Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Materials Letters 60 (2006) 1433 – 1436
materials letters
www.elsevier.com/locate/matlet

Electronic structure of some mono-, semi-titanium boride and diboride

B. Mouffok [a], H. Feraoun [a,b], H. Aourag [a,b,*]

[a] Laboratoire de Synthèse de l'Information Environnemental, Université de Sidi-belabbes 22000, Algeria
[b] Laboratoire d'Etude et de Prédiction de Matériaux, URMER, Université de Tlemcen, 13000, Algeria

Received 10 July 2005; accepted 10 November 2005
Available online 3 January 2006

Abstract

The electronic structure and chemical bonding mechanism of TiB, Ti_2B and TiB_2 are studied on the basis of charge density and total density of states and band structure calculations using the full-potential linearized augmented-plane-wave method (FP-LAPW). Results demonstrate the origin of the bonding formation in these compounds.

Keyword: Electronic structure

1. Introduction

Within the actual increasing interest and impetus in the search for materials possessing specific and desired properties, the transition metal borides are essentially interesting because they have some unique properties such as high melting point, hardness, durability, wear resistance, chemical stability and metallic properties: high thermal conductivity, low electrical resistivity and low work function. More precisely, the titanium diboride compound is a target candidate for the development of light-weight high-temperature structural materials [1], since it has the highest melting point and largest cohesive energy. Instead of the large number of both experiments and theoretical explanations of the bonding nature of this compound, it still remains not very clear. We have tried to explain the bonding nature in this compound using comparison with the mono- and semi-titanium borides (TiB and Ti_2B), and the titanium diboride (TiB_2).

We present the results of Full Potential Linear Augmented Plane Wave (FP-LAPW) calculations on mono- and semi-titanium borides (TiB and Ti_2B), and the titanium diboride (TiB_2). In the following sections, the calculation method is illustrated; the crystalline structures of the studied compounds are presented with the calculated parameters which were optimized in the present calculations. Next, the density-of-state histograms and the electron charge density plots are used to discuss the bonding nature in these.

2. Method of calculation

Our calculations were performed using the Full Potential Linear Augmented Plane Wave method (FP-LAPW) as embodied in the WIEN2k-code [2] in a scalar relativistic version without spin orbit coupling [3], which has proven to be one of the most accurate methods for the computation of the electronic structure of solids within density functional theory. In the FP-LAPW method, the unit cell is divided into two parts: atomic spheres centred on the atomic sites and an interstitial region. Inside the atomic spheres, the basis set used to describe electronic states employs atomic-like functions, while in the interstitial region, plane waves are used. Exchange and correlation effects were treated using the generalized gradient approximation (GGA) as described by Perdew et al. [4].

3. Results and discussion

3.1. Crystal structure

The transition metal diboride crystallizes in the AlB_2 type structure that is designated as C32 [5]. It has a simple hexagonal symmetry (D_{6h}) with space group *P6/mmm*, in which close packed TM layers alternate with graphite like boron sheets. The boron atoms form hexagons with three nearest neighbours in the same plane (Fig. 1a). The TM atoms lie

* Corresponding author. Laboratoire d'Etude et de Prédiction de Matériaux, URMER, Université de Tlemcen, 13000, Algeria.
E-mail address: h_aourag@mail.univ-tlemcen.dz (H. Aourag).

0167-577X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.11.085

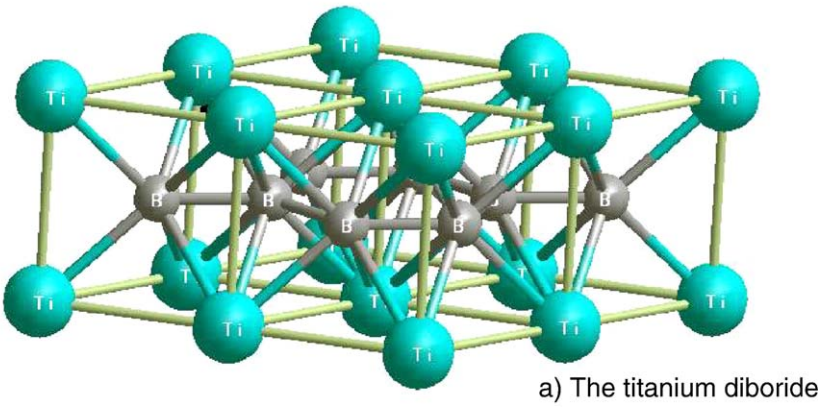

Fig. 1. The crystalline structures of for titanium diboride (a) and for titanium semiboride (b).

exactly on the centre of the B-hexagons, with six TM nearest neighbours. Hence, even they seem to be layered compounds, the interlayer interaction is very strong in the TMB_2 crystal structure. Taking one formula per unit cell, the TM atoms would occupy the (0,0,0) position when the two boron atoms would be positioned at (1/3,2/3,1/2) and (2/3,1/3,/1/2). This structure attracts a large interest due to the discovery of high T_c superconducting MgB_2 [6].

There is no general agreement on the crystal structure of the monoborides, even if it is believed to exhibit cubic symmetry. Pearson [7] reported the titanium monoboride in the NaCl structure. The semi-borides have a body centred tetragonal (Al_2Cu type) structure (D_{4h}^{18}) [8] with space group *I4/mcm*. There are, hence, six atoms in the conventional tetragonal cell that are TM(1/6,2/3,0), TM(5/6,1/3,0), TM(1/3,1/6,0), TM(2/3,5/6,0), B(0,0,1/4) and B(0,0,3/4) (Fig. 1b).

For each compound, the crystalline structures were optimized with respect to the total energy to determine the lattice parameters: *a*, *c* and *c*/*a* ratio. The total energy variations with respect to volume change were then fitted to the Murnaghan equation of state [9] to determine the bulk modulus and its derivative. For the mono-borides, selected crystalline structures were compared and the results confirm that that of the B_1 is the most stable (in agreement with Pearson [7]). Tables 1–3 summarize the results compared to experiments and other calculations when available.

Table 1
Structural properties of TiB_2

	a_0 (Å)	c_0 (Å)	V_0 (Å^3)	B (Mbar)	c/a
Actual work	3.031	3.231	25.77	2.538	1.066
Ref [10]	3.029	3.229	25.65	2.400	1.066
Ref [11]	3.030	3.230	25.68	–	1.066

Table 2
Structural properties of TiB

	V_0 (Å^3)	a_0 (Å)	c_0 (Å)	B (Mbar)	c/a	E_0 (eV)
B1_TiB	23.38633	4.5395	4.5395	1.704672	1.	−23,916.96536
B2_TiB	21.71961	3.5153	3.5153	1.749248	1.	−23,916.24386
$L1_0$_TiB	21.37099	4.20617	3.4166	1.743072	0.8123	−23,916.46082

Table 3
Structural properties of Ti_2B

	V_0 (Å^3)	a_0 (Å)	c_0 (Å)	B (Mbar)	c/a	E_0 (eV)
Actual work	76.32431	5.666	4.754	1.611	0.839	−94,313.68788
Ref [12]	74.89378	5.864	4.356	2.61	0.742	–