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# Quantum-chemical analysis of the chemical stability and cohesive properties of hexagonal $TiB_2$, $VB_2$, $ZrB_2$ and $NbB_2$

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**The cohesive properties and chemical stability of diborides $MB_2$ have been analysed using the results of full-potential LMTO calculations. A comparison of interatomic M–M, M–B and B–B interactions in $MB_2$ phases (M = Ti, V, Zr, Nb) shows that the changes in the cohesive properties are mainly controlled by the strength of the covalent M–B bonds.**

Among the known transition metal (TM) borides the hexagonal diborides of IVa and Va group metals ($MB_2$) possess the highest melting temperatures, hardness and chemical stability.[1,2] The stability and thermomechanical properties of $MB_2$ depend on the kind of metal and get noticeably worse with the growth in TM atomic number ($z$) in the period and with reduction of $z$ in the group of the Periodic Table.[1,2]

In the phenomenological models of the electronic structure of $MB_2$ phases their properties are attributed to one of several possible types of interatomic interactions (see reviews 3 and 4). For example, it is supposed[5] that B–B interactions are responsible for the structural peculiarities of diborides. The calculations of energy band structure were carried out by the authors of refs. 6 and 7 for some $MB_2$ phases. Based on the total and local densities of states (TDOS, LDOS), the cohesive properties of $MB_2$ (with the growth of $z$ in the period) were explained by the changes in occupation of antibonding states with valence electron concentration (vec) in the cell. This approach[6,7] is widely employed to interpret the thermodynamic properties of diborides such as melting temperature, entropy characteristic energies, *etc.*[8] The model fails, however, to explain the differences in the properties of isostructural and isoelectronic $MB_2$ (for example, $TiB_2$ and $ZrB_2$ or $VB_2$ and $NbB_2$).[1,2]

In the present paper the first-principle analysis of the chemical stability of $MB_2$ (M = Ti, V, Zr, Nb) is performed and the contributions of different types of interatomic interactions to the cohesive energy of these phases are considered. The electronic energy band structure of $MB_2$ was calculated using the self-consistent full-potential linear muffin-tin orbitals method (FP-LMTO).[9] The structural data for diborides were taken from ref. 2.

TDOS and LDOS of $ZrB_2$, $NbB_2$ are given in Figure 1. It was found that, in conformity with previous computations (reviews 3 and 4), the characteristic feature of the electronic structure of $MB_2$ is the local TDOS minimum (pseudogap) between the bands of bonding (Md–Bp) - and antibonding Md*, Bp-states. For $ZrB_2$ (vec = 3.33 e atom$^{-1}$), the Fermi level ($E_F$) is located at this TDOS minimum. This corresponds to the condition of maximum chemical stability of the crystal: bonding states are completely occupied and antibonding states are vacant. Going to $NbB_2$ (vec = 3.67 e atom$^{-1}$) the bands of the antibonding states become partially occupied and DOS on the Fermi level [$N(E_F)$] increases: $N(E_F)$ = 4.35 and 15.56 Ry$^{-1}$ for $ZrB_2$ and $NbB_2$, respectively. According to the traditional band concept of stability of chemical compounds,[10,11] this determines a decrease in cohesive energy and chemical stability of $NbB_2$ as compared with $ZrB_2$. Analogous conclusions can be drawn from the TDOS for $TiB_2$ and $VB_2$.

From numerous experimental data[1,2] it follows that in accordance with cohesive properties these diborides make up the series $ZrB_2 > NbB_2 > TiB_2 > VB_2$. In the framework of the FP-LMTO[9] method the cohesive energy of the system is

**Table 1** Cohesive energies ($E_{dif}$/Ry cell$^{-1}$) of Ti, V, Zr, Nb diborides and energies of different types of bonds according to FP-LMTO calculations.

| Phase | $-E_{dif}(MB_2)$ | $-E$(M–M) [a] | $-E$(B–B) [a] | $-[E$(M–M) + $E$(B–B)] | $-E$(M–B) |
|---|---|---|---|---|---|
| $TiB_2$ | 1.58 | 0.36 | 0.86 | 1.22 | 0.36 |
| $VB_2$ | 1.53 | 0.40 | 0.88 | 1.28 | 0.25 |
| $E^b$ | 0.05 | –0.04 | –0.02 | –0.06 | 0.11 |
| $ZrB_2$ | 1.78 | 0.44 | 0.82 | 1.26 | 0.52 |
| $NbB_2$ | 1.78 | 0.56 | 0.85 | 1.41 | 0.37 |
| $E$ | 0.00 | –0.12 | –0.03 | –0.15 | 0.15 |

[a] $E$(M–M) and $E$(B–B) correspond to the $E_{dif}$ values from a calculation of hypothetical $M\square_2$ and $\square B_2$ compounds. [b] $E$ is the energy difference for 3d- and 4d-metal borides.

