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Electronic and bonding properties of TiB_2

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Abstract

The structural and electronic properties of TiB_2 have been calculated using the first-principles total-energy pseudopotential method based on density functional theory. It is shown that the calculated lattice constants and heat of formation of TiB_2 are in good agreement with the experimental results. By analyzing the band structure, density of states and Mulliken population, it is found that the bonding nature in TiB_2 is a combination of ionic, covalent and metallic. The 2s–2p interaction exists in the close-packed layer of boron atoms. The hybridization of Ti-3d and B-2p from different layers is the main reason for the creation of pseudogap and results in the strong interlayer covalent bonding. In the same time, the charge transfer from titanium to boron is as significant as 1.16 electrons in the present case. The d–d resonance and free-electron 3d states of titanium atoms contribute to the covalent and metallic bonding in the layer of titanium atoms.

Keywords: TiB_2; First-principles total-energy calculations; Electronic structure

1. Introduction

As one of the AlB_2-type transition-metal diborides, TiB_2 possesses many unique physical properties, such as high melting point, hardness, chemical stability, high thermal conductivity, low electric resistivity and low work function [1]. The application of TiB_2 mainly includes the in situ particulate-reinforced composites, grain refiner, light-weight high-temperature structural materials, impact resistant armor, cutting tools, wear resistant coatings, and so on [2–5]. The reports on experimental and theoretical TiB_2 studies cover many fields including physics, chemistry and materials sciences at present. Many papers have been published on the structural and physical properties of the diborides in the past decades. Perkins and Sweeney calculated the band structure of TiB_2 by a tight-binding method and found the existence of the graphite band structure [6]. By virtue of the augmented plane-wave (APW) calculations and X-ray photoelectron spectroscopy (XPS), Ihara et al. figured out that the band structure of ZrB_2, whose structure is similar to TiB_2, is determined by the sp^2 hybrid state and p_z state of boron and the d and s states of zirconium, and the bonding nature of ZrB_2can be explained by a combination of the graphite model of the boron network and the hcp-metal bonding model of zirconium [7]. On the basis of orbital overlap, the electronic structures of solid metal borides with the AlB_2-type structure were studied by Burdett et al. [8]. It was found that the interaction of the orbitals of the transition-metal with those of a planar, graphite-like net of boron atoms and the interaction with those of other metals are both important in influencing the properties of these species. Subsequently, Tian et al. also calculated the electronic structure of TiB_2 using the self-consistent linear muffin-tin orbitals (LMTO) with the atomic sphere approximation (ASA) [9,10]. They found that the Ti–B covalent bonding is as important as other bonds in influencing the physical properties of TiB_2. Recently, Vajeeston et al. further investigated the electronic structure and ground-state properties of AlB_2-type diborides using the tight-binding LMTO method [11]. However, they considered that the TM–TM (transition-metal) and TM–B interactions are less significant than the p–p covalent interaction of boron atoms. Meanwhile, making use of the electron-energy-loss spectroscopy (EELS) and full potential linearized augmented plane-wave method (LAPW), Lie et al. studied the unoccupied electronic states of TiB_2 and observed the hybridized electronic states between the boron-p and titanium-d bands [12,13]. With regard to the bonding nature of the transition-metal diborides, the present results of the above approaches are not consistent with each other. In this paper, the electronic and bonding properties of TiB_2, as one of the transition-metal diborides, are investigated using the

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first-principles total-energy plane-wave pseudopotential method based on density functional theory (DFT) and the results are compared with experiments and other theoretical calculations.

2. Crystal structure and computational details

The crystal structure of TiB_2 is AlB_2-type with the space group symmetry *P6/mmm* which is designated as *C32*. It adopts a layered hexagonal structure with alternating close-packed hexagonal layers of titanium and graphite-like boron layers. The atoms are positioned at Ti (0, 0, 0), B (1/3, 2/3, 1/2) and B (2/3, 1/3, 1/2) in the unit cell with lattice parameters of $a = 3.028$ Å and $c = 3.228$ Å. The crystal structure and Brillouin zone (BZ) of TiB_2 have been reported in earlier publications [8,9].

