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Mechanical, Electronic and Optical Properties of Two Phases of NbB$_4$: First-Principles Calculations

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Abstract: As transition metal borides have been successfully synthesised, the study of the combination of transition metal and boron is another effective way to investigate the properties of boride. We have predicted the novel phase Amm2-NbB$_4$. Using the Cambridge Serial Total Energy Package (CASTEP) code, we further researched on the mechanical, electronic and optical properties of C2/c- and Amm2-NbB$_4$. It is found that both the phases of NbB$_4$ are dynamically and mechanically stable at 0 and 100 GPa. Their Vickers hardness values are both 34 GPa, which indicate that they are hard materials. The band gap of C2/c-NbB$_4$ is 0.145 eV, which indicates that it is a semiconductor (or metalloid) at 0 GPa. For the Amm2-NbB$_4$, the band structure without band gap indicates it is a metal at 0 GPa. The optical properties of these two structures are similar. At 0 eV, the real part of dielectric function is 28.8 for C2/c-NbB$_4$, and the real part value for Amm2-NbB$_4$ is 43. We hope our work will provide some help to the experimental work about the technology of the material.

Keywords: Electronic Properties; First-Principles Calculations; Mechanical Properties; NbB$_4$; Optical Properties.

1 Introduction

Super-hard materials are widely used as grinding, polishing, cutting, drilling tools, and surface-protective coatings due to their superior mechanical properties [1–3]. Transition metals are previously known to form borides with high boron content [4]. Transition metal borides (TMBS) possess several unique properties such as high melting points, hardness, chemical stability, and metallic properties. Until recently, some TMBS have been synthesised and they all have good properties [5–9]. For example, ReB$_4$ [5] and WB$_4$ [10, 11] were discovered to be super-hard materials based on the measured hardness of about 48 and 43 GPa. And some potentially super-hard materials found and investigated extensively include OsB$_4$ (37 GPa) [8], IrB$_{1.1}$ (43 GPa) [9] and RhB$_{1.1}$ (44 GPa) [9]. However, these transition metals (TMs) such as Os, Re, W, Ir and Rh are so expensive that people began to find lighter TMs to replace them.

Luckily, CrB$_4$ was synthesised by Niu et al. [12] having hardness of 48 GPa. The calculated hardness values of Amm2- and Cmcm-ZrB$_4$ are both about 42 GPa [4]. It shows that these lighter TM borides are possible choices for super-hard materials. Ge et al. [13] did a systematic investigation on TM boride, MBn (the TMs include M=Y, Zr, Nb, Mo, Tc, Ru, p n ≤8). The geometries, stabilities, electronic and magnetic properties of MBn clusters were investigated. The results showed that the doped-M atoms improve the chemical activity of the host clusters in most cases. The magnetic properties of 4d impurity in B clusters are mainly affected by symmetry, by coordination number and by atomic distance. The relative orientation between the magnetic moments of the M atoms (M=Zr, Nb, Mo, Tc, Ru) and those of its neighbouring B atoms exhibit ferromagnetic or antiferromagnetic alignment in contrast to the ferromagnetic alignment of YBn. Li et al. [14] predicted new ultra-incompressible phases of NbB$_4$ (C2/c-NbB$_4$, and Amm2-NbB$_4$) using particle swarm optimisation algorithm. Their phase stability, dynamic stability, elastic properties and electronic properties are investigated by using first-principles calculations. It is found that the C2/c phase transforms to Amm2 phase at about 42 GPa, and both phases are dynamically and mechanically stable at ambient conditions. Both the phases of NbB$_4$ have high bulk and shear moduli and a low Poisson’s ratio and can be classified as ultra-incompressible materials because the Nb-based borides have some characteristics such as low cost, high hardness, high elastic modulus and excellent thermal stability. At present, the study focuses on the Nb-B binary compounds’ properties especially the structure and mechanical properties.

In this paper, according to the Amm2-ZrB$_4$ phase in the Zhang’s work [15], we predict the novel Amm2 phase of NbB$_4$, whose atom positions are different from the atom positions in Li’s work. Moreover, based on Li’s C2/c-NbB$_4$...
phase work, the properties of $C2/c$-$NbB_4$ phase are also further analysed. Both mechanical properties and phonon dispersion spectra under the pressure of 0 and 100 GPa are calculated. Their phase stabilities and dynamical stabilities are analysed. The electronic band structures and optical properties are calculated by PBE0 at 0 GPa. This work will be an important base for further experiments on NbB₄.

