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The electronic structure and chemical stability of the AlB_2 -type transition-metal diborides

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Abstract. The electronic structures of the AlB_2 -type transition-metal diborides TMB_2 ($TM=Sc, Ti, V, Cr, Mn, Y, Zr, Nb, Mo, Hf, Ta$) have been calculated by using the self-consistent LMTO-ASA method. The binding mechanism is discussed and the rigid-band model is shown to provide a fairly good description of their electronic structures. The existence of a pseudogap in the total density of states is found to be a common feature of these compounds. The variation of the chemical stabilities of these diborides is analysed and we find that the trends can be understood in terms of the band-filling concept of the bonding states. The results are compared with other theoretical and experimental work.

1. Introduction and method

The AlB_2 structure is one that is adopted by many of the transition-metal diborides TMB_2 ($TM=Sc, Ti, V, Cr, Mn, Y, Zr, Nb, Mo, Hf, Ta$) (see table 1). These diborides possess some unusual properties, such as high melting points, hardness, and metallic properties (Matkovich *et al* 1977). Their study has both fundamental scientific and technological significance. In a previous paper (Tian and Wang 1992), we have studied the electronic structure and equation of state of TiB_2 . From analysing the partial density of states of TiB_2 , we argued that the pseudogap at the Fermi energy in the band structure can be attributed to the competition of the hybridization between the Ti 3d and B 2p states and the Ti d resonances. On the basis of discussions on the formation of the pseudogap, we concluded that the Ti–B covalent bonding is very important in the electronic structure and therefore in influencing the physical properties of TiB_2 . In this paper we further study the electronic structures of the AlB_2 -type transition-metal diborides—as was done for transition-metal monoborides by Mohn and Pettifor (1988) and for semiborides by Mohn (1988). We find that the existence of a pseudogap in the total density of states is a common feature of these diborides. The binding mechanism is discussed and a comparison of our results with other theoretical work and experimental result is made. The fact that they are isostructural and their similar atomic configurations make these diborides an ideal system to study when investigating the band-filling effect. We try to understand the variation of the chemical stability across the constituent transition-metal series using band-structure concepts.

The self-consistent linear muffin-tin orbitals (LMTO) with the atomic sphere approximation (ASA) (Andersen 1975) is used in our calculations. Within the method, the

Table 1. Occurrence of transition-metal diborides with the AlB_2 structure.

Sc	Ti	V	Cr	Mn
Y	Zr	Nb	Mo	
	Hf	Ta		

volume of the unit cell is the sum of the total volumes of the overlapping atomic spheres. Inside an atomic sphere, two terms contribute to the effective one-electron potential: the Coulomb and the exchange–correlation potentials. The Coulomb potential consists of a nuclear potential, an electron–electron repulsive potential obtained by solving the Poisson equation, and the Madelung potential which represents the interaction between the electron and the charge centred at other atomic spheres. The calculations are semi-relativistic: the non-relativistic limit of the Dirac equation is taken and corrected to the order $1/c^2$; the spin–orbit coupling is not included. The AlB_2 structure is designated C_{32} with the space group symmetry $P6/mmm$. It is a simple hexagonal lattice in which Al layers alternate with graphite-like B layers (see figure 1 of Tian and Wang 1992). By choosing appropriate primitive lattice vectors, the atoms are positioned at $(0,0,0)$ Al, $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ B and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$ B in the unit cell. Table 2 gives the crystallographic parameters (Samsonov *et al* 1975) and transition-metal atomic configurations of these diborides. The $2s^2 2p^1$ configuration of the boron atom is adopted for the valence electrons. The 4f states in HfB_2 and TaB_2 are included in the core states. It is noticeable that the TM–B distances are only slightly larger than the sum of the atomic radius of the TM and that of B, and one would guess that the interaction between the electronic states of TM and B atoms is strong. The B–B distances are almost unchanged at 1.78 Å—about twice the value of the boron atomic radius—and the B atoms are thus in quite close contact with one other. This structure is rather closely packed; this can be coped with efficiently and accurately by using the LMTO–ASA method (Skriver 1984).

