

Structure Determination of the 4d Metal Diborides: A Quantum Mechanical Study

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Metal diborides (MB_2) often have interesting thermal, mechanical, and superconducting properties. MgB_2 was put into focus some years ago for its high transition temperature (39 K) in combination with its simple AlB_2 structure. The boron structure in MB_2 is assumed to be dependent on the electron transfer from the nearby positioned metal atoms. An electronic and structural comparison has been performed here for various initially planar and puckered transition-metal borides, using quantum mechanical density functional theory (DFT) calculations under periodic boundary conditions. In comparison to MgB_2 , the experimentally planar transition-metal diborides (ZrB_2 , NbB_2 , and MoB_2) and the experimentally puckered ones (TcB_2 , RuB_2 , RhB_2 , and PdB_2) have been examined. The results indicate that the energetic stability generally follows the experimentally obtained results. The metals that are less electronegative than boron donate electrons to boron, which in turn induce planar boron structures (graphitic-like). The metals that prefer to be planar donate more than one electron, while the trend for metals which favor puckered B structures is that they donate less than one electron per metal atom. Two donated electrons per metal atom (or very close to) will result in the most stable AlB_2 structure.

Introduction

A few years ago superconductivity was observed for hexagonal bulk magnesium diboride, MgB_2 , with a transition temperature, T_C , of 39 K.¹ This was a great discovery due to the high transition temperature of MgB_2 in combination with its simple layered hexagonal AlB_2 structure.² Other high-temperature superconductors have otherwise quite complicated structures which make them hard and expensive to synthesize.³ Metal diborides other than MgB_2 were examined earlier due to their interesting thermal, mechanical, and superconducting properties.^{4,5} However, the observed superconducting transition temperatures for these compounds were unfortunately too low.^{3,6}

The planar B skeletons in some MB_2 compounds have similarities to the graphite structure. The geometrical boron structure of MB_2 is assumed to be influenced by the electron transfer to the boron atoms from neighboring metal atoms. Boron is an element with only three valence electrons, which makes it ideal to form compounds with metals that possess low electronegativity values. For the transition-metal compounds, TM, this is due to their high conductivity properties and larger density of states at the Fermi level (compared to the main group elements) a very interesting group of materials.³ Within modern technology various transition-metal diborides, TMB, are practically useful because of several properties such as high melting points, hardness, and high thermal electric conductivity.⁷ Hence, the TMB compounds are very interesting for further investigations of materials properties such as superconductivity.^{3,7} The superconductivity of other metal boron superconductors is believed to depend on the existence of d-electron atoms within the outer electron shell of the metal, which however the Mg element in MgB_2 does not possess.⁶ This circumstance, in addition to the discovery of superconductivity in the AlB_2 -type CaSi_2 phase at 14 K, has made it advantageous to examine several other types of diborides with the AlB_2 structure.³

The present study is the first one in a series of investigations where the influence of various metals and metal combinations on the geometrical structure and superconductivity properties will be thoroughly illuminated on an atomic level. The purpose with the first (and present) study is to elucidate the effect of various metals (also including transition metals) on the geometrical structure of the boron skeleton. The metals include Zr, Nb, Mo, Tc, Ru, Rh, and Pd.

It is of great importance to examine the structures for various transition-metal diborides since high-temperature superconductors have been found to have a planar, graphitic B layer (MgB_2). An obtained deeper knowledge concerning the underlying causes to the formation of planar MB_2 structures is, hence, important for future design and development of new high-temperature superconducting materials.

Methods

The electronic and structural properties of various planar and puckered transition-metal borides have been investigated within the framework of density functional theory (DFT) using the program package CASTEP from Accelrys, Inc. One commonly applied approximation in DFT for exchange and correlation effects is the generalized gradient approximation (GGA-PW91) developed by Perdew and Wang.⁸ GGA-PW91 introduces inhomogeneity by a density gradient expansion and has been found to be more accurate for calculations of bond energies.^{9,10} The total energy was in the present work minimized by varying plain wave basis sets with a kinetic energy cut off frequency of 300.0 eV. These are varied self-consistently using a preconditioned conjugate-gradient technique which expands the wave functions in terms of plane waves.¹⁰ The number of k points used was 32, which were generated by using the Monkhorst–Pack scheme. This scheme produces a uniform mesh of k points in reciprocal space, which is more satisfactory than linear or quadratic methods.¹¹

