

高压下 CrB_4 的结构和电子性质的第一性原理计算

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摘要: 该论文对新合成超硬材料 CrB_4 的结构和电子性质从 0~100 GPa 的压力范围内, 采用密度泛函理论下的第一性原理计算进行了详细地理论研究. 在零压力下的结果与现有的理论和实验值吻合得很好. 计算了 CrB_4 的结构, 键长, B-B、Cr-B 键的 Mulliken 重叠布居, 态密度(DOS)和 PDOS 等随压力的依赖, 并进行了讨论. 计算出的结构性质与压力的关系表明, 结构参数和 CrB_4 共价键对压力不敏感, 有力地支持了 CrB_4 化合物的高硬度是来自于 B-B 笼这一特点.

关键词: CrB_4 ; 第一性原理计算; 电子性质; 高压

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First-principles calculations of structural and electronic properties of CrB_4 under high pressure

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Abstract: We present a detailed theoretical study for the structural and electronic properties of the new synthesized hard material CrB_4 under pressure ranging from 0 to 100 GPa by first-principles calculations with density functional theory in this paper. The results at zero pressure are in good agreement with the available theoretical and experimental values. The pressure dependence of structure, bond length, the Mulliken overlap population of B-B bonds and Cr-B bond, density of states (DOS) and PDOS are successfully calculated and discussed. The calculated pressure dependence of structural property shows that both structural parameters and covalent bonds of CrB_4 are insensitive to the pressure, the results strongly support that the high hardness of CrB_4 compounds is derived from the feature of B-B bonds cage. The B-B covalent bonds as bonds cage enhance the resistance to shear deformation and improve the hardness.

Keywords: CrB_4 ; First-principles calculation; Electronic property; High pressure

1 Introduction

In recent years, superhard materials become an important class of function material because they have been found possess unique physical and chemical properties, such as high hardness, high melting point, high chemical stability and good e-

lectrical conductivity, and have wide range of industrial applications^[1-4]. With the development of modern industry, the importance of superhard materials in steady growth, so it is an urgent mission for the researchers to synthesize new superhard materials with superior properties. Many new superhard materials have been synthesized up

to now, since diamond was first synthesized in 1955. Recently, Xu *et al.*^[5] and Wang *et al.*^[6] investigated the structural stability and elastic modulus of CrB₄ compound by first-principle approach. They found that the orthorhombic CrB₄ has the high shear modulus (312 GPa) compared with the WB₄ (129 GPa). However, Pan *et al.*^[7] investigated the structural formation, elastic properties, hardness and electronic structure of CrB₄ compounds using first-principles approach. They found that the high hardness of CrB₄ compounds is derived from the feature of B-B bonds cage. The B-B covalent bonds as bonds cage enhance the resistance to shear deformation and improve the hardness. And they predict that the CrB₄ compounds with CrB₄-type are the potential superhard materials.

Although above researches suggest that CrB₄ may play roles mainly in high pressure conditions, we find the pressure effect on the structural and electronic properties of CrB₄ has rarely been reported to date. So, in this paper, we aimed to study the pressure-induced changes of the structural and electronic properties of CrB₄ at pressures ranging from 0 to 100 GPa to understand its properties deeply. For this purpose, we performed density functional theory calculations, which are widely employed to calculate the structural and electronic properties as a supplement to experiment, to investigate the lattice constants, bond length, the densities of states (DOS) and the charges of the atoms for CrB₄ at different pressures.

2 Model and computational method

The underlying calculations were performed with the projector-augmented wave (PAW) method^[8-11] implemented with the Vienna ab initio simulation package (VASP)^[12-14]. The generalized gradient approximation (GGA)^[15] was used to describe the exchange-correlation function. The atomic calculations are performed for Cr 3d⁵4s¹ and B 2s²2p¹. Geometry optimization was performed using the conjugate gradient algorithm

method with a plane-wave cutoff energy of 360 eV. The calculations were conducted with 10×12×20 for the predicted phases with space groups Immm. Monkhorst-Pack k-points were used to ensure that all structures are well-converged to better than 5×10^{-6} eV/atom and the maximum force on the atom is below 5×10^{-3} eV/Å. The structures were relaxed with respect to both lattice parameters and atomic positions.

3 Results and discussion

3.1 Pressure-induced structural changes

CrB₄ crystallizes in the orthorhombic structure with the space group IMMM (No. 71). There are two chromium and eight boron atoms in the unit cell of CrB₄. In present calculations, we chose primitive cell as initial structure, and fully optimized the lattice and internal coordinates without any restrictions under hydrostatic pressure ranging from 0 to 100 GPa. The obtained lattice parameters $a = 4.744$ Å, $b = 5.479$ Å, $c = 2.846$ Å at zero pressure are very close to the experimental data of S. Andersson *et al.* ($a = 4.744$ Å, $b = 5.477$ Å, $c = 2.854$ Å)^[16]. The lattice parameters a , b , c and the Cr-B bond and B-B₁₋₃ bond lengths of CrB₄ compounds are listed in Tab. 1, together with the available theoretical^[5-7] and experimental data^[16,17]. As seen in Tab. 1, the calculated data for CrB₄ compounds at 0 GPa in this study are in good agreement with theoretical results previously reported by Xu *et al.*^[5] and Pan *et al.*^[7], as well as the experimental values by Andersson *et al.*^[16]. The good performance makes us feel confidence in following investigations using the chosen methods.

To investigate the effect of pressure on the structures of CrB₄, we plotted the variations of ratios a/a_0 , b/b_0 , c/c_0 , and normalized volume ν (V/V_0) with pressure in Fig. 1, in which a_0 , b_0 , c_0 and V_0 are the zero pressure equilibrium structural parameters. All ratios depicted in Fig. 1 decrease smoothly with pressure. The crystal cell along a -axis is more compressible than along b and c -axis. When the applied pressure is up to 100

GPa, they are shortened by only about 7.5%, 5.4% and 9.5%, respectively. The volume of primitive cell decreases only about 19.8% despite that the pressure is up to 100 GPa, which sug-

gests the compound is an incompressible material. We make a fitting for these ratios and obtain the following quadratic function relationships^[18]:

Tab. 1 The calculated and experimental values of the lattice parameters (a, b, c in Å) and the Cr-B bond and B-B₁₋₃ bond lengths (in Å) for CrB₄ compounds at 0 GPa

a	b	c	B-B ₁	B-B ₂	B-B ₃	Cr-B	Ref.
4.748	5.479	2.846	1.854	1.726	1.822	2.093	Present work(GGA-PBE)
4.750	5.489	2.854	—	—	—	—	Theor. ^a (GGA-PBE)
4.961	5.685	3.008	—	—	—	—	Theor. ^b (LDA)
4.742	5.476	2.849	1.854	1.727	1.822	2.092	Theor. ^c (GGA)
4.744 ^d	5.477 ^d	2.854 ^d	1.721 ^e				Expt.

^a Ref. [5]; ^b Ref. [6]; ^c Ref. [7]; ^d Ref. [16]; ^e Ref. [17].

$$a/a_0 = 0.99931 - 0.00107p + 3.30784 \times 10^{-6}p^2$$

(1)

$$b/b_0 = 0.99989 - 0.00073p + 1.8988 \times 10^{-6}p^2$$

(2)

$$c/c_0 = 0.999160 - 0.00133p + 3.99926 \times 10^{-6}p^2$$

(3)

$$V/V_0 = 0.999540 - 0.00310p + 1.0468 \times 10^{-6}p^2$$

(4)

In above equations, the unit of pressure is GPa.

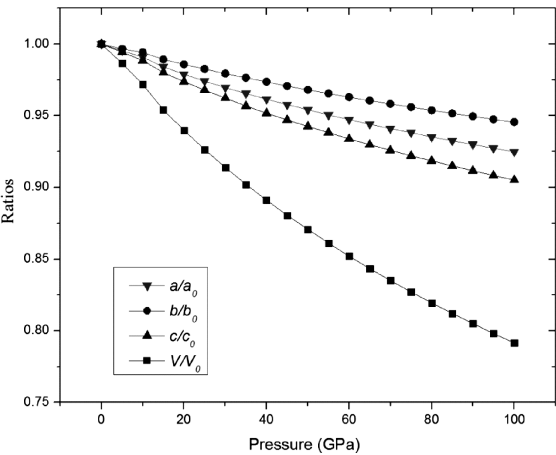


Fig. 1 Variation of ratios a/a_0 , b/b_0 , c/c_0 and v as a function of pressure

The changes of structural parameters and volume of crystal originate from the changes of the bonds in the cell of CrB₄ with pressure. In order to reveal the origin of high hardness, the bond characteristic of CrB₄-type compounds is studied in detail. According to the report of Pan *et al.*^[7], that the bond strength of B-B covalent