2 Method

In this work, all the properties are calculated by using the Cambridge Serial Total Energy Package (CASTEP) code [1, 16] based on the density function theory [17]. Among them, the structural optimisation and mechanical properties for $C2/c$-$NbB_4$ and Amm2-$NbB_4$ are calculated by using the generalised gradient approximation with PBE function [18]. The optical and electronic properties of the two phases of NbB₄ are calculated by using PBE0 [19]. The cut-off energy and number of k-points are two important parameters in this work. The cut-off energy can decide the number of plane waves, while the number of special k-points determines the Brillouin zone [20]. For $C2/c$ and Amm2-$NbB_4$, the values of plane-wave cut-off energy are set as 650 eV. The k-points are $10 \times 10 \times 3$ and $9 \times 9 \times 3$ in the first irreducible Brillouin for $C2/c$ and Amm2-$NbB_4$. For all the calculations, we set the value of self-consistent field tolerance threshold as $5 \times 10^{-7}$ eV/atom and the convergent value of the total energy difference is less than $5 \times 10^{-6}$ eV/atom. In addition, the maximum Hellmann–Feynman force is taken as 0.01 eV/Å and the maximum stress is set as $5 \times 10^{-3}$ Å. The lattice parameters under 0 and 100 GPa are calculated at 0 and 100 GPa as shown in Table 1. Based on the Born Guidelines, the mechanical stability criteria of the orthorhombic phase and monoclinic phase are shown as:

$$\begin{align*}
C_{ij} &> 0 \quad (i=6) \\
\left[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})\right] &> 0 \\
\left[C_{11} + 2C_{12} - 2C_{23}\right] &> 0 \\
\left[C_{11} + C_{13} - 2C_{23}\right] &> 0 \\
\left[C_{22} + C_{13} - 2C_{23}\right] &> 0
\end{align*}$$

$$\begin{align*}
C_{ij} &> 0 \quad (i=6) \\
\left[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})\right] &> 0 \\
\left[C_{11} - C_{33} - C_{13}^2\right] &> 0 \\
\left[C_{22} - C_{12} - 2C_{13}\right] &> 0 \\
\left[C_{22}(C_{13}C_{23} - C_{12}^2) + 2C_{23}C_{23}C_{33} - C_{23}^2C_{33} - C_{13}^2C_{33}\right] &> 0 \\
\left[C_{15}C_{25}(C_{13}C_{12} - C_{33}C_{23}) + C_{25}^2C_{33} - C_{15}^2C_{33}\right] &> 0 \\
\left[C_{15}(C_{15}C_{25} - C_{25}^2) + C_{15}^2C_{25}^2\right] &> 0 \\
\left[C_{13}C_{25}(C_{11}C_{22}C_{13} - C_{12}^2) + C_{25}^2C_{33} - C_{13}^2C_{33}\right] &> 0 \\
\left[C_{25}C_{35}(C_{11}C_{22}C_{23} - C_{12}^2) + C_{35}^2C_{33} - C_{25}^2C_{33}\right] &> 0 \\
g = C_{11}C_{12}C_{13} - C_{11}^2C_{33} - C_{12}^2C_{33} - C_{13}^2C_{33} + 2C_{15}C_{13}C_{33}
\end{align*}$$

By using the CASTEP program [22], all the elastic stiffness constants for the two phase crystals can be calculated at 0 and 100 GPa as shown in Table 1. Based on the value of $C_{ij}$ in Table 1, it is shown that both $C2/c$-NbB₄ and Amm2-NbB₄ phases are mechanically stable under 0 and 100 GPa. In addition, the bulk modulus $B$ and shear modulus $G$ can be calculated directly by Voigt's

3 Results and Discussion

3.1 Structure Properties

It is necessary to explore the crystal structure in order to understand the properties of materials. For both monoclinic $C2/c$ phase and orthorhombic Amm2 phase, the four NbB₄ f.u. are contained in the unit cell. After the structural optimisation at 0 GPa, the lattice constants of the $C2/c$-NbB₄ are shown as $a = 3.647$, $b = 5.303$, $c = 10.610$, $\alpha = \gamma = 90^\circ$ and $\beta = 102.2^\circ$. The lattice constants of Amm2-NbB₄ are $a = 9.967$, $b = 5.285$, $c = 3.113$, $\alpha = \gamma = 90^\circ$. Because the $C2/c$ phase belongs to monoclinic and the Amm2 phase belongs to orthorhombic, we show the section structures of $C2/c$-NbB₄ in the y–z plane and x–z plane in Figure 1a,b. The section structures of Amm2-NbB₄ in the x–z plane and x–y plane are shown in Figure 1c,d. In Figure 1, the small green balls represent atom B and the big pink balls represent the atom Nb. In addition, the volume of per formula is 41.34 Å³/formula for $C2/c$-NbB₄ and 41.00 Å³/formula for Amm2-NbB₄, respectively. The lattice constants are close to the calculated values [14], which indicate that the crystal structures are available and we can do further work for two phases of NbB₄.

3.2 Mechanical Properties

The bulk modulus $B$ and shear modulus $G$ are two important parameters under mechanical properties. The bulk modulus $B$ is a physical quantity, which allows the material to estimate rigidity, while the shear modulus $G$ is applied to determine the ductility of a material [21]. For crystals, elastic stiffness constants are orthogonally applied to consider the symmetry of the crystals ($C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$ for Amm2-NbB₄; $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$, $C_{ij}$ for $C2/c$-NbB₄). Based on the Born Guidelines, the mechanical stability criteria of the orthorhombic phase and monoclinic phase are shown as:

$$\begin{align*}
C_{ij} &> 0 \quad (i=6) \\
\left[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})\right] &> 0 \\
\left[C_{11} + 2C_{12} - 2C_{23}\right] &> 0 \\
\left[C_{11} + C_{13} - 2C_{23}\right] &> 0 \\
\left[C_{22} + C_{13} - 2C_{23}\right] &> 0
\end{align*}$$

$$\begin{align*}
C_{ij} &> 0 \quad (i=6) \\
\left[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})\right] &> 0 \\
\left[C_{11} - C_{33} - C_{13}^2\right] &> 0 \\
\left[C_{22} - C_{12} - 2C_{13}\right] &> 0 \\
\left[C_{22}(C_{13}C_{23} - C_{12}^2) + 2C_{23}C_{23}C_{33} - C_{23}^2C_{33} - C_{13}^2C_{33}\right] &> 0 \\
\left[C_{15}C_{25}(C_{13}C_{12} - C_{33}C_{23}) + C_{25}^2C_{33} - C_{15}^2C_{33}\right] &> 0 \\
\left[C_{15}(C_{15}C_{25} - C_{25}^2) + C_{15}^2C_{25}^2\right] &> 0 \\
\left[C_{13}C_{25}(C_{11}C_{22}C_{13} - C_{12}^2) + C_{25}^2C_{33} - C_{13}^2C_{33}\right] &> 0 \\
\left[C_{25}C_{35}(C_{11}C_{22}C_{23} - C_{12}^2) + C_{35}^2C_{33} - C_{25}^2C_{33}\right] &> 0 \\
g = C_{11}C_{12}C_{13} - C_{11}^2C_{33} - C_{12}^2C_{33} - C_{13}^2C_{33} + 2C_{15}C_{13}C_{33}
\end{align*}$$

By using the CASTEP program [22], all the elastic stiffness constants for the two phase crystals can be calculated at 0 and 100 GPa as shown in Table 1. Based on the value of $C_{ij}$ in Table 1, it is shown that both $C2/c$-NbB₄ and Amm2-NbB₄ phases are mechanically stable under 0 and 100 GPa. In addition, the bulk modulus $B$ and shear modulus $G$ can be calculated directly by Voigt's
and Reuss’s schemes, according to the Voigt–Reuss–Hill approximation [23], given as follows:

\[
B_v = \frac{1}{9} \left[ C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) \right]
\]  
\[
G_v = \frac{1}{15} \left[ C_{11} + C_{22} + C_{33} + 3(C_{12} + C_{13} + C_{23}) - (C_{12} + C_{13} + C_{23}) \right]
\]

\[
B_R = \frac{1}{3} \left[ S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23}) \right]
\]  
\[
G_R = 15 \left[ \frac{1}{4} (S_{11} + S_{22} + S_{33}) + S_{44} + S_{55} + S_{66} \right]
\]

\[
G_v = 15 \left[ \frac{1}{4} (S_{11} + S_{22} + S_{33}) + 3(S_{44} + S_{55} + S_{66}) - 4(S_{12} + S_{13} + S_{23}) \right]
\]

\[
B = \frac{1}{2} (B_v + B_R), \quad G = \frac{1}{2} (G_v + G_R)
\]

Figure 1: Crystal structures of NbB₄: (a) section structure of C2/c-NbB₄ in y–z plane, (b) section structure of C2/c-NbB₄ in x–z plane, (c) section structure of Amm2-NbB₄ in x–z plane and (d) section structure of Amm2-NbB₄ in x-plane.

Table 1: The elastic constants of both phases of NbB₄ at 0 and 100 GPa.

<table>
<thead>
<tr>
<th>Space group</th>
<th>C₁₁</th>
<th>C₂₂</th>
<th>C₃₃</th>
<th>C₄₄</th>
<th>C₅₅</th>
<th>C₆₆</th>
<th>C₁₂</th>
<th>C₁₃</th>
<th>C₂₃</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2/c-NbB₄</td>
<td>0 GPa</td>
<td>619</td>
<td>639</td>
<td>559</td>
<td>188</td>
<td>224</td>
<td>241</td>
<td>110</td>
<td>136</td>
<td>106</td>
</tr>
<tr>
<td>C2/c-NbB₄</td>
<td>0 GPa</td>
<td>708</td>
<td>620</td>
<td>697</td>
<td>233</td>
<td>290</td>
<td>257</td>
<td>140</td>
<td>139</td>
<td>139</td>
</tr>
<tr>
<td>C2/c-NbB₄</td>
<td>100 GPa</td>
<td>1042</td>
<td>1145</td>
<td>1103</td>
<td>478</td>
<td>427</td>
<td>363</td>
<td>377</td>
<td>378</td>
<td>322</td>
</tr>
<tr>
<td>Amm2-NbB₄</td>
<td>0 GPa</td>
<td>527</td>
<td>597</td>
<td>623</td>
<td>230</td>
<td>211</td>
<td>217</td>
<td>146</td>
<td>134</td>
<td>75</td>
</tr>
<tr>
<td>Amm2-NbB₄</td>
<td>0 GPa</td>
<td>676</td>
<td>693</td>
<td>607</td>
<td>245</td>
<td>251</td>
<td>298</td>
<td>118</td>
<td>154</td>
<td>146</td>
</tr>
<tr>
<td>Amm2-NbB₄</td>
<td>100 GPa</td>
<td>1022</td>
<td>1128</td>
<td>1130</td>
<td>334</td>
<td>307</td>
<td>307</td>
<td>390</td>
<td>328</td>
<td>286</td>
</tr>
<tr>
<td>Amm2-ZrB₄</td>
<td>0 GPa</td>
<td>554</td>
<td>576</td>
<td>454</td>
<td>223</td>
<td>243</td>
<td>254</td>
<td>50</td>
<td>113</td>
<td>122</td>
</tr>
</tbody>
</table>

Ref. [14] and [15].
where $S_{ij}$ is the element of compliance matrix. There is a relation between the compliance matrix $S$ and the elastic stiffness matrix $C (S = C^{-1})$ [24]. The Young’s modulus $E$ and Poisson’s ratio $\nu$ can be calculated as follows [25]:

$$E = \frac{9BG}{3B + G}, \quad \nu = \frac{3B - 2G}{2(3B + G)}$$  \hspace{1cm} (8)

The bulk modulus $(B)$, shear modulus $(G)$, Young’s modulus $(E)$ and Poisson’s ratio $(\nu)$ are given in Table 2 for two phases of $\text{NbB}_4$ at 0 and 100 GPa, with the value of $\text{Amm2-ZrB}_4$ under 0 GPa.

From Table 2, it is seen that both $\text{Amm2}$ phases of $\text{NbB}_4$ have higher bulk modulus than phases of $\text{ZrB}_4$ at 0 GPa. Young’s modulus can also indicate the stiffness of materials. The high value of Young’s modulus indicates that the material has good hardness and the low value of Young’s modulus indicates that the material has good flexibility.

In addition, the Vickers hardness $H_v$ which can describe the hardness of materials directly, is calculated by an empirical model given as follows [26]:

$$H_v = 2(G^3 / B^3)^{0.585} - 3$$  \hspace{1cm} (9)

According to Table 2, the Vickers hardness values of $\text{Amm2}$- and $\text{C2/c-NbB}_4$ are both 34 GPa, which indicate that the $\text{Amm2-NbB}_4$ and $\text{C2/c-NbB}_4$ belong to the category of hard materials.

In order to research the dynamic stabilities of two phases of $\text{NbB}_4$, the phonon dispersion curves under pressure of 0 and 100 GPa are shown in Figure 2. The absence of negative frequencies indicates that $\text{Amm2-NbB}_4$ and $\text{C2/c-NbB}_4$ crystals are dynamically stable at 0 and 100 GPa. And from the phonon density of state (DOS) as shown in Figure 2, we can observe that in the lower frequency, the total DOS is mainly from the states of atom Nb, while the states of atom B provide mainly DOS in the higher frequency due to the atoms’ different mass.

The mechanical and dynamical stabilities indicate that $\text{Amm2}$- and $\text{Cmcm-NbB}_4$ are stable. Based on these, the electrical properties and optical properties are analysed by PBE0.

### 3.3 Electronic Properties

Electronic properties can be used to determine the type of the compound (metal, semiconductor or insulator). The electrical properties of $\text{Amm2}$- and $\text{Cmcm-ZrB}_4$ are calculated along high symmetry directions of the Brillouin zone. The band gap between the valence and conduction bands can be observed from the electronic (DOS) and band structure in Figure 3. In the band structure, the dot-line presents the Fermi level. In Figure 3a, it can be noted that the band structure curves do not pass through the Fermi level and the band gap is 0.145 eV, which indicates that $\text{C2/c-NbB}_4$ is a semiconductor but has good metallic properties at 0 GPa. So $\text{C2/c-NbB}_4$ can conduct electricity as long as the appropriate conditions of excitation energy can be satisfied. From Figure 3b, the band structure curves pass through the Fermi level, which indicates that $\text{Amm2-NbB}_4$ is a metal at 0 GPa.

The DOS can provide more information about the electronic structure revealing the mechanism of the elastic properties and fundamental structural stability. The electronic DOS of $\text{C2/c-NbB}_4$ and $\text{Amm2-NbB}_4$ are shown in Figure 3 in the energy range from –20 to 10 eV.

In Figure 3a, we can see that the total DOS of $\text{C2/c-NbB}_4$ is mainly contributed from B-p and Nb-d in the energy range from –7 to 7 eV. Between –10 and –4 eV, the total DOS is mainly contributed by B-p with some contribution from Nb-d, and between 1 and 4 eV, the total DOS is mainly Nb-d’s contribution and some B-p’s contribution. From –18 to –10 eV, the DOS is mainly determined by B-p and B-s whose contributions are similar.

In Figure 3b, the total DOS of $\text{Amm2-NbB}_4$ is mainly contributed by B-p and Nb-p in energy range from –12 to –5 eV and from 5 to 9 eV. The partial DOS of the B-p and Nb-p are very similar, which shows that there is a strong bond. Between –2 and 4 eV, the Nb-d is the main factor. Between –18 and –12 eV, the B-s contribution is major.

### 3.4 Optical Properties

Optical properties is an important property of materials and includes dielectric function, refractive index, absorption spectrum, reflectivity and conductivity. The dielectric function is the most general property of a material and

**Table 2:** The bulk modulus $(B)$, shear modulus $(G)$, Young’s modulus $(E)$ and Poisson’s ratio $(\nu)$ for both phases of $\text{NbB}_4$ at 0 and 100 GPa.

<table>
<thead>
<tr>
<th>Space group</th>
<th>$B$</th>
<th>$G$</th>
<th>$E$</th>
<th>$\nu$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NbB}_4$</td>
<td>$\text{C2/c}$</td>
<td>279</td>
<td>225</td>
<td>531</td>
<td>0.182</td>
</tr>
<tr>
<td>$\text{Amm2}$</td>
<td>273</td>
<td>223</td>
<td>526</td>
<td>0.178</td>
<td>Present</td>
</tr>
<tr>
<td>$\text{C2/c}$</td>
<td>310</td>
<td>264</td>
<td>613</td>
<td>0.173</td>
<td>[14]</td>
</tr>
<tr>
<td>$\text{Amm2}$</td>
<td>313</td>
<td>262</td>
<td>617</td>
<td>0.168</td>
<td>[14]</td>
</tr>
<tr>
<td>$\text{ZrB}_4$</td>
<td>$\text{Amm2}$</td>
<td>241</td>
<td>229</td>
<td>522</td>
<td>[15]</td>
</tr>
<tr>
<td>100 GPa</td>
<td>$\text{NbB}_4$</td>
<td>$\text{C2/c}$</td>
<td>605</td>
<td>399</td>
<td>981</td>
</tr>
<tr>
<td>$\text{Amm2}$</td>
<td>611</td>
<td>355</td>
<td>892</td>
<td>0.257</td>
<td>Present</td>
</tr>
</tbody>
</table>
Figure 2: Phonon dispersion curves and phonon DOS of two phases of NbB₄: (a) C2/c-NbB₄ (0 GPa); (b) Amm2-NbB₄ (0 GPa); (c) C2/c-NbB₄ (100 GPa); and (d) Amm2-NbB₄ (100 GPa).

Figure 3: Band structure and electronic density of states: (a) C2/c-NbB₄ and (b) Amm2-NbB₄.
can characterise how a material responds to the incident electromagnetic wave [27]. The real part of dielectric function is related to the electric polarisation characteristics of the material [28]. In general, the optical properties and the band structure mainly reflect the behaviour of the electrons. With an increase in the incident energy, the phenomenon of electronic transition happens. In this process, electrons will radiate energy outwardly and the optical phenomenon will happen. Based on the definition of direct transition and Kramers–Kronig relation [29], the real and imaginary parts of the dielectric function, absorption coefficient, reflectivity coefficient, etc. can be derived:

$$\varepsilon_2 = \frac{C}{\omega^2} \sum_{K} \left| e \cdot M_{C \nu}(K) \right|^2 \frac{d^3k}{2\pi} \delta \left( E_C(K) - E_{\nu}(K) - \hbar \omega \right)$$  

$$\varepsilon_1 = 1 + C \sum_{K} \left| e \cdot M_{C \nu}(K) \right|^2 \frac{d^3k}{2\pi} \frac{\hbar}{E_C(K) - E_{\nu}(K)}$$

$$\frac{E_C(K) - E_{\nu}(K)}{\hbar^2} - \hbar^2 \omega^2$$

$$I(\omega) = \sqrt{2(\omega)\left| \varepsilon_2(\omega)^2 - \varepsilon_1(\omega)^2 - \varepsilon_1(\omega) \right|^2}$$

$$R(\omega) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

where the subscript C and V represent the conduction band and valence band, BZ is the first irreducible Brillouin, K is the reciprocal lattice, h is the Planck’s constant, $|e \cdot M_{C \nu}(K)|^2$ is the momentum transition matrix element, $\omega$ is the angular frequency, $C_\nu$ and $C_\nu$ are the constants and $E_C(K)$, $E_\nu(K)$ is the intrinsic level on the conduction band and valence band. The values $n$ and $k$ are the reflectivity coefficient and extinction coefficient. In addition, other properties can be derived from the dielectric function. In Figure 4, dielectric function, refractive index, absorption spectrum, reflectivity, and conductivity of two phases of NbB are shown.

Figure 4a shows the real and imaginary parts of the dielectric function for $C_2/c$-NbB and Amm2-NbB. It can be observed that the real part value of dielectric function is about 43 at photon energy of zero for $C_2/c$-NbB, and the real part value of dielectric function for Amm2-NbB is about 11.92 at 0.92 eV. This peak can be due to the transitions of Nb-d and B-p electrons from valence band to conduction band. Similarly, the peak value of dielectric function for Amm2-NbB is about 16.01 at 1.4 eV. This peak can be due to the transitions of Nb-d, B-p and Nb-p electrons from valence band to conduction band. These refer to Figure 3. In Figure 4, the value range of the imaginary part is about from 0 to 18 eV. In Figure 3, the DOS value range of the valence band is from –18 to 0 eV, within this range, there are electron transitions. The values of the imaginary part of the dielectric constant are related to the strength of the electron transitions.

Reflection spectrum is the most direct manifestation of band system, spectrum of each peak belongs to different inter-band transition. Figure 4b shows the reflectivity of both phases. The reflectivity is the ratio of the energy of reflective wave to the energy of the incident wave. And it also shows that the reflectivity of Amm2-NbB is better than that of $C_2/c$-NbB. The absorption coefficient defines the ability to absorb incident wave energy for a material. Figure 4c shows the absorption spectrum of $C_2/c$- and Amm2-NbB. It is shown that the strongest absorption peaks for both phases of NbB are about 13.5 eV.

The refractive index is an important property under optical properties. The real part $n$ indicates the dispersion of the medium, and the imaginary part $k$ indicates the absorption loss. For $C_2/c$-NbB, the static refractive index $n(0)$ is about 5.38 as shown in Figure 4d; the $n$ gets to the minimum value at about 17.6 eV. The $k$ increases to 1.7 at about 4.3 eV and then approaches zero above 18 eV. Similarly, for Amm2-NbB, the $n$ starts from 6.60 and gets to the minimum value at about 18.8 eV. When Figure 4a, d are compared, the shapes of curves are similar. The refractive index is related to the transition of electrons. We can also observe that light propagates through the material difficulty in the range from 9.67 to 19.69 eV for $C_2/c$-NbB and in the range from 10.13 to 19.36 eV for Amm2-NbB.

Figure 4e shows that conductivities of both structures are similar when incident photon energy ranges from 0 to 30 eV. The optical conductivity is a good gauge of photoconductivity, which could shed light on the electrical conductivity of the material [30]. It is shown that the real parts of conductivity for two phases are always more than zero. It can also be due to the excitation of electrons. The peaks (4.37, 7.3 and 10.2 eV) for $C_2/c$-NbB can be considered as the performance of main B-p and some Nb-d, B-p, main B-p and some B-s electronic transitions, respectively, as shown in Figure 3a. Similarly, all the peaks (3.8, 6 and 10.7 eV) for Amm2-NbB can be seen as the expression for excitation of B-p and Nb-p electrons.
Conclusions

First-principles calculations were performed to research about the elastic, electronic and optical properties of C2/c-NbB4 and novel Amm2-NbB4. For two phases of NbB4, their values of $C_{ij}$ satisfy the mechanical stability criteria of the monoclinic phase and orthorhombic phase, respectively. The absence of negative frequencies of the phonon spectra indicates that Amm2-NbB4 and C2/c-NbB4 crystals are mechanically stable and dynamically stable at 0 and 100 GPa. The Vickers hardness values of Amm2- and C2/c-NbB4 are both 34 GPa, which show that Amm2-NbB4 and C2/c-NbB4 belong to the category of hard materials. For C2/c-NbB4, the band gap is 0.145 eV, which

Figure 4: Optical properties: (a) dielectric function, (b) reflectivity, (c) absorption spectrum, (d) refractive index and (e) conductivity.

4 Conclusions
indicates that it is a semiconductor (or metalloid) but has good metallic properties at 0 GPa. For Amm2-NbB4, the band structure indicates it is a metal at 0 GPa. The optical properties of these two structures are similar. The real part of dielectric function is about 28.8 for C2/c-NbB4, and the real part value for Amm2-NbB4 is about 43 at 0 eV. For the imaginary part of dielectric function, the peak value of the imaginary part for C2/c-NbB4 is about 11.92 at 0.92 eV, and the peak value for Amm2-NbB4 is about 16.01 at 1.4 eV.

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References