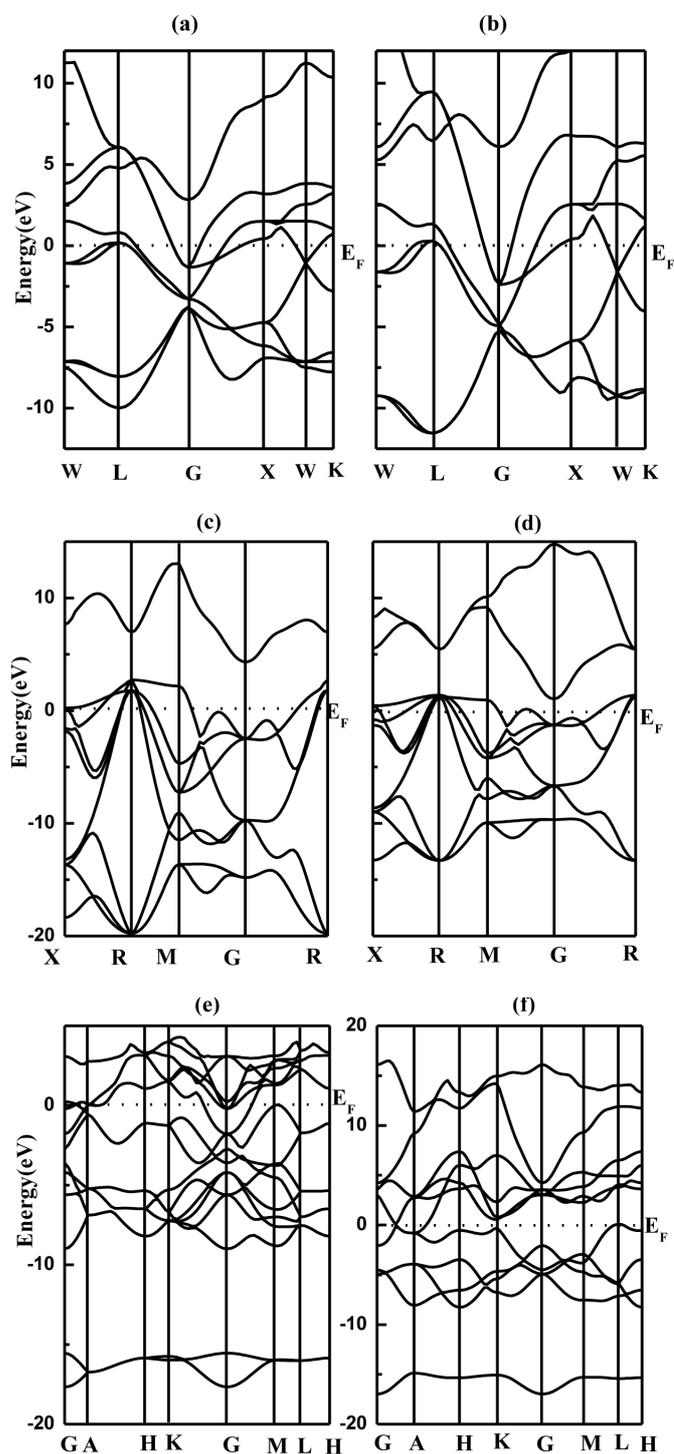


Figure 4: Band structures for NbN in (a) the NaCl structure at  $P = 0$ , (b) the NaCl structure before the transition, (c) the CaCl structure after the transition, (d) the CsCl structure at  $P = 0$ , (e) the  $\delta$ -NbN at  $P = 0$ , and (f) the  $\epsilon$ -NbN at  $P = 0$ .

## 4 Conclusions

In summary, we have investigated structural, elastic and electronic properties for different phases of niobium nitride using *ab initio* plane-wave pseudopotential density functional theory method. The lattice parameters, bulk modulus and the phase transition pressure are obtained. The present work predicted that the hexagonal phases  $\delta$  and  $\epsilon$  are more energetically stable than cubic phases. It has been shown that the ground structure is  $\epsilon$ -NbN. The obtained bulk modulus values indicate that these phases of NbN are low compressible materials. It is also found that the phase transition pressure from NaCl structure to CsCl structure are 290 GPa. The elastic constants, Debye temperature and elastic anisotropies of NbN in five structures are also obtained. It is found that Debye temperature is in agreement with theoretical data. The anisotropies of ZB-NbN, NaCl-NbN, CsCl-NbN gradually increases. For hexagonal structure, the anisotropies of  $\epsilon$ -NbN are stronger than that of  $\delta$ -NbN. The electronic properties of NbN under pressure are also calculated, and it is found that NbN exhibits a metallic behavior and the hybridizations between atoms becomes more stronger under pressure.

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