bond is stronger than that of Cr-B bond and the B-B covalent bond plays an important role in intrinsic hardness for these CrB₄ compounds. The Cr atom is located in the center of B-B bonds cage and the Cr-B bonds are formed in the inner of B-B bonds cage. It must be worth to note that the Cr-B bond is surrounded by B-B covalent bonds. So we chose three B-B covalent bonds and one Cr-B bond in the B-B bonds cage, and investigated their variations with pressure and plotted in Fig. 2. The four B-B bonds are B-B₁, B-B₂, B-B₃ and Cr-B, respectively, and we label them B-B₁, B-B₂, B-B₃ and Cr-B in this paper. We have drawn the crystal structure of CrB₄ in Fig. 3, and marked the B, B₁, B₂, Cr atom. It can be seen from Fig. 2 that all bonds decrease smoothly with pressure. When the applied pressure is up to 100 GPa, they are shortened by only about 9.1%, 6.8%, 6.9% and 5.6%, respectively. We also make a fitting for these variations and obtain the following quadratic function relationships^[18]:

$$L_{B-B_1} = 1.852960 - 0.00245p + 7.9766 \times 10^{-6}p^2$$

(5)

$$L_{B-B_2} = 1.726330 - 0.00164p + 4.8768 \times 10^{-6}p^2$$

(6)

$$L_{B-B_3} = 1.822190 - 0.00175p + 4.9936 \times 10^{-6}p^2$$

(7)

$$L_{Cr-B} = 2.092430 - 0.0016p + 4.3076 \times 10^{-6}p^2$$

(8)

In above equations, the unit of bond length is

Å and the unit of pressure is GPa.

To further investigate the effect of pressure on the bonding and antibonding states of B-B bonds and Cr-B bond, we plotted the Mulliken overlap population of B-B bonds and Cr-B bond with pressure in Fig. 4. It can be seen from Fig. 4 that the positive value of overlap population for B-B covalent bonds is slowly increasing with pressure, and the negative value of overlap population for Cr-B bond is obviously decreased with pressure. When the applied pressure is up to 100 GPa, The Mulliken overlap population of B-B1, B-B2 and B-B3 bonds are increased by about 2.1%, 6.8%, and 11.2%, respectively. And Mulliken overlap population of Cr-B bond is obviously reduced by about 169%. These results indicate that the bond strength of B - B covalent bond is stronger than that of TM- B bond and the B-B covalent bond plays an important role in intrinsic hardness for these CrB₄ compounds.