The degree of electron transfer between the transition metal

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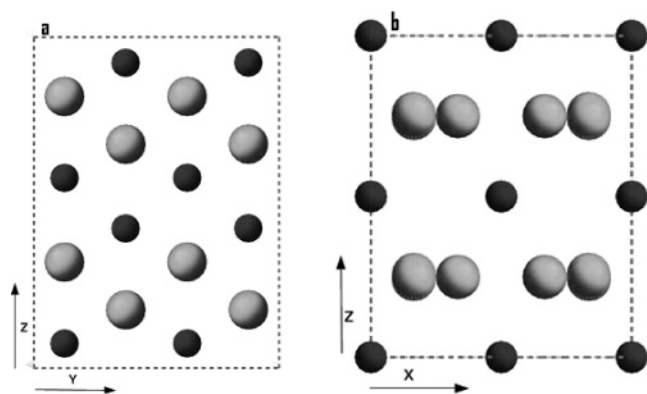


Figure 1. B and M atoms are demonstrated as large and small spheres, respectively: (a) puckered MB_2 structure and (b) planar MB_2 structure.

and boron element has been estimated in this work by calculating the individual atomic charges (for each compound and for both planar and puckered structures). In addition, the covalent bond strengths within the $\text{M}-\text{B}$ bonds were estimated by calculating the electron bond populations. The atomic charges and bond populations were then calculated by projecting the plane wave states onto the localized basis set by means of Mulliken analysis.¹²

The calculations were based on periodic boundary conditions, where the metal boride models were constructed as periodically repeated super cells, see Figure 1. All MB_2 compounds were in the present investigation initially modeled as a planar and puckered super cell that consisted of 16 boron and 8 metal atoms, respectively. The puckered structures were orthorhombic with similarities to tetragonal carbon.¹³ The planar structures had the hexagonal AlB_2 type. For every structure, all atoms, in addition to super cell parameters, were allowed to move freely in a geometry optimization procedure using the BFGS algorithm (Broyden–Fletcher–Goldfarb–Shanno).¹⁴

Extensive test calculations were performed to ensure the accuracy of the model template and the theoretical parameters. Different numbers and combinations of k points and cut off frequencies were evaluated in order to receive the most optimal values of structural stabilization energies. The results of the test calculations showed that 32 k points and a cut off-frequency of 300.0 eV is adequate to use within the present investigation. A difference of less than $1.7 \times 10^{-4}\%$ was obtained using 32 vs 40 k points and the puckered RuB_2 structure. The corresponding result for the planar RuB_2 structure was $3.2 \times 10^{-4}\%$. The results obtained when varying the cutoff frequency were also almost identical when using 300 vs 340 eV for both types of structures. Hence, 32 k points and a cutoff frequency of 300 eV have been chosen to be used within the present investigation.

Results and Discussion

A. General. The interaction and control by the 4d transition metals (Y, Zr, Nb, Mo, Tc, Ru, Rh, and Pd) on the geometrical structure of the boron skeleton in the MB_2 compounds have been investigated theoretically here using DFT under periodic boundary conditions. The energetic stability of two disparate structures (planar versus puckered) have been calculated and compared for each of the metal boride compounds. It should be emphasized that not all of the compounds (Y, Zr, Nb, Mo, Tc, and Ru) have been observed (or synthesized) experimentally. In addition, these have naturally shown only one stable structure (planar or puckered). Hence, to more thoroughly investigate the structural stability of the various elements one has to start with more artificial yet plausible structures onto which geometrically

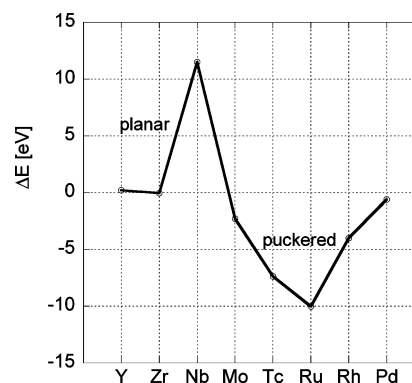


Figure 2. Energy difference (initially puckered minus initially planar structures) from geometry optimization calculations.

relaxation will be performed in the calculations. In addition, one has to use identical planar versus puckered structures for all different MB_2 compounds. The choices of these structures within the present study are planar MoB_2 and puckered RuB_2 , which both were synthesized earlier. MoB_2 is a hexagonal AlB_2 type with $a = b = 3.05$ Å and $c = 3.113$ Å.¹⁵ RuB_2 is orthorhombic with $a = 4.6443$ Å, $b = 2.8668$ Å, and $c = 4.0449$ Å.¹⁶