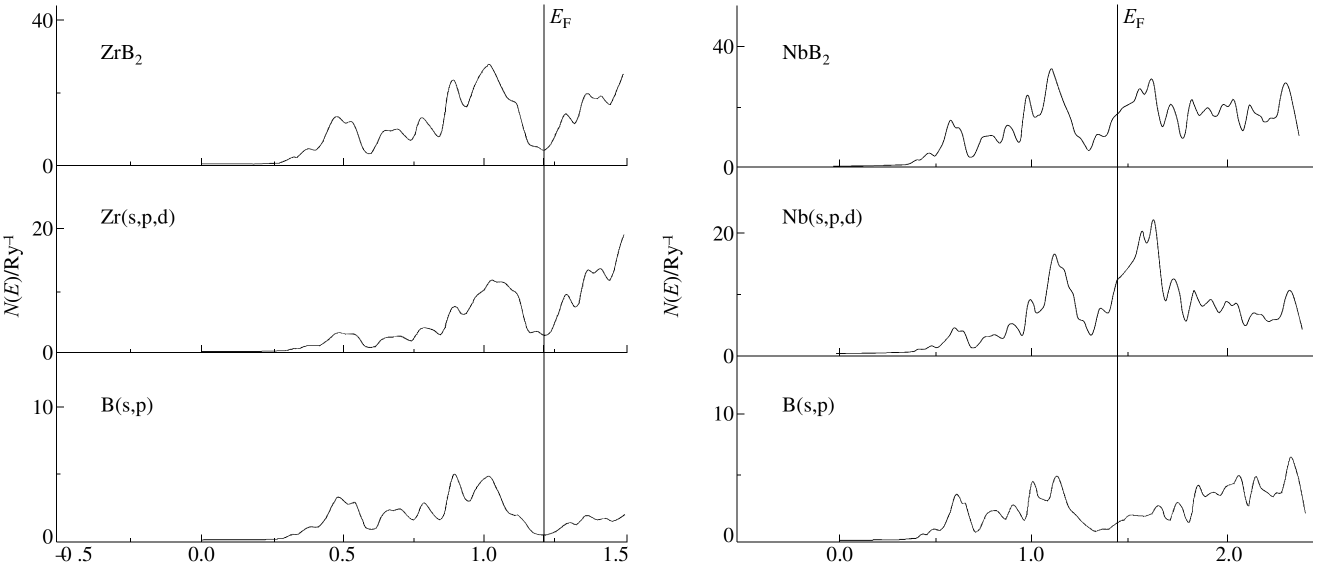

**Figure 1** Total and local densities of states of $ZrB_2$ and $NbB_2$.

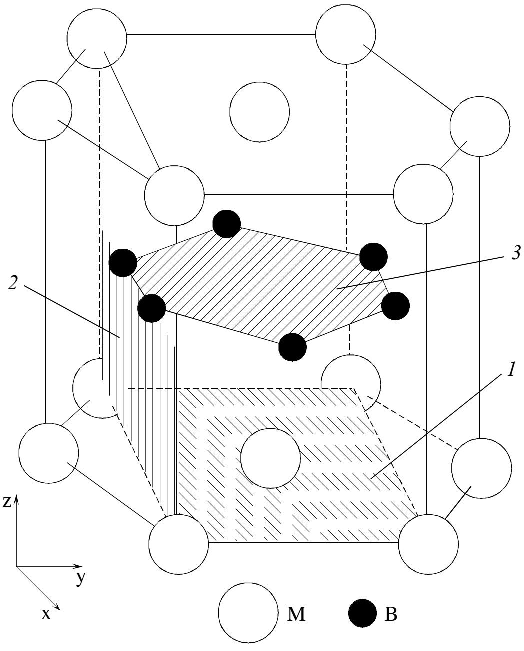

**Figure 2** Fragment of the crystal structure of diborides $MB_2$. Designated are the planes of metallic atoms (*1*), boron atoms (*3*) and 'interlayer' plane (*2*).

