First-principles study on properties and electron structure of CrB_2(0001) surface

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Abstract: Based on a first-principles density functional plane-wave ultrasoft pseudopotential method, the surface properties of two different types of terminated CrB_2 (0001) are calculated and compared, such as surface relaxation, surface energy and electricity structure. The results of surface relaxation show surface interlayer distance converges rapidly for both terminated CrB_2(0001) when the number of the atoms layers reaches 9. Through analysis of charge density difference and partial density of states (PDOS), it can be concluded that CrB_2 (0001) models with B termination have smaller interface energy, stronger electronic interaction than another models and the form of termination is more stable.

Key words: density functional calculations (DFT); surface relaxation; surface energy; CrB_2(0001)

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0 Introduction

Boron and borides are, generally wear-resistant high-temperature materials, highly desirable and widely used in chemical industry, metallurgy and national defense[1]. Particularly because of superconducting transition temperature of $MgBr_2$, borides have attracted the attention of researchers in the field of physics all over the world[2-3]. There is a great scientific interest in effectiveness and reliability of boron for grain refinement of pure Al and Al alloys in practice. There is growing concern about AlB_2 characterized by high hardness, high melting point and antioxidant capacity. The potency of AlB_2 inoculation for grain refinement of Al-Si alloys has been demonstrated[4].

The theoretical studies about surface properties have the important guiding sense to grain refining mechanism of the solidification structure of the light metallic structural materials, such as Mg, Al and Ti alloys. The first-principles calculations with density functional theory (DFT) is the ideal research approach to surface properties[5-6]. First-principles calculations make it possible to deeply explore surface properties in theory and practice. In this paper, surfaces properties of CrB_2 (0001) are studied by using the first-principles method, such as surface relaxation, charge density difference and partial density of states (PDOS).

1 Methodology and details

The data associated with surface properties are performed with Cambridge sequential total energy package (CASTEP) package of materials studio. In order to ensure the accuracy of the test data, generalized gradient approximation (GGA) is used for the exchange correlation between electrons in this work. Ultrasoft pseudopotentials that allows the calculation to be performed at a lower energy cutoff is utilized[7-8]. The value of plane-wave cutoff energy is set to 400 eV by a test. The value of k point is set to $12\times 12\times 12$ for bulk, and $10\times 10\times 1$ for both terminated CrB_2(0001). Self-consistent field (SCF) tolerance of energy calculation is set to 1.0×10^{-5} eV/atom.

2 Results and discussion

2.1 Bulk properties

The surface is established by periodic slabs. Some critical parameters such as k-point sampling grids, cut-off are identified after several tests to control calculated results within an acceptable energy range. The CrB_2 phase is hexagonal structure similar to AlB_2[4]. The space group symmetry is P6/mmm. By means of geometry optimization, the calculated

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lattice constant for bulk of CrB_2 is obtained. The calculated values $a=2.96$ Å, $c=2.687$ Å are almost consistent with the experimental values $a=2.969$ Å, $c=3.066$ Å[9]. There is reason to believe that the selection of the critical parameters in geometry optimization is accurate and reliable.

2.2 Surface convergence

Determination of the number of slabs is critical to show the bulk-like characteristic interiors. There is no doubt that the more the number of slab layer is set, the more accurate the results obtained by this method. Considering the high cost of computational time, the number of slab layer is selected reasonably. Surface relaxation tests on the CrB_2(0001) slabs are bound to carry out firstly to ascertain slab thickness. Both Cr-terminated CrB_2 (0001) and B-terminated CrB_2 (0001) are fabricated on the surface of CrB_2(0001). The convergence test is conducted by choosing five different kinds of atoms model with 3, 5, 7, 9 and 11 slabs. A vacuum gap (thickness = 10 Å) is inserted to eliminate periodical effect in Z direction.

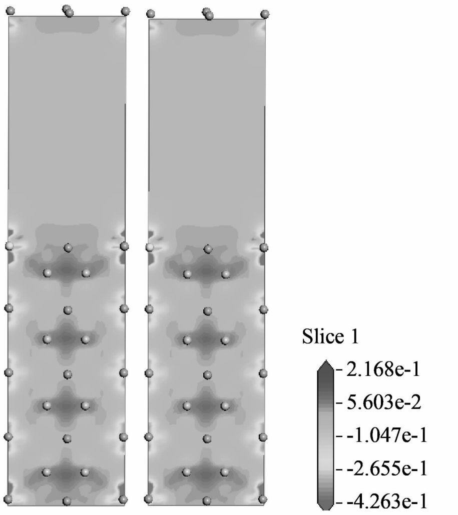
After full relaxation of surface structure, surface electrons are redistributed to achieve a more stable structure (shown as Table 1). Table 1 shows the change of adjacent slabs distance in percent of the distance in the bulk for two different terminations. According to the result of relaxation, the fluctuation range of the interlayer spacing increases obviously and when the number of layers reaches 9 slabs, surface relaxation tends to converge. No matter how many layers and what kind of terminated form, the more outer atomic layers is, the more obvious the changes of the interlayer distances of both terminations are.

Table 1 CrB_2(0001) surface relaxations change (Δ_{ij}) convergence on termination and atom layers

Interlayer	Termination	Atoms layers of slab			
		5	7	9	11
Δ_{12}		14.93	−17.02	−18.16	18.02
Δ_{23}		2.2	5.3	6.59	7.06
Δ_{34}	Cr		−3.2	−5.4	−6.57
Δ_{45}				0.1	0.2
Δ_{56}					0.1
Δ_{12}		4.5	5.91	5.47	6.23
Δ_{23}		−4.9	6.09	−5.52	−6.61
Δ_{34}	B		0.8	5.3	7.43
Δ_{45}				−0.2	0.3
Δ_{56}					0.2

2.3 Electronic structure

The total valence electron densities for the 9 relaxed CrB_2(0001) models are shown in Fig. 1. By comparing Figs. 1(a) and (b), some significant differences in the surface bonding characteristics can be found. Negative value indicates losing electron area and positive value indicates obtaining electron area for charge density difference scale in Fig. 1. The value of charge density difference for B atoms is the positive values. Charge distribution is possessed of the marked directivity. A very large number of positive charges are accumulated between B atoms in the same layer. According to the above characteristic, it is concluded that adjoining B atoms exist in the form of covalent bond way. A finite amount of charge is transferred from Cr to B between adjacent layers. The adjacent layers have strong ionic bond. By contrast, Cr-B ionic bond of Fig. 1(a) is stronger than that of Fig. 1(b) and electronic interaction of 1st layer in Fig. 1(a) is stronger than that of 1st layer in Fig. 1(b), which indicate B-termination is more stable than Cr-termination.



(a) B-termination (b) Cr-termination

Fig. 1 Charge density difference for CrB_2(0001)

2. 4 Surface energies of CrB_2(0001)

Surface energy is an important physical parameter. Surfaces with the lowest surface energy are supposed to the most stable. So, the surface energy are often used to determine about nucleation potency of some particles for liquid metal melts from the viewpoint of thermodynamics. The surface energy can be expressed by the equation as follows[10]

$$\gamma_s = \frac{1}{2A_s}(E_{\text{slab}}(N) - NE_{\text{bulk}}), \tag{1}$$

where $E_{\text{slab}}(N)$ is the total energy of surface slabs, N is the total of surface super-cell slab, E_{bulk} is the total energy per atom of bulk after energy optimization. But, for surface energy of CrB_2 (0001), which is characterized by non-stoichiometry, Cr and B_2 chemical potentials should be synthetically put into consideration. So, the surface energies of both terminated CrB_2 can be expressed as[11-14]

$$\gamma = \frac{1}{2\mathring{A}}(E_{\text{slab}} - N_B\mu_B - N_{Cr}\mu_{Cr} + PV - TS), \tag{2}$$

where $\mathring{A}$ is surface area of slab.

Based on 0 K and constant pressure conditions, PV and TS can be ignored. Chemical potential of bulk material is[13-14]

$$\mu_{CrB_2}^{\text{bulk}} = \mu_{Cr} + 2\mu_B. \tag{3}$$

For the non-stoichiometric CrB_2 (0001) models, the surface energy γ can be ascertained as

$$\gamma = \frac{1}{2\mathring{A}}[E_{\text{slab}} - N_{Cr}\mu_{CrB_2}^{\text{bulk}} + (2N_{Cr} - N_B)\mu_B]. \tag{4}$$

Fig. 2 shows that B-terminated is smaller than that of Cr-terminated one under the B-rich condition. On the contrary, Cr-terminated surface engery is smaller under the Cr-rich condition. According to the theory of thermodynamics, the $\mu_{CrB_2}^{\text{bulk}}$ equals the sum of CrB_2 formation heat $\Delta H_f^0(CrB_2)$ and chemical potentials of bulk Cr and B_2

$$\mu_{CrB_2}^{\text{bulk}} = \mu_{Cr}^{\text{bulk}} + 2\mu_B^{\text{bulk}} + \Delta H_f^0(CrB_2). \tag{5}$$

Using Eq. (4), the value of formation enthalpy of bulk is −0. 936 3 eV. The chemical potential of each element in the slab have to be less than that of its bulk as: $\mu_B \leqslant \mu_B^{\text{bulk}}$ and $\mu_{Cr} \leqslant \mu_{Cr}^{\text{bulk}}$, which is the base for the formation of the stable slabs structure. The following inequity can be obtained[15]

$$\frac{1}{2}\Delta H_f^0(CrB_2) \leqslant \mu_B - \mu_B^{\text{bulk}} \leqslant 0. \tag{6}$$

According to above conditions, the linear relationship between surface energies of CrB_2 (0001) and chemical potential difference between before and after relaxation for boron can be obtained in Fig. 2.

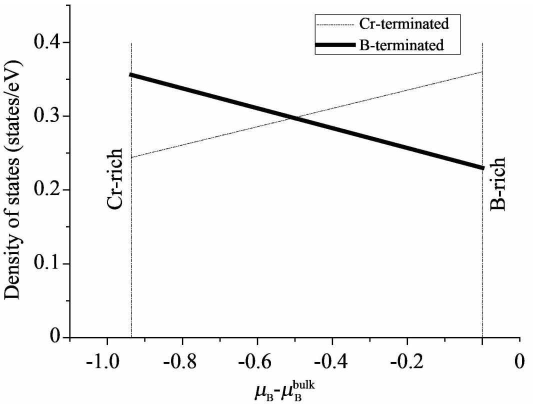
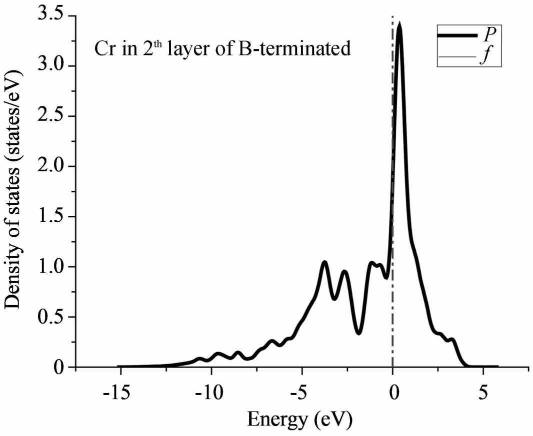


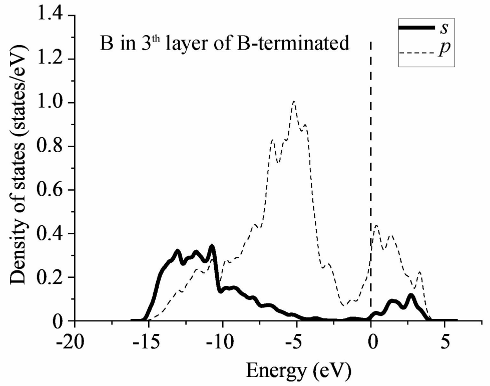
Fig. 2 Linear relationship between surface energies of CrB_2 (0001) and chemical potential difference

2. 5 Interfacial bonding

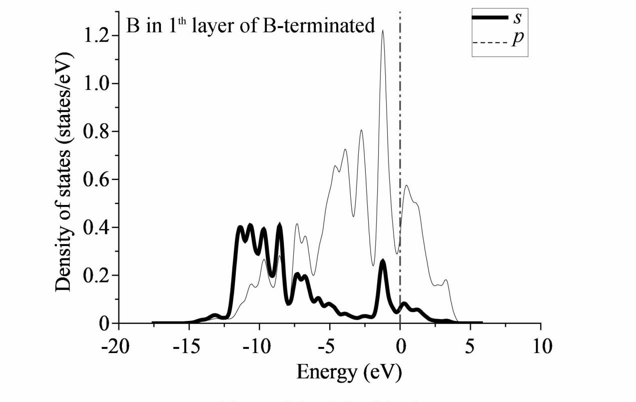
The PDOS of three different structures: B-terminated and Cr-terminated bulk are shown as Figs. 3—5. In the analysis of PDOS, the different atom layers are examined. Some critical information can be gained from the PDOS.



(a) Partial DOS of 2nd layer Cr

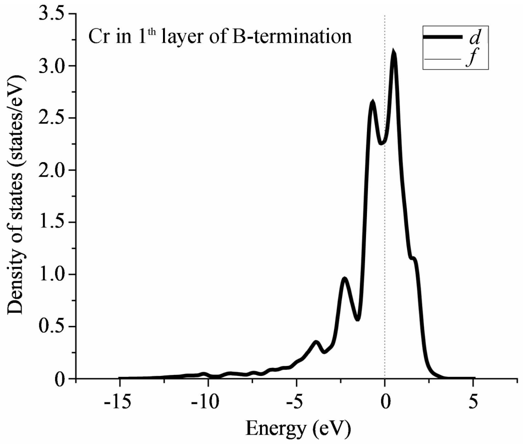


(b) Partial DOS 3 rd layer B

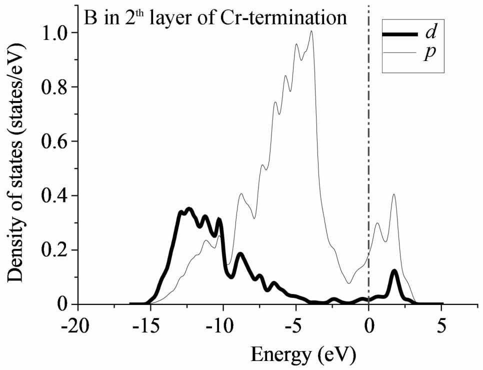


(c) Partial DOS of 1st layer B

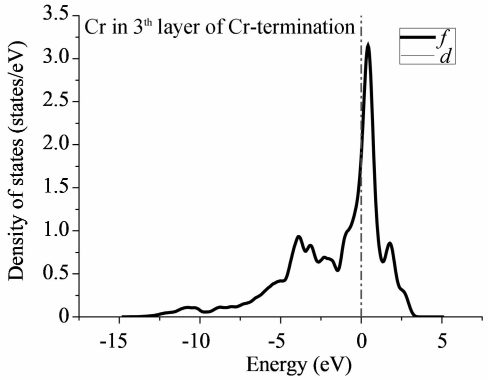
Fig. 3 Partial DOS of B-terminated surface



(a) Partial DOS of 1st layer Cr



(b) Partial DOS of 2nd layer B



(c) Partial DOS of 3rd layer Cr

Fig. 4 Partial DOS of Cr-terminated surface

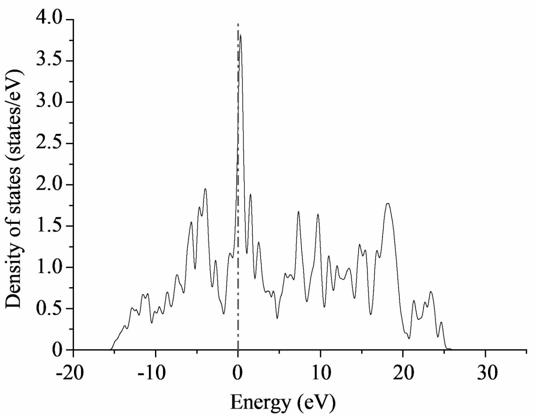


Fig. 5 DOS of bulk

There is pseudogap near the Fermi level among PDOS of bulk. This phenomenon are caused by B-B covalent bonds. The PDOS curves' shape of CrB_2(0001) are sharp and localized near the Fermi surface, which indicates CrB_2(0001) has the typical metallic features. The PDOS of B in 1st layer of B-termination shows more occupied states near the Fermi level than that of other layers. So, the B atoms exhibit the metallic property, but the curves of B in other lay tend to be similar, as shown in Figs. 2(b—c) and Fig. 3(b). The curves of Cr atoms distribute near the Fermi level more concentratively in both terminated surface (Fig. 2(a) and Fig. 3(a—c)). There is the valley of Cr in 1st layer around Fermi level (Fig. 3). That is radically different from other layers when pseudogap never exists (Fig. 2(a) and Fig. 3(c)). These phenomenon demonstrate that the first layer of B-terminated CrB_2 (0001) has covalent features than the third layer.

3 Conclusion

The plane-wave soft-pseudopotential method based on density functional theory is adopted to calculate the surface properties. According to the interlayer space variation of 11 layers, it is easy to find surface interlayer distance converges rapidly, as slab thickness increases and primarily takes place in the top four layers. Surface energy of B-terminated CrB_2(0001) is smaller than that of Cr-terminated one under the B-rich condition. On the contrary, Cr-terminated CrB_2 (0001) surface energy is smaller under the Cr-rich condition. On the whole, B-terminated CrB_2(0001) surfaces has smaller surface energy and more thermodynamically stable than the Cr-terminated one. The first layer of B-terminated CrB_2(0001) has exhibited more covalent feature over the first layer of Cr-terminated CrB_2 (0001) characterized by more metallic feature. The outermost electronic interaction of B-terminated (0001) is much stronger and surface structure is more stable.

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CrB_2(0001)表面特性和电子结构的第一性原理研究

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摘　要： 基于第一性原理的密度泛函平面波赝势方法，对两种不同终端 CrB_2(0001)的表面性能：表面弛豫、表面能和电子结构等进行了计算和分析。当 CrB_2(0001)表面结构原子层数达到 9 时，表面层间距快速收敛。通过分析差分电荷密度和态密度(PDOS)，可以得出硼终结 CrB_2(0001)表面结构比铬终结CrB_2(0001)具有较小的界面能和较强的电子相互作用，表面更稳定。

关键词： 密度泛函计算(DFT)；表面弛豫；表面能；CrB_2(0001)

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