

THE ELECTRONIC STRUCTURE AND GROUND STATE PROPERTIES OF Ti_2B , TiB and TiB_2 .

P. Vajeeston, and R. Asokamani

Department of Physics
Anna university
Chennai- 600 025.

In this paper, the electronic structure and ground state properties of the Titanium borides (Ti_2B , TiB and TiB_2) calculated using the self consistent Tight-Binding Linear Muffin-Tin Orbital method are reported. We have carried out a systematic electronic structure studies for these Titanium borides for different volumes. We deduced from the above high pressure studies the equilibrium volume, Bulk modulus (B_0) and its pressure derivative (B_0'), cohesive energy (E_c), heat of formation (ΔH) and electronic specific heat coefficient (γ). These values are compared with the available experimental and other theoretical calculations. The bonding nature of these borides is analysed via the charge density histogram. The existence of pseudo gap in the total density of states is found to be a common feature for these compounds.

Introduction

Transition-metal borides have several unique properties such as high melting point, hardness, chemical stability and metallic property. They have attracted researchers in different fields. Many experimental and theoretical studies have been done on these materials. However, the bonding nature of these compounds is not very clear¹. The transition-metal semi borides of the form TMB_2 form a class of essentially intermetallic compounds. All known transition metal semi borides crystallize in the Al_2Cu (I_4/mcm) structure². Besides the transition-metal – transition-metal interaction, the bonding mechanism also exhibits Ti-d, B-p hybridization. The mono borides have INVAR behavior³ and the glass-forming ability of boron in transition metals. Pettifor and Padloucky have explained the structure of the p-d bonded A-B compounds⁴. The TiB crystallize in FeB structure⁵. A tight binding calculation of TiB_2 was performed by Perkins and Sweeney⁶ who found strong evidence of graphite band structure. Burdett et al⁷ studied the electronic structure of transition-metal borides with the AlB_2 structure and found that the interaction of the orbitals of the transition metal with those of other metals are both important in influencing the properties of these species. The purpose of this paper is to study the electronic structure, bonding nature and other properties of Ti_2B , TiB

and TiB_2 through the self consistent Tight-Binding Linear Muffin-Tin Orbital(TBLMTO) method with the atomic sphere approximation(ASA). The results are compared with experimental and other theoretical investigations.

The crystallographic structure of the titanium borides

The crystal structure of the titanium semi boride described in this paper is isomorphous to the body centered tetragonal (Al_2Cu - type) structure²: space group D_{4h}^{18} ($I4/mcm$). The tetragonal unit cell contains four atoms. These atoms are found in the following special positions of the space group specified⁵ at $B(0\ 0\ 1/4)$, $B(0\ 0\ 3/4)$, $Ti(1/6\ 2/3\ 0)$, $Ti(-1/6\ -1/3\ 0)$, $Ti(2/3, -1/6\ 0)$ and $Ti(-1/3\ -1/6\ 0)$. There exists an ambiguity regarding the crystal structure of TiB . Wyckoff⁵ reported TiB in FeB structure, whereas Pearson⁸ and Landolt-Börnstein⁹ report NaCl and ZrS structure respectively. However, recent investigations³ have confirmed the FeB configuration. In our calculations, we have taken the Orthorhombic FeB structure with the unit cell containing four molecular units. The atomic arrangement for the FeB structure is based on the space group $Vn1b(pbnm)$ with all atoms in symmetry planes². The atomic positions are $Ti(-.058,-1/4,.591)$, $Ti(.54\ 1/4\ -.591)$, $Ti(.942\ -1/4\ .154)$,

Ti(-.942 ¼ .154), B(0.354 ¼ -.154), B(-.354 -1/4 -.183), B(.646 -1/4 -.56) and B(-.646 ¼ .562). The boron atoms are in very close contact with one another as well as with the surrounding metal atoms. Each boron atom has two boron neighbors. The crystal structure of TiB₂ is A1B2 type which is designated as C32. It is a simple-hexagonal lattice in which HCP Ti layers alternative with graphite like B layers. By choosing appropriate primitive lattice vectors, 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^{1,10}. This structure is quite close packed, and can be dealt with efficiently and accurately by the TBLMTO-ASA method. In Table 1 we have listed the calculated and experimental crystallographic parameters of Ti₂B, TiB and TiB₂, the calculated values are in very good agreement with the experimental data.

Computational details

The conventional LMTO-ASA method as well as its transformation to a localized representation (TB-LMTO)¹¹⁻¹³ are well described in literature. We have performed self-consistent scalar relativistic calculations using the 'frozen core' approximation and von-Barth-Hedin¹⁴ parameterization of the exchange - correlation potential. Combined correction has been taken into account. 554, 145 and 1456 K-points are taken in the irreducible wedge of the Brillouin zone (IBZ); for the tetrahedron method of integration¹⁵ for Ti₂B, TiB and TiB₂ respectively. In ASA, the crystal is divided into space-filling, and therefore slightly overlapping, spheres centered on each of the atomic sites. The ground state total energies have been calculated self-consistently as a function of unit cell volume for each compound and the corresponding total energies were evaluated (Fig.1). The bulk modulus are calculated by using the Vinet's equation of state (EOS)¹⁶. The heat of formation and cohesive energy are calculated as following procedure similar to what we have made earlier.^{17,18}

Results and discussion

A detailed comparative study on the three compounds Ti₂B, TiB and TiB₂ on the thermal, chemical and cohesive properties is reported. Nature of bonding in these compounds are analyzed using the charge density histogram and the charge transfer between the atoms.

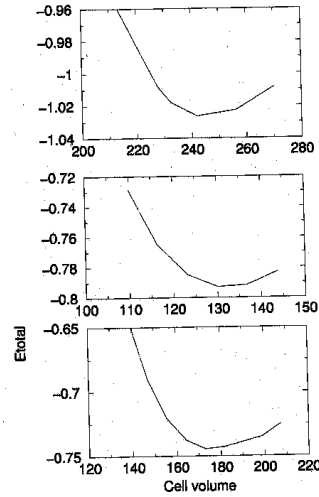
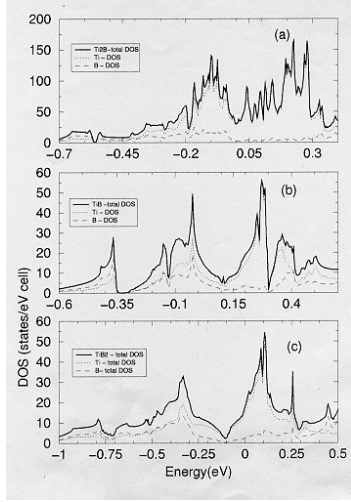


Fig.1 Total cell volume versus total energy curve for Ti₂B, TiB and TiB₂.

Table 1. The crystallographic data for transition-metal titanium borides.

Compound	Lattice parameter	
	Calculated	Experimental
Ti ₂ B	A=5.864	A=6.100
	C=4.356	C=4.53
TiB	A=6.034	A=6.120
	B=3.002	B=3.060
	C=4.537	C=4.560
TiB ₂	A=3.026	A=3.028
	C=3.213	C=3.228

The essential contribution to the cohesion of the transition metal compounds is the broadening of transition metal(TM) d band and the hybridization between TM-d and the B-p states, filling bonding or antibonding states will increase or decrease the cohesion(or stability). Since the rigid-band model describes the electronic structure of the borides well, band filling can be regarded as being responsible for the variations of their electronic structure and related properties. W_v and W_p denote the energy distance from bottom of valance band to the Fermi level(the width of the valance band) and the pseudogap, respectively. Since W_v represents the width of occupied states and W_p the width of bonding states, W_v/W_p can be used to describe the occupied portion of the bonding states. When W_v/W_p is larger than unity, the bonding states can no longer accommodate their valence electrons and the non-bonding states have to be filled, W_v/W_p decides the stability of the system.



TiB₂ is a stabler compound with $W_v/W_p \approx 1$ followed by Ti₂B with $W_v/W_p = 0.906$ and finally TiB with $W_v/W_p = 0.8$. This sequence of stability is further enclosed by their $N(E_F)$ values as seen in Table 2.

Table 2. The cohesive energy (E_{coh} in eV/atom), heat of formation ($-\Delta H$ in eV/atom), bulk modulus (B_o in Mbar), bulk modulus derivative (B_o'), the width of the valence band W_v that of the bonding states W_p , W_v/W_p , electronic specific-heat coefficient (γ in $mJ mol^{-1}K^{-2}$) and $N(E_F)$ (States/Ry/Cell) of titanium borides.