The obtained differences in geometrical stabilities have been analyzed and discussed by investigating the correlation with other related parameters such as (i) energetic stabilization between planar and puckered structures as described above, (ii) a comparison of tabulated values of electronegativity for the various elements in the present study, (iii) electron transfer between the metal atom and the neighboring boron atoms, and (iv) electron bond populations and (v) by comparing relative atomic sizes. The electron transfer is estimated from calculated atomic charges, and the electron bond population is an estimation of the density of electrons within the bonds (i.e., being a measure of covalent bond strength). The electronegativity is generally expected to be strongly correlated to electron-transfer possibilities. Elements with high electronegativity will attract electrons from neighboring (binding) atoms.¹⁷ In addition, the relative atomic size may influence the final geometrical results by causing severe steric hindrances.

B. Energetic Stabilization of Planar vs Puckered Structures. The energetic and structural results of the geometrical relaxation of the initially planar vs puckered structures of the various MB_2 compounds can be seen in Figures 1 and 2. The ΔE diagram (Figure 2) shows the calculated energy difference between the initially planar and initially puckered models. Hence, a positive ΔE value implies that the initial planar structure is energetically the most stable one (compared to an initially puckered structure). The maxima to the left of the inflection point in Figure 2 will, hence, support a conclusion that the NbB_2 compound prefers to be planar, see Figure 1. Correspondingly, the negative ΔE values to the right of the inflection point in Figure 2 imply puckered B skeleton structures, and hence, Tc, Ru, and Rh may prefer a puckered structure.

There are four MB_2 compounds that have ΔE values very close to zero. This means in practice that the final results after geometry optimization gave almost identical total energies. This is quite understandable if the final geometries, after relaxation of the initial planar and puckered structures, were in principle identical for each of the four different compounds. Another explanation is that both the planar and puckered structures have extremely similar total energies. The MoB_2 compound, which according to experimental results prefers a planar B skeleton, has corresponding ΔE values in the nearest vicinity to the

TABLE 1: Electronegativities (Pauling Scale)

metal	Mg	Y	Zr	Nb	Mo	Tc	B	Ru	Rh	Pd
electronegativities	1.2	1.3	1.4	1.6	1.8	1.9	2.0	2.2	2.2	2.2

inflection point in Figure 2, i.e., ΔE is about zero.¹⁷ Generally, the ΔE values are the results from subtraction between two very big numbers. Hence, it is in principle not possible to draw any conclusions regarding structural stabilities when the ΔE values are that close to zero, which is the situation for the MoB₂ compound. The values can thus be either positive or negative. The approximations for the electron exchange and correlation will induce small errors that not necessarily have to be identical for both structure types. Therefore, the conclusion that can be drawn from the MoB₂ results is that there is no obvious preference for one geometrical structure in favor of the other since there is this very small total energy difference between the planar and puckered structures. Hence, kinetic effects during the synthesis of the MoB₂ compound can be very decisive for the final results.

It is also very interesting to note that zero values for ΔE can also be observed in Figure 2 for Y and Zr (to the left) and Pd (to the right). The results for YB₂ and ZrB₂ are quite understandable since both the initial planar and puckered structures (for both of the compounds) ended up as planar ones as a result of geometry optimizations. Hence, the present calculations show that there, from a thermodynamic point of view, exist severe problems in synthesizing puckered forms of these two compounds. Also, the difference in energy for Pd is almost zero but still has a small value, which implies a tendency for a puckered structure.

C. Coupling to Elemental Electronegativities. An obvious trend is observed when comparing the obtained structural stabilization energies (presented in Figure 2) with the corresponding elemental electronegativity values by Pauling (see Table 1). The metals that are less electronegative than boron (Y, Zr, Nb, Mo, and Tc) (i.e., have a larger ability to donate electrons to neighboring boron atoms) may also have the capability to induce a planar boron structure (graphitic-like).¹⁸ As can be seen in Figure 2, all of these metals have, with one exception (TcB₂), MeB₂ structures with planar B skeletons. The Mo and Tc metals have electronegativity values that are very similar to the value for B, which may therefore explain the discrepancy in results in Figure 2. As can also be seen in Figure 2, all three of the highly electronegative metals from Table 1 (Ru, Rh, and Pd) prefer a puckered boron structure. MgB₂ is included in Table 1 for comparison since this compound has been obtained experimentally and also has superconducting properties. The boron skeleton within MgB₂ is planar, and the low electronegativity value of MgB₂ agrees well with the conclusions presented above, i.e., its high ability to donate electrons to neighboring boron atoms could induce a planar boron structure.