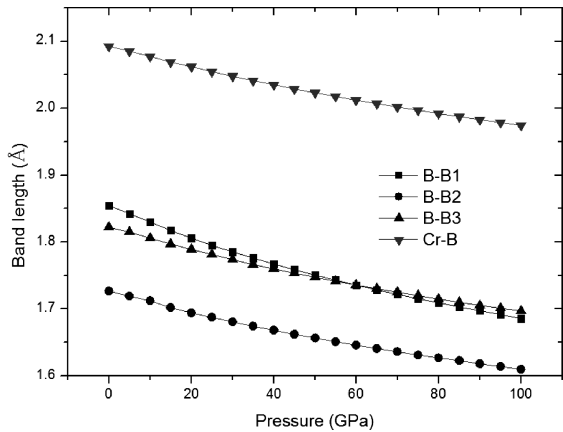


Fig. 2 Variation of bond lengths as a function of pressure

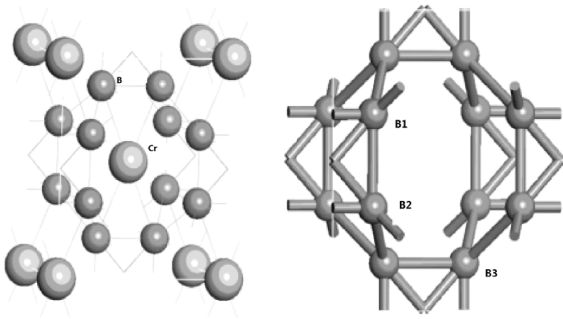


Fig. 3 Crystal structure of CrB₄

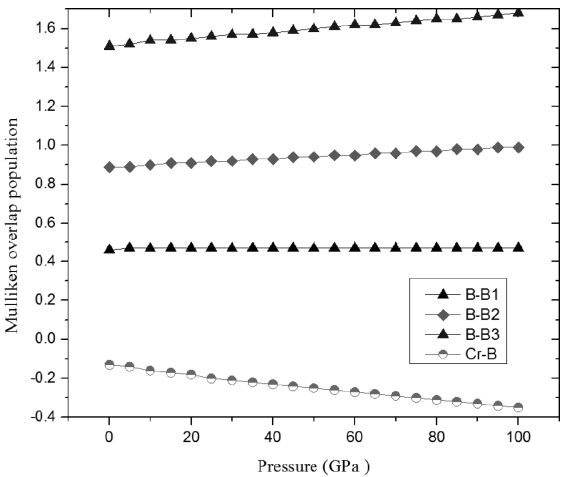


Fig. 4 The Mulliken overlap population of CrB₄ as a function of pressure

3.2 Pressure-induced electronic changes

Understanding the electronic property in detail is essential for further investigation of hard material [19]. In this study, the density of state (DOS) and partial density of state (PDOS) are calculated to investigate the electronic property of CrB₄. The DOS and PDOS of CrB₄ near the Fermi level (set to 0 eV) at zero pressure are shown in Fig. 5. As seen in Fig. 5, CrB₄ is metallic because the value of DOS at the Fermi level (E_F) is not zero, which is in accordance with the result of Pan *et al.* [7]. It can be seen from Fig. 5 that there are four distinct peaks that can be identified in the DOS of CrB₄, two in valence band and two in conduct band. For convenience, we labeled the four peaks V1, V2, C1 and C2, respectively. In order to interpret the formation of the DOS, we also depicted the obtained PDOS in Fig. 5. The calculated results show that the 3d-shell of Cr and 2s-shell and 2p-shell orbitals of B atom play an important role in electron contribution and bond strength, and the electronic distribution has obvious locality. Combining with the PDOSs of Cr and B atoms also shown in Fig. 5, we find the peak V1 is mainly formed by hybridization of B-2p and Cr-3d states; 2p orbital of B atom exhibits strong hybridization with 3d orbital of Cr atom, which results in the formation of the another peak in valence band V2. The overlap means the covalent chemical bonds exist between B atom and Cr

atom, which may be responsible for the high hardness of CrB₄; The peak near the Fermi level C1 is formed mainly by B-2p and Cr-3d states; The peak located in conduct band C2 is dominated by the Cr-3d with a small contribution of B-2p, B-2s and Cr-3d states. Moreover, we calculated the density of state (DOS) at several pressures to investigate the effect of pressure on electronic property of CrB₄.

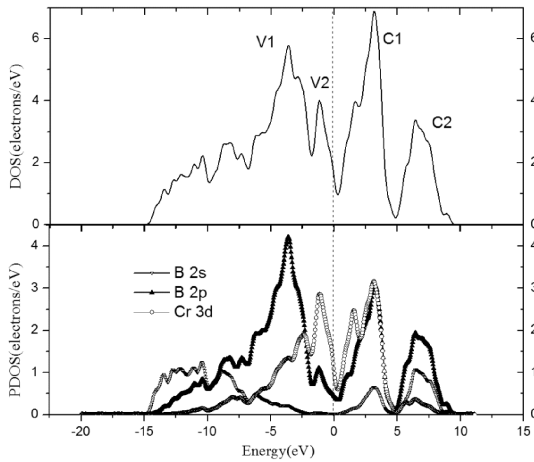


Fig. 5 The DOS and PDOS of CrB₄ at zero pressure

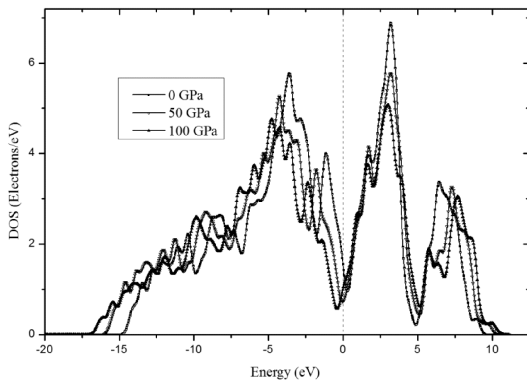


Fig. 6 The DOS of CrB₄ at 0, 50, and 100 GPa

For comparison, we present the DOSs of CrB₄ under 0, 50 and 100 GPa in Fig. 6. From Fig. 6, we find there are general features of the DOS despite the pressure. As pressure increases, the peaks in the bonding region shift a little to the left and the peaks in the antibonding region shift to right. Moreover, all peaks lower their heights with increasing pressure, indicating the reduction in the hybridization energy under high pressure. In Fig. 6, we noticed that the pressure has great

influence on the DOS at E_F , which is an important parameter because the value closely related to the superconductivity of a material.