Calculated parameters	Ti ₂ B		TiB		TiB ₂	
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
E_{coh}	0.835	---	0.469	--	1.225	---
$-\Delta H$	0.0362	---	0.356		0.0674	---
B_o	2.61	---	2.42	2.40	2.24	2.38 ²⁰
B_o'	3.191	---	2.98	---	2.1	---
W_v	0.68	---	0.60	---	0.99	0.96
W_p	0.75	---	0.85	---	0.98	0.97
W_v/W_p	0.906	---	0.83	---	1.01	0.90
γ	14.52	---	2.95	---	0.74	1.08
$N(E_F)$	83.723	---	17.03	---	4.27	1.20

Fig.2 The total densities of states of the (a)Ti₂B (b) TiB and (c) TiB₂, with Fermil energy = -0.0464, -0.054 and -0.076 eV, respectively.

The presence of pseudogap is a common feature of all binary transition metals. Pseudogap is observed in these compounds as seen from density of states histograms as shown in Fig.2. The pseudogap is due to the competing effect of the d-d resonance and the strong hybridization between Ti - 3d and B-2p states. A strong Ti-B interaction leads to a high melting point and hardness in TiB₂ than the hcp titanium.

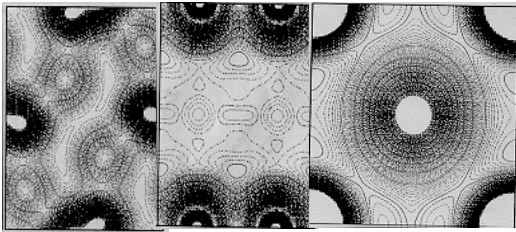


Fig.3 Charge density plot for Ti₂B, TiB and TiB₂

The bonding charge density is response of electron distribution. The valence electron charge density plot as shown as Fig.3 for Ti₂B, TiB and TiB₂. The Fig.3 clearly indicate that these compounds have mixed bonding nature i.e Ionic, metallic and covalent bonding nature. As the charge density histograms reveals directionality in bonding, we suggest that due to the nature of bonding TiB₂ may not be an exact layered compound. Further, a charge transfer of 1.39 electrons for Ti to B has been observed which indicates the presence of ionic bonding. Finite $N(E_F)$ (Fig. 2) contributes to the nature of metallic bonding. Thus, from the above observation, we conclude that the nature of bonding in TiB₂ as a mixed bonding consisting of ionic, metallic and covalent natures. It is to be noted that TiB₂ is more ionic as the charge transfer from Ti to B is higher than TiB and Ti₂B. The existence of the covalent bonding is the reason for low ductility and high hardness and melting point of TiB₂.

The calculated values of cohesive energy, heat of formation, bulk modulus and its derivative, electronic specific heat coefficient, and number of electrons at the Fermi energy ($N(E_F)$) are compared in Table 2 for Ti_2B , TiB and TiB_2 . $N(E_F)$ is the highest in Ti_2B and γ is also high for Ti_2B compared to the other two compounds. This higher electronic specific-heat coefficient will lead to a good thermal conductivity and thus this leads to high energy loss, which is undesirable for the aerospace applications. TiB_2 is preferred as aerospace material with lowest γ value.

For cubic systems, the lower value of bulk modulus leads to higher hardness²² and melting temperature, where as in the non-cubic systems, shear modulus decides the hardness of the material. But the present work shows that TiB_2 having lower bulk modulus possesses higher stability and hardness even though these systems are non-cubic in nature. As we move from titanium semiboride and to mono boride and then to diboride, the bulk modulus decreases revealing the progressive increment in strength and hardness.

Conclusion

In conclusion, our self-consistent band calculation of titanium borides (Ti_2B , TiB and TiB_2) provides an accurate description of their electronic structure. The Tm-B interaction is important in influencing their stability and hardness. The chemical stability of these species has been discussed using band concepts and the trends can be understood via band filling of the bonding state. The nature of bonding in TiB_2 is of mixed bonding consisting of ionic, metallic and covalent natures. Among the three titanium borides, TiB_2 has more stability, hardness and higher melting point.

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