D. Electron Transfer between Transition-Metal and Boron Atoms. An explanation for the differences in the structural stability of puckered vs planar B skeletons in the present study

has been looked at by studying electron-transfer processes between the transition-metal and boron atoms for each compound. As can be seen in Table 2, the number of electrons that transferred from the metal atoms to neighboring boron ones decreases from yttrium to palladium (from left to the right in the periodic system); this is the situation for both the initial planar and puckered structures. MgB₂ is included in Table 2 for comparison.

When comparing Table 2 with Figure 2, there is a close correlation in the observed results. As can be seen in Table 2, more than one electron has been transferred to B in the initially graphitic-like (planar) B skeleton for the compounds to the left of Tc. A somewhat smaller, but similar, observation has been made for the initially puckered structures to the left of Nb. The more pronounced electron transfer discovered for the planar B skeleton in MoB₂ does strongly correlate with experimental observations as well as with the results shown in Figure 2 (where also the planar structures were found to be the energetically preferred). It must once again be stressed that the very small ΔE value in Figure 2 indicates an unclear preference for B geometrical structure within MoB₂. Figure 2 shows a negative value of ΔE , but there is a large probability for a positive value as well.

The transition-metal atoms that are located to the right of Mo in Figure 2 will, with one exception, donate less than (or equal to) one electron to the neighboring borons. Hence, the puckered B structure that was found to be the most stable in section B will be formed when less than one electron is transferred from the metal to the neighboring borons.

The binary borides that have shown superconducting properties have planar, graphite-like boron skeletons within an AlB₂ structure. One explanation is that the boron structure has to be planar to receive superconductivity.⁶ The number of expected donated electrons is, however, unknown. According to the theory by Mulokzi, two electrons donated from each metal atom would give the most stable planar AlB₂ structure.¹⁸ The number of delocalized electrons drawn from two boron atoms (within one B layer) to the empty d orbital of a neighboring metal atom or from the metal to the boron atoms was calculated using the sum obtained from Pauling's single-bond radii in combination with the experimental atomic radii (see ref 18). In addition to the 4d transition metals studied in this theoretical investigation, MgB₂ has also been included. The planar, layered structure of MgB₂, which has been observed experimentally, shows superconducting properties.² Although Mg is not a transition metal, it has shown similar behavior concerning the electron transfer between Mg and B.¹⁵ As can be seen in Table 2, in the present study the magnesium in MgB₂ has been found to donate two electrons to the B element. It is, hence, possible to draw the conclusion that one way to receive a planar metal diboride is for the metal atom to donate two electrons, one to each neighboring boron atom.

E. Electron Bond Populations. An electron bond population (i.e., electron density between two atoms) is generally regarded to be a measure of the covalent bond strength. The results of

TABLE 2: Changes in Atomic Charge as a Result of Electron Transfer from One Metal Atom to Two Neighboring Boron Atoms

metal	Mg	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
initially planar									
ΔB charge [e]	-1.0	-0.6	-0.65	-0.6	-0.55	-0.5	-0.45	-0.6	-0.4
ΔM charge [e]	2.0	1.2	1.3	1.2	1.1	1.0	0.9	1.2	0.8
initially puckered									
ΔB charge [e]	-0.8	-0.6	-0.6	-0.45	-0.4	-0.4	-0.35	-0.45	-0.3
ΔM charge [e]	1.9	1.2	1.2	0.9	0.8	0.8	0.7	0.9	0.6

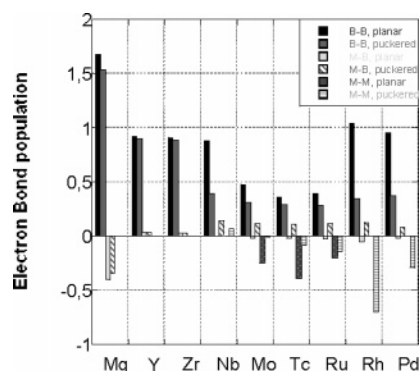


Figure 3. Electron bond populations for planar and puckered 4d metal diborides.