4 Conclusions

In this paper, the structural and electronic properties of CrB₄ have been studied by using plane-wave pseudopotential density functional theory within the generalized gradient approximation (GGA). The obtained results at ambient pressure are in good agreement with the experimental and theoretical values. Our attention has been focused on the pressure-induced structural and electronic changes. The calculated pressure dependence of structural property shows that both structural parameters and covalent bonds of CrB₄ are insensitive to the pressure, which is significant for its applications under high pressure. Also the density of states (DOS) of CrB₄ versus pressure is successfully calculated. We find high pressure may lower the peak heights of DOS and change its profile.

References:

- [1] Kaner R B, Gilman J J, Tolbert S H. Designing superhard materials [J]. Science, 2005, 308: 1268.
- [2] Varin R A, Chiu C, Li S, *et al.* Application of controlled and electrical discharge assisted mechanical alloying for the synthesis of nanocrystalline MgB₂ superconducting compound [J]. J Alloy Compd, 2004, 370: 230.
- [3] Basu B, Raju G B, Suri A K. Processing and properties of monolithic TiB₂-based materials [J]. Int Mater Rev, 2005, 51: 352.
- [4] Montoya J A, Hernandez A D, Gregoryanz E, *et al.* OsN₂: crystal structure and electronic properties [J]. Appl Phys Lett, 2007, 90: 011909.
- [5] Xu H B, Wang Y X, Lo V C. First - principles study of CrB₄ as a high shear modulus compound [J]. Phys Stat Soli R, 2011, 5: 13.
- [6] Wang B, Wang D Y, Cheng Z X, *et al.* Phase stability and elastic properties of chromium borides with various stoichiometries [J]. ChemPhysChem, 2013, 14: 1245.
- [7] Pan Y, Zheng W T, Guan W M. First-principles study on the structure, elastic properties, hardness

and electronic structure of TMB_i ($TM=Cr, Re, Ru$ and Os) compounds [J]. *J Solid State Chem*, 2013, 207: 29.

[8] Blöchl P E. Projector augmented-wave method [J]. *Phys Rev B*, 1994, 50: 17953.

[9] Kresse G, Joubert D. From ultrasoft pseudopotentials to the projector augmented-wave method [J]. *Phys Rev B*, 1999, 59: 1758.

[10] Hohenberg P, Kohn W. Inhomogeneous electron gas [J]. *Phys Rev*, 1964, 136: B864.

[11] Kresse G, Hafner J. Ab initio molecular dynamics for liquid metals [J]. *Phys Rev B*, 1993, 47: 558.

[12] Kresse G, Hafner J. Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium [J]. *Phys Rev B*, 1994, 49: 14251.

[13] Kresse G, Furthmüller J. Efficiency of ab initio total-energy calculations for metals and semiconductors using a plane-wave basis set [J]. *Comp Mater Sci*, 1996, 6: 15.

[14] Kresse G, Furthmüller J. Efficient iterative schemes for ab-initio total-energy calculations using a plane-wave basis set [J]. *Phys Rev B*, 1996, 54: 11169.

[15] Perdew J P, Burke K, Ernzerhof M. Generalized gradient approximation made simple [J]. *Phys Rev Lett*, 1996, 77: 3865.

[16] Andersson S, Lundstrom T. The crystal structure of CrB_4 [J]. *Acta Chem Scand*, 1968, 22: 3103.

[17] Okada S, Atoda T, Higashi I. Structural investigation of Cr_2B_3 , Cr_3B_4 , and CrB by single-crystal diffractometry [J]. *J Solid State Chem*, 1987, 68: 61.

[18] Zhou M, Lu Z P, Tao Y Q, *et al.* Elastic and electronic properties of $CuAlSe_2$ under pressure: a first-principle study [J]. *J Sichuan Univ: Nat Sci Ed*(四川大学学报: 自然科学版), 2017, 54: 771.

[19] Ao T G, Ying C, Zhao E J. First principles studies on mechanical properties of ZrB_3 and NbB_3 under high pressure [J]. *J Sichuan Univ: Nat Sci Ed*(四川大学学报: 自然科学版), 2017, 54: 547.

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