The calculations of the electronic structure and ground-state properties of TiB_2 were performed using a total-energy plane-wave pseudopotential method based on DFT, which employs special point integration over the BZ and a plane-wave basis set for the expansion of the wave functions [14–17]. The minimum total-energy of the structure is achieved by automatically relaxing the internal coordinates using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [18]. The ultrasoft pseudopotential was used for all atoms, which generated that the atomic configurations of Ti and B were $3s^2 3p^6 3d^2 4s^2$ and $2s^2 2p^1$, respectively [19]. Two separate approximations to the exchange-correlation functional were used: the traditional local density approximation (LDA-CA-PZ) [20,21] and the generalized gradient approximation (GGA-PBE) [22]. The plane-wave cutoff energy of 380 eV was employed in the calculations, which assured a total-energy convergence of 10^{-6} eV atom^{-1}. BZ sampling was performed using a $10 \times 10 \times 8$ Monkhorst-Pack k-points mesh [23]. Mulliken charges population was also calculated according to the formalism described by Segall et al. [24,25].

3. Results and discussion

3.1. Optimization of structure

The results for the lattice parameters, equilibrium volume, cohesive energy and heat of formation of TiB_2 calculated by GGA and LDA are shown in Table 1, where the experimental results and other calculations are also presented. It is found that the lattice constants calculated by GGA are in more satisfactory agreement with the experimental values than those calculated by LDA in our results, Hartree–Fock method and TB-LMTO in other calculations. The LDA lattice constants, *a* and *c*, are 1.28% and 2.2% smaller than experimental results, which comes from the "overbinding" commonly found in LDA calculations. The values of cohesive energy achieved by GGA, LDA and TB-LMTO differ largely. Being lack of experimental data, it is difficult to judge which result is more precise. Both GGA and LDA more accurately reproduce the experimental heat of formation of TiB_2, as compared to the TB-LMTO. Overall, it is concluded that the GGA yields the best agreement with experiment, and the following calculation results are based on the GGA.

3.2. Electronic structure of TiB_2

Fig. 1(a) and (b) presents, respectively, the energy bands of TiB_2 along high-symmetry lines of the Brillouin zone and the total density of states (DOS) of TiB_2. The curves in Fig. 1 are similar to those in earlier literature [6,8–11]. The DOS of TiB_2 possesses finite value at the Fermi level, which indicates the metallic feature of TiB_2 in its crystalline state. Therefore, TiB_2 occupies excellent thermal conductivity and low electric resistance. There are five main peaks (A, B, C, D and E) in the total DOS curve of TiB_2. The peaks A and B in the lower energy part of the DOS curve arise from the Ti-3s and -3p states, respectively, which are localized and contribute little to the bonding of TiB_2. The broad peaks C, D and E corresponding to the B-2s, -2p and Ti-3d, -4s states are mainly bonding states of TiB_2 and a "pseudogap" exists between the peaks D and E.

The bonding properties of TiB_2 can be seen from the partial DOS near the Fermi level, as shown in Fig. 2. Vajeeston et al. considered that the B-s electrons in TiB_2 are localized and naturally its effect on bonding is very small [10]. It is seen from Fig. 2(e) that the width of the B-2s states is from −15 eV to 20 eV and there are a number of peaks in the B-2s states. In the same time, the integrated intensity of the B-2s states below the Fermi energy is about one, which indicates there is only one valence electron on the 2s states of B atom after bonding. These features of the B-2s states imply that there are s–p interactions

Table 1
Comparison of lattice parameters, equilibrium volume (V_0), cohesive energy (E_{coh}) and heat of formation (ΔH) for TiB_2; HF: Hartree–Fock, Exp.: experimental results

	a (Å)	*c* (Å)	*c*/*a*	V_0 (Å^3/cell)	E_{coh} (eV/cell)	$-\Delta H$ (eV/cell)
GGA[a]	3.0292	3.2196	1.063	25.585	20.9109	3.382
LDA[a]	2.9891	3.1568	1.056	24.426	24.2048	3.391
TB-LMTO[b]	3.070	3.262	1.063	26.628	53.8459	3.197
HF[c]	3.027	3.240	1.0704	–	–	–
Exp.	3.028[d]	3.228[d]	1.060[d]	25.632[d]	–	3.401[e]

[a] Present results.
[b] Ref. [11].
[c] Ref. [26].
[d] Ref. [27].
[e] Ref. [28].