Table 2. Crystallographic parameters and atomic configurations. TM–TM and B–B denote the distances between neighbouring atoms.

Compound	a (Å)	c (Å)	TM–B (Å)	B–B (Å)	TM configuration
ScB ₂	3.148	3.516	2.53	1.82	3d ¹ 4s ²
TiB ₂	3.028	3.228	2.35	1.75	3d ² 4s ²
VB ₂	2.998	3.057	2.28	1.73	3d ³ 4s ²
CrB ₂	2.969	3.066	2.26	1.73	3d ⁵ 4s ¹
MnB ₂	3.009	3.037	2.31	1.74	3d ⁵ 4s ²
YB ₂	3.303	3.842	—	—	4d ¹ 5s ²
ZrB ₂	3.165	3.547	2.50	1.83	4d ² 5s ²
NbB ₂	3.086	3.306	2.38	1.78	4d ⁴ 5s ¹
MoB ₂ †	3.040	3.060	—	—	4d ⁵ 5s ¹
HfB ₂	3.14	3.47	2.47	1.81	5d ² 6s ²
TaB ₂	3.097	3.225	2.48	1.78	5d ³ 6s ²

† Data for MoB₂ are taken from Spear (1976).

The energy bands are calculated on a uniform mesh of 64 points in the irreducible wedge of the Brillouin zone. The radii of Wigner–Seitz spheres are chosen according to the equality of the potentials at different spheres. The convergence of the eigenvalues is within 1 mRyd.

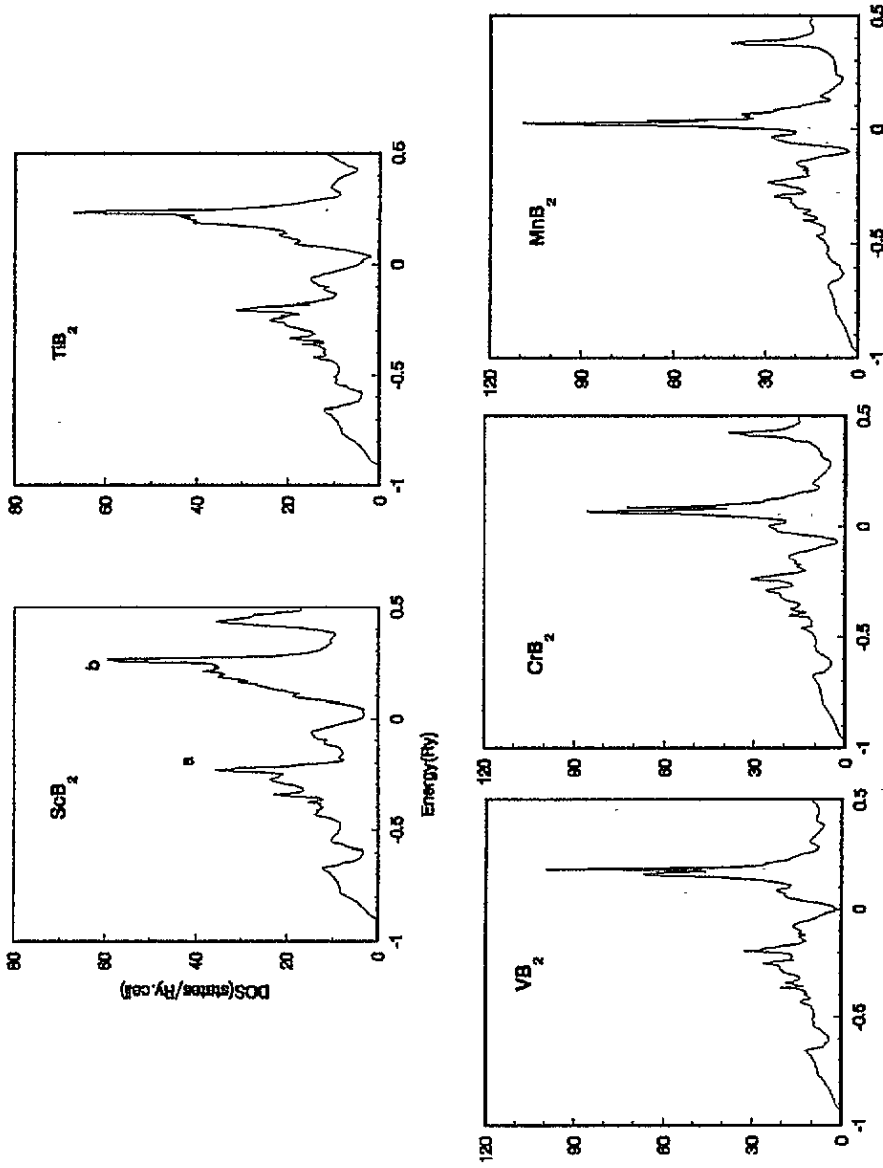


Figure 1. The total densities of states of the AlB₂-type transition-metal diborides ScB₂, TiB₂, VB₂, CrB₂, and MnB₂, with Fermi energy = -0.08, 0.04, 0.08, 0.04, and 0.01 Ryd, respectively.

2. The electronic structures

In our previous paper (Tian and Wang 1992), the formation of a pseudogap in the electronic structure of TiB_2 was discussed; it was attributed to the competition between the strong Ti-B hybridization and the Ti 3d resonance. Since the diborides investigated have the same crystal structure, it can be expected that their electronic structures will show similar features to that of TiB_2 . Shown in figures 1 to 3 are the total densities of states (DOS) of all the diborides investigated (the results for TiB_2 in this paper are taken from Tian and Wang 1992). One can see that the curves have close similarity. For a series going from left to right, the DOS curves resemble each other. The DOSs have non-vanishing values at the Fermi energy, indicating that all these diborides exhibit metallic behaviour in their crystalline state. As is evident from the partial densities of states (which have not been shown here—the reader is referred to Tian and Wang (1992), and Ihara *et al* (1977)), the band structures of the TM_2B_2 can be regarded as being determined by the sp^2 hybrid state and the p_z state of boron as well as the d and s state of the TM. The boron sublattice has the planar graphite-like structure and this is reflected in the DOS by the lowest-lying peak. The existence of a pseudogap in the DOS is seen to be a common feature of these diborides. Above the pseudogap stands the sharp non-bonding TM d states, which divide the DOS into bonding (below) and anti-bonding (above) states. According to Pasturel *et al* (1985), a pseudogap arises from strong chemical interactions and is a sign of enhancement of the cohesive energy. Since the TM d-B p hybridization is strong enough in these species to produce a pseudogap, these diborides cannot be called exactly layered compounds, since the interlayer interaction is strong even though the TM layers alternate with the B layers in their crystal structure. Table 3 gives a comparison of the results from the present work with other theoretically calculated values and experimental values of the electronic specific-heat coefficient γ . The theoretical values are calculated directly from a free-electron approximation: $\gamma = \pi k_B^2 N(E_F)/3$, using the calculated density of states at the Fermi energy $N(E_F)$. γ^{RB} refers to the values calculated from the rigid-band model, obtained by fixing the bands of TiB_2 , ZrB_2 and HfB_2 for the three series, respectively. γ^{ex} is the experimental value taken from Castaing *et al* (1969). The comparison shows good agreement. In particular the values of the calculated values γ^{cal} and the values γ^{RB} obtained from rigid-band model do not significantly differ. The so-called rigid-band model provides a good description of their electronic structures. The discrepancies between the calculated and experimental values for some compounds may be caused by the neglect of the electron-phonon interaction in our calculations.

Although the rigid-band model describes the electronic structures of these diborides fairly well, there are some differences between the band structures as expected. Near the pseudogap, there are two main peaks (see the DOS curve of ScB_2). The lower one (peak a) arises from the TM-B hybridization, while the higher one (peak b) reflects the TM d resonance. On going from left to right of a series, there is an increase in the bandwidth, and a lowering of peak a and a raising of peak b in the densities of states. This may be attributed to the increasing resonance strength of the d electrons as one goes from left to right. In contrast, for TM_2B_2 of one group, while going from top to bottom, the density of peak a increases and that of b decreases. We think this effect indicates the increasing TM-B hybridization from top to bottom.

Like the transition-metal monoborides (Mohn and Pettifor 1988) and semiborides (Mohn 1988), the transition-metal diborides are also examples of the metal-metalloid compounds described by Gellatt *et al* (1983) and Weaver *et al* (1984). On the one hand, the d-band bonding becomes weaker since the dilution of boron atoms makes the average distance between TM atoms larger. On the other hand, the TM d states interact with the boron p

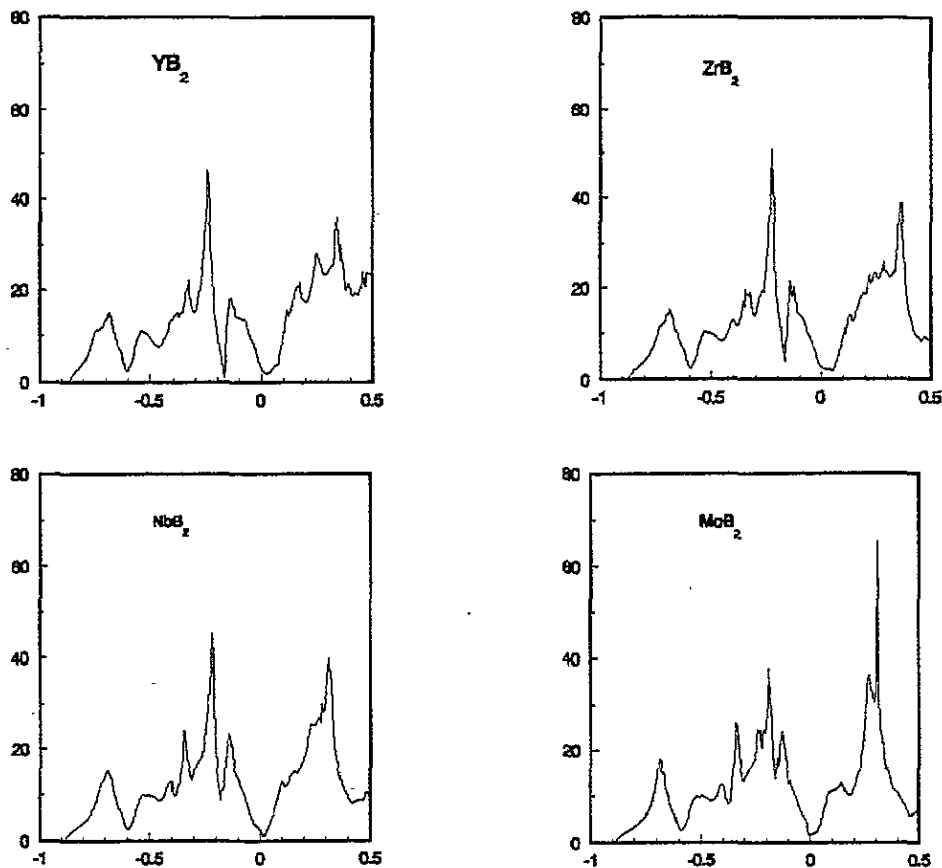


Figure 2. The total densities of states of the AlB₂-type transition-metal diborides YB₂, ZrB₂, NbB₂, and MoB₂, with $E_F = -0.1, 0.04, 0.14,$ and 0.22 Ryd, respectively.

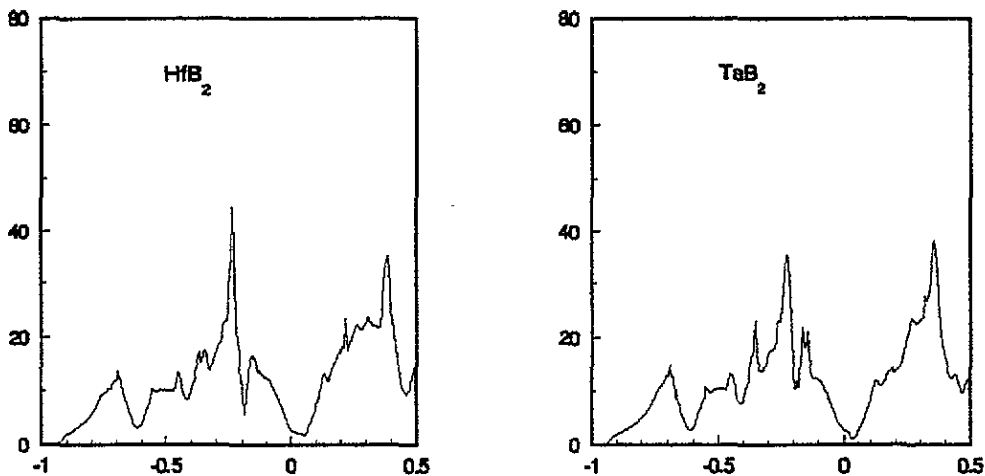


Figure 3. The total densities of states of the AlB₂-type transition-metal diborides HfB₂ and TaB₂, with $E_F = 0.04$ and 0.16 Ryd, respectively.

states (with an interaction that is strong enough to produce a pseudogap in the diborides),

Table 3. A comparison of the theoretical and experimental electronic specific-heat coefficient γ (in unit of $\text{mJ mol}^{-1} \text{K}^{-2}$).

Compound	γ^{cal}	γ^{RB}	γ^{\dagger}	γ^{ex}
ScB ₂	2.48	2.46	1.12	2.2
TiB ₂	0.38	—	0.88	1.08
VB ₂	3.62	3.78	3.09	4.84
CrB ₂	5.84	5.56	3.60	13.6
MnB ₂	8.09	6.10	—	4.45
YB ₂	2.38	2.45	—	—
ZrB ₂	0.36	—	0.527, 0.718 \ddagger	—
NbB ₂	2.44	2.64	—	2.33
MoB ₂	2.76	3.20	—	3.58
HfB ₂	0.34	—	—	—
TaB ₂	2.37	2.11	—	1.70

\dagger Computed from the rigid-band values of $N(E_F)$ by fixing the band of CrB₂ (Liu *et al* 1975).

\ddagger The two values correspond to KS exchange and Slater exchange (Ihara *et al* 1977), respectively.

forming bonding and anti-bonding hybrids, which is important in the stabilization of the lattice. From the viewpoint of orbital overlap, Burdett *et al* (1986) also found that the interaction of the orbitals of TM atoms with the boron atoms and interaction with those of other metals are both important in influencing the properties of these species. We should emphasize, however, that the boron–boron interaction in these diborides is also significant. This is different from what is found for the transition-metal semiborides (Mohn 1988), where boron–boron interaction is not strong.

3. Chemical stability

It's well known that a high melting point is always associated with high chemical stability. We note from experimental data (Matkovich *et al* 1977) that there is a systematic decreasing of the melting point from Ti to Cr, Zr to Nb, and Hf to Ta. Hence the order of chemical stability is TiB₂>VB₂>CrB₂, ZrB₂>NbB₂, HfB₂>TaB₂. We aim to explain this trend using the band-structure concepts.

According to Friedel's (1969) theory of cohesive energy for TM and the conceptual picture of chemical bonding for ordered TM and non transition-metal compounds given by Williams *et al* (1983), the essential contribution to the cohesion of the TM compounds is the broadening of 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). This idea has been shown to be successful by Xu and Freeman (1989) in the analysis of the phase stability of cubic trialuminides (YAl₃, ZrAl₃ and NbAl₃). Since the rigid-band model describes the electronic structures of the diborides rather well, the band filling can naturally be regarded as being responsible for the variations of their electronic structure and related properties.

We use W_v , W_p to denote the energy distance from bottom of valence band to the Fermi level (the width of the valence 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. These values for the TMB₂ concerned have been given in table 4. The melting points of these diborides are also listed. It is seen that though W_v apparently changes for different compounds, W_p keeps almost constant at

about 0.96 Ryd (~ 10 electrons).

Table 4. The width of the valence band W_v , that of the bonding states W_p , W_v/W_p , and the melting points of the diborides.

Compound	W_v (Ryd)	W_p (Ryd)	W_v/W_p	Melting point ($^{\circ}$ C)
ScB ₂	0.85	0.95	0.90	—
TiB ₂	0.96	0.97	0.99	2980
VB ₂	1.00	0.97	1.03	2400
CrB ₂	1.04	0.93	1.12	2200
MnB ₂	1.03	0.91	1.13	—
YB ₂	0.71	0.93	0.76	—
ZrB ₂	0.95	0.96	0.99	3040
NbB ₂	1.01	0.99	1.02	2900
MoB ₂	1.05	0.92	1.14	—
HfB ₂	1.03	1.01	1.02	3250
TaB ₂	1.15	1.01	1.14	3200

In the direction from Sc to Mn, there is an increase of the number of valence electrons (VES) of the diborides. ScB₂ has nine valence electrons, and the bonding states are not fully filled ($W_v/W_p < 1$). Putting more VES into the band will probably increase the stability. From VB₂ to MnB₂, the values of W_v/W_p are larger than unity. That means that the bonding states can no longer accommodate their valence electrons, and non-bonding states have to be filled. Hence the cohesion is reduced. Considering the increasing values of W_v/W_p , the chemical stability must decrease from VB₂ to CrB₂ to MnB₂. For TiB₂, the bonding state has just enough room to accommodate its ten valence electrons, so it can be expected to be the most stable in this series. Similar analysis reveals that ZrB₂ is the most stable among the second series, and NbB₂ has better chemical stability than MoB₂. For the third row, HfB₂ is more stable than TaB₂. These discussions agree completely with experiment. Therefore, the variation of chemical stability of these AlB₂-type diborides can be understood in terms of the band filling of bonding states.

It's still noteworthy that when going from TiB₂ to ZrB₂ and to HfB₂, there is also a systematical increase in the chemical stability. A similar trend is also found in the group VB₂, NbB₂ and TaB₂. We think that this effect could be arising from the d-band widening (as can be seen from the DOS curve), as well as the increasing TM-B hybridization from TiB₂ to HfB₂, VB₂ to TaB₂ (which is evident from the new pseudogap produced by TM-B hybridization).

From the above analysis, one can see that the more stable the crystal, the smaller $N(E_F)$, and naturally the larger the resistivity. Therefore the band-filling idea can be successfully used to explain the structural stability and electronic transport in these diborides. It is interesting to note that this is also true for quasicrystalline solids (Phillips 1993).

In the work of Burdett *et al* (1986), the measured values of the heat of formation (see Topor and Kleppa 1985) for the compounds from ScB₂ to MnB₂ was noted and explained. It was suggested that the experimentally observed variation in the heat of formation is crucially dependent upon the extent of occupation of the metal-boron orbital set. For a given d count the available electrons will first fill TM-B bonding orbitals and then, as the electron count increases, eventually anti-bonding orbitals. Filling bonding orbitals leads to a positive slope in the curve, and filling anti-bonding orbitals leads to a negative slope. This discussion on the variation of the heat of formation is consistent with our analysis of the chemical stability of these diborides. We think that the analysis of Topor and Kleppa was

in fact saying the same thing as we did in the earlier discussions of this section, although the terms used are different (*orbital set* in their study and *band* in ours), and our analysis is somewhat more qualitative.

4. Conclusions

In conclusion, our self-consistent band calculation of the of the AlB_2 -type diborides TMB_2 ($TM=Sc, Ti, V, Cr, Mn, Y, Zr, Nb, Mo, Hf, Ta$) provide an accurate description of their electronic structures. The band structures of these diborides can be regarded as being determined by the sp^2 hybrid state and the p_z state of boron as well as the d and s states of TM . We find that their total density of states are characterized by a pseudogap between bonding and anti-bonding states. The $TM-B$ interaction is important in influencing their stabilities. The rigid-band model provides a good description of the electronic structure of these diborides. Our results have been compared with other theoretical work and experimental results. Variation of the chemical stability of these species has been discussed using band concepts and the trends can be understood via band filling of the bonding states.

Acknowledgment

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