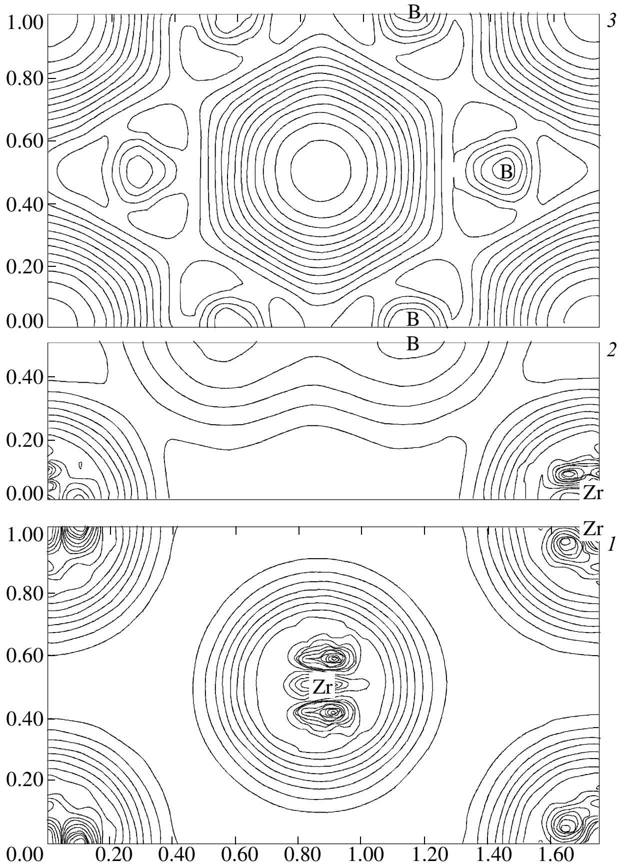

**Figure 3** Contour maps of total charge density of $ZrB_2$ in different planes of the unit cell [(*1*)–(*3*), Figure 2] showing the main types of interatomic interactions in the crystal: Zr–Zr (*1*), Zr–B (*2*) and B–B (*3*). FP-LMTO calculations.

calculated as $E_{dif} = E_{tot} - E_{at}$, where $E_{tot}$ is the total energy of the crystal and $E_{at}$ is the energy of free atoms constituting its lattice. $E_{dif}$ was found to decrease in the order $ZrB_2 \sim NbB_2 > TiB_2 > VB_2$ (see Table 1), *i.e.* in conformity with the experimentally established regularity.

The value of $E_{dif}$ is an integral characteristic of chemical bonding and describes the overall energy effect of atomic interaction rearrangement in the lattice. Therefore, our next aim was to determine the role of separate interatomic interactions in the formation of the cohesive properties of $MB_2$. The main types of chemical bonding in diborides are M–M, B–B interactions in metal and boron plane nets (Figure 2) and the covalent 'interlayer' M–B bond. These types of interatomic bonds in different planes of the $ZrB_2$ unit cell are visually illustrated in Figure 3. To evaluate the energy contributions of separate bonds [$E$(M–M), $E$(B–B) and $E$(M–B)] to $E_{dif}$, the electronic structure of isolated diboride sublattices – hypothetical defect structures $M\square_2$ and $\square B_2$ — (M = Ti, V, Zr, Nb; $\square$ = = vacancies in the corresponding sublattice) was calculated with retention of their geometry in real phases. The energies of M–M and B–B bonds were then determined as

$$E(\text{M–M}) = E_{dif}(M\square_2) = E_{tot}(M\square_2) - E_{at}(M),$$
$$E(\text{B–B}) = E_{dif}(\square B_2) = E_{tot}(\square B_2) - 2E_{at}(B).$$

The energy of the covalent M–B interaction was defined as the difference between the cohesion energy of the real phase and the sum of the cohesive energies of its non-interacting sublattices

$$E(\text{M–B}) = E_{dif}(MB_2) - [E_{dif}(M\square_2) + E_{dif}(\square B_2)].$$

It follows from Table 1 that the main contribution to the chemical bonding for diborides is due to strong B–B bonds. The bonding between B atoms dominates both M–M and M–B interactions. $E$(B–B) in hypothetical $\square B_2$ compounds depends only on the interatomic distances B–B in the structure of $MB_2$ and closely follows any changes occurring in them.[2] The values of $E$(M–M) for $M\square_2$ correlate with the known cohesive energies for pure 3d, 4d-metals (Nb > Zr > V > Ti).[11,12] The sum of $E_{dif}$ for two non-interacting sublattices ($M\square_2 + \square B_2$) gives a change in chemical stability: $NbB_2 > VB_2 > ZrB_2 > TiB_2$. Thus, the interlayer M–B interaction has a determining effect on the integral $E_{dif}$ value for these phases (see Table 1).

The first-principle analysis of chemical stability and cohesive properties of diborides performed here makes it possible to draw the following conclusions. The thermomechanical properties of $MB_2$ result from the strength of the M–M, M–B and B–B bonds. In spite of the leading role of B–B interatomic interactions they are not responsible for the variety of diboride properties, as proposed in some phenomenological models.

Depending on the nature of the metallic sublattice the changes in separate types of bonding take place in different ways. The cohesive energy of these diborides changes mainly owing to interlayer covalent M–B interactions and $E$(M–B) increases with the growth of metal atomic number $z$ in the group and decreases as $z$ grows in the period. Hence, it is possible to assert that the relative change in chemical stability and cohesive properties of the diborides considered is controlled by the covalent boron-metal interaction.

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