the calculated electron bond populations can be seen in Figure 3. It should be emphasized that the metal–metal (M–M) bond populations will become negative (i.e., antibonding) for Mo (initially planar structure only) and for the elements to the right (both puckered and planar structures) in Figure 3. The M–M electron bond populations for the puckered structures are in principle zero for Mo, while it has the most negative value for Rh (−0.7). For the initial planar structures only three metals to the right of Mo show M–M bond populations (Mo, Tc, and Ru), and they are all negative. These results imply that the structures that energetically preferred to be puckered in section B have antibonding M–M character. It is then possible to draw the conclusion that M–M bonds will not be formed for puckered structures. It furthermore correlates well with the work by Burdett et al., in which a theoretical study has been made (using band-structure calculations of the extended Hückel type) on some solid metal borides with the AlB_2 structure.¹³ It was there indicated that the puckering of the boron skeleton in the TcB_2 and RuB_2 structures is not due to the effects of the charge transfer but to strong metal–metal repulsions (overlap population) perpendicular to the nonmetal sheets.¹³ However, the overlap populations presented in ref 11 were calculated for the first-row (3d) transition metals. It must be stressed that their results correlate well with the results in the present study. In ref 11 the overlap populations for the elements to the left of Cr (group 6) are in principle zero (nonbonding), while the corresponding values for the elements to the right of Cr are slightly negative (antibonding).¹³ In this paper the metals to the left of Mo (also group 6) are also in principle zero, while they are slightly negative to the right of Mo, see Figure 3.

In the present study the metal–boron (M–B) bond populations for the initial planar structures were found to be almost zero for all elements except Mg, which has a bond population of about −0.4. For all the other elements the bond populations for the initially puckered structures are small and positive (<0.2). Hence, the M–B bond populations seem to be of no major importance for structural formation of the transition-metal borides.

As can further be seen in Figure 3, the boron–boron (B–B) bond populations are all positive (bonding) and numerically rather large. The initial planar structures have (compared to the puckered B ones) larger (or almost equal) B–B bond populations for all transition metals studied. It is worth noting that Mg has the highest bond population for both the initial planar and puckered structures (1.75 vs 1.55). These results support the conclusion that the B–B bond populations are not of any guidance in explaining the preferential structure formation.

F. Influence of Radius. The radius values of M and B are included to decide whether this “physical” number can influence

TABLE 3: Metallic (atomic) Radii of the Metal Atoms, and Covalent Radius for the Boron Atom^a

element, E	B	Mg	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
radius, r [pm]	88	160	178	159	143	136	135	133	134	138
r_M/r_B		1.82	2.02	1.81	1.63	1.55	1.53	1.51	1.52	1.57

^a The metallic radius is one-half of the shortest interatomic distance within the bulk metal. The covalent radius is the single-bond interatomic distance in diatomic molecules of B.¹⁹

the structural properties, as opposed to the effect of electronic properties of the various elements. As can be seen in Table 3, the radii for the transition 4d metals (Y to Pd) generally decrease from left to right in the periodic table.¹⁹ This is hence also the situation for the radius values between M and B within each MB_2 compound (r_M/r_B). The MB_2 compounds that, according to the energetic stabilization in section B prefer puckered boron structure (Mo, Tc, Ru, Rh and Pd), show a radius of around 1.50. The MB_2 compounds for which the planar B sheets are the energetically most preferred ones in section B (Y, Zr, and Nb), have a radius above 1.60. As can be seen in Figure 2 and Table 3, there is a clear correlation between the obtained results and the radius values.

Conclusion

The energetically most preferred structures of some 4d transition-metal diborides in the present investigation have been studied theoretically using density functional theory (DFT) under periodic boundary conditions. Two different initial structures were used and compared for each compound: the puckered RuB_2 structure (with puckered B layers) and the planar MoB_2 structure (with graphitic-like B layers). The purpose was to receive a deeper understanding about the underlying causes of the different structures of the 4d transition-metal diborides.

The calculated results show that the energetic stability generally follows the experimentally obtained results. The structures to the left of Mo (Y, Zr, and Nb) in the periodic table prefer the planar AlB_2 structure, while the structures to the right (Tc, Ru, Rh, and Pd) prefer a puckered structure. However, MoB_2 has no obvious preference for either of the two structures since there is a very small energy difference between the two structures. Both the initially puckered YB_2 and ZrB_2 became planar after geometry optimization. Hence, it is not possible to form the puckered structures of these two compounds.

Furthermore, there are observations that make us believe that the electronic redistribution is important for the finally obtained structure. The metals that are less electronegative than boron will more easily donