First-Principles Study on Ground State Properties of ZrB2 Crystal

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Abstract: The lattice constants, electronic structure, elastic constants, and the Debye temperature of ZrB2 crystal were calculated by first-principles total energy pseudo-potential methods based on density function theory. The results show that the balance lattice constants a and c of ZrB2 calculated by the general gradient approximation (GGA) exchange correlation function approximation method and ultrasoft pseudopotential scheme are 0.316 81 nm and 0.353 53 nm, with the relative errors of 0.058% and 0.058%, respectively, compared to the experimental data. The covalent electron hybridization between 2p orbitals of B atom and 4d orbitals of Zr atom is supposed as the main cause of “pseudo-gap”. The Mulliken population analysis indicates that a part of Zr electrons transfer to B atoms, leading to the ionic bonding in ZrB2 crystal. In order to investigate the effect of strain amplitude on the calculated results, four different strain amplitudes of the elastic constants were applied. According to the presetting strain and stress method, the theoretical values of elastic matrix for ZrB2 single crystal are similar to the experimental data. The Debye temperature of ZrB2 calculated based on elastic constants is 927 K, coincided with the experimental value (910 K).

Keywords: first-principles; zirconium diboride crystal; ground state; lattice constant; elastic constants

1 Introduction

ZrB2 possesses some unique physical properties like high melting point, hardness, chemical stability, high thermal conductivity, low electrical resistivity and low work function. The application of such a material is related to the interesting combination of mechanical, chemical, thermal and electrical properties, i.e., cutting tools, armor, refractory materials, electrode, etc.\[1\].

Recently, Takamura et al.\[2\] investigated the growth of ZrB2 epitaxially on Si to form GaN films, which exhibits some promising photoluminescence properties. However, there are still many open questions related to the ground state properties in ZrB2 crystal.
In this paper, the electronic structures and elastic properties of \( \text{ZrB}_2 \) were investigated by the first principles total-energy plane-wave pseudopotential (PW-PP) method. In addition, the elastic constants and the Debye temperature of \( \text{ZrB}_2 \) were also analyzed. The calculated results were compared to the available experimental data.

2 Computational methodology

Density functional theory calculations are performed with plane-wave ultrasoft pseudo-potential by using the general gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) function as implemented in the CASTEP code (Cambridge Sequential Total Energy Package)[3]. The ionic cores are represented by ultrasoft pseudo-potentials for Zr and B atoms. For Zr atom, the configuration is \([\text{Kr}] 4d^{2}5s^{2}\), where the \(4d^{2}\) and \(5s^{2}\) electrons are explicitly treated as valence electrons. For B atom, the configuration is \([\text{He}] 2s^{2}2p^{1}\), where \(2s^{2}\) and \(2p^{1}\) electrons are explicitly treated as valence electrons. The plane-wave cut off energy is 450 eV and the Brillouin-zone integration is performed with the \(27 \times 27 \times 30\) grid sizes by the Monkorst-Pack method for structure optimization. This set of parameters assure the total energy convergence of \(5.0 \times 10^{-6}\) eV/atom, the maximum force of 0.1 eV/nm, the maximum stress of 0.02 GPa and the maximum displacement of \(5.0 \times 10^{-5}\) nm.

3 Results and discussion

3.1 Equilibrium geometry

The crystal structure of \( \text{AlB}_2\)-type transition-metal diborides is designated as \(C_{32}\) with the space group symmetry of \(\text{P}6_{3}/\text{mmm}\) (191). \(\text{ZrB}_2\) crystal is in the hexagonal when \(Z = 1\), the Zr atom is on the \(1a\) Wyckoff site, and the B atoms are on the \(2d\) Wyckoff site. The experimental lattice parameters of \(\text{ZrB}_2\) are \(a_0 = 0.3169\) and \(c_0 = 0.3523\) nm [4].

In order to check the applicability and accuracy of the ultrasoft pseudo-potential, the GGA calculation of the perfect bulk \(\text{ZrB}_2\) is carried out to determine the optimized cell parameters, i.e., \(a\) and \(c\). The resulting \(a\) and \(c\) are 0.316 81 nm and 0.353 53 nm, respectively, which are close to the experimental values, with the relative errors of 0.058% and 0.058%, respectively.

3.2 Band structure and density of states (DOS)

Figures 1 and 2 show the band structure along high-symmetry points in the Brillouin zone and the total density of states (DOS), respectively. Clearly, in Fig. 1, no band gap appears in the band structure. According to the crystal field theory (CFT), the energy level of \(3d\) orbitals in Zr atoms is divided due to the influence of the ligand B atoms, where \(4d_{x^2-}y^2\) orbital decreases as double degenerate state, \(4d_{x^2-y^2}\) orbital decreases a little, and \(4d_{2z^2-r^2}\) orbital increases as double degenerate state. Fig. 1 also shows the energy bands of the orbitals above.

3.3 Charge density and differential charge density in \(\text{ZrB}_2\) crystal

Figures 3 and 4 show the calculation results of electron charge density and differential charge density on the faces of the \(\text{ZrB}_2(0001)\), (0002) and \((11 \overline{2} 0)\), respectively, to analyze the bond behavior of \(\text{ZrB}_2\). It is seen that the interaction between Zr and Zr atoms is weak (see Fig. 3(a)), and the distribution of the charge density between Zr and Zr atoms is flat. In Fig. 3(b), there are the...
obvious covalent bonds between B atoms and their charge density is the highest due to the interaction between the electrons on the 2s and 2p orbitals in the honeycomb faces of the B atoms. Besides, the more intense interaction between Zr and B atoms cannot be ignored. This testifies “pseudo-gap” in the ZrB₂ crystals resulting from the intense interaction between the electrons of 4d orbitals in Zr atoms and of 2p orbitals in B atoms again. In Fig. 3(c), there are small peaks on the distribution of charge density between Zr and B atoms, showing the intense interaction of covalent bonds between the layers.

Figure 4 shows the theoretical results of the differential charge density. Clearly, some charge transfers from Zr to B atoms, though it exists intense covalent hybrid effects between the electrons of 4d orbitals in Zr atoms and of 2p orbitals in B atoms. The Mulliken population analysis also explains some charge transfers of Zr atoms, as shown in Table 1. The charge transfer from 5s orbitals of Zr atoms to B atoms indicates that the interaction between Zr and B atoms is a hybrid interaction of covalent and ionic bonding. Besides, the
bond length between Zr and Zr atoms is not the shortest, and their interaction is much weak. The density of state indicates that the interaction between Zr–Zr atoms is composed of intense metal bonding and a little covalent bonding.

(a) (0001) face

(b) (0002) face

(c) (11 2 0) face

Fig. 4  Difference charge density (relative to the isolated atoms) of ZrB$_2$

### Table 1  Mulliken population analysis of ZrB$_2$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Species</th>
<th>s orbit</th>
<th>p orbit</th>
<th>d orbit</th>
<th>Total charge</th>
<th>Charge</th>
<th>Bond</th>
<th>Population</th>
<th>Length/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td></td>
<td>0.97</td>
<td>2.61</td>
<td>0.00</td>
<td>3.57</td>
<td>–0.57</td>
<td>B1–B2</td>
<td>2.45</td>
<td>0.182 897</td>
</tr>
<tr>
<td>B2</td>
<td></td>
<td>0.97</td>
<td>2.61</td>
<td>0.00</td>
<td>3.57</td>
<td>–0.57</td>
<td>B1–Zr</td>
<td>0.15</td>
<td>0.254 393</td>
</tr>
<tr>
<td>Zr</td>
<td></td>
<td>1.97</td>
<td>6.11</td>
<td>2.77</td>
<td>10.85</td>
<td>1.14</td>
<td>B2–Zr</td>
<td>0.15</td>
<td>0.254 393</td>
</tr>
</tbody>
</table>

3.4 Elastic constants of ZrB$_2$ single crystal

Table 2 shows the calculated results about elastic constants of ZrB$_2$ single crystal. Clearly, the $C_{13}$ values obtained from different strain amplitude are coincided with each other very well. The experimental data and the other calculated results obtained by the pseudo-potential plane wave are more accurate than those previous results [6]. Mahmud et al. [7] used the linear combination atom orbitals (LCAO) method to obtain the deviant theoretical results. This is because the method ignores the effect of exchange association, so as to cause the “bound” effect of the lattice. The simulated results obtained by the PWPP method [6] are similar to our work. Compared to the experimental results by use of the single crystal ultrasonic measurement [8], the theoretical calculation in this work is more accurate than those from others.

Table 2  Calculated results of elastic constants of hexagonal ZrB$_2$ single crystal

<table>
<thead>
<tr>
<th>Maximum strain amplitude/nm (Four steps)</th>
<th>Elastic constant/GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{11}$</td>
</tr>
<tr>
<td>0.000 2</td>
<td>555.845</td>
</tr>
<tr>
<td>0.000 4</td>
<td>556.603</td>
</tr>
<tr>
<td>0.000 6</td>
<td>556.082</td>
</tr>
<tr>
<td>0.000 8</td>
<td>556.179</td>
</tr>
<tr>
<td>Experiments [8]</td>
<td></td>
</tr>
<tr>
<td>LCAO [7]</td>
<td>581</td>
</tr>
<tr>
<td>564</td>
<td>52</td>
</tr>
<tr>
<td>606</td>
<td>54</td>
</tr>
</tbody>
</table>
3.5 Debye temperature

As an important physical parameter, the Debye temperature \((\theta_D)\) is closely related to the other important physical properties of solid, such as elastic constants, heat capacity and melting point. Based on the solid state physics, the lattice vibration is mainly affected by acoustic branch at a low temperature. Therefore, at low temperature, heat capacity can be calculated through elastic constants rather than the experimental method. The calculated Debye temperature is 927 K, which is close to the experimental value \((i.e., 910 \text{ K})\)\(^{[9]}\), indicating the reliability of the calculations in this paper. The Debye temperature of ZrB\(_2\) is greater than that of TiB\(_2\) \((i.e., 743 \text{ K})\)\(^{[10]}\).

4 Conclusions

1) The balance lattice constants of ZrB\(_2\) crystal obtained by the GGA exchange correlation function approximation method and super soft constraint potential scheme were accurate, and the relative errors were only 0.058% and 0.058%, respectively, compared to the experimental data.

2) Based on the calculation results about band structure and density of states in ZrB\(_2\), the “pseudo band gap” was supposed to resulting from the strong hybridization of the covalent electrons between 2p orbitals of B atom and 4d orbitals of Zr atom. The Mulliken population analysis indicated that a part of Zr electrons transferred to B atoms, leading to the ionic bonding in ZrB\(_2\) crystal.

3) The elastic matrix of single ZrB\(_2\) crystal was calculated according to the presetting strain and stress method, and the calculated results were similar to the experimental data. The Debye temperature of ZrB\(_2\) calculated by elastic constants was 927 K, which was close to the experimental value and greater than that of TiB\(_2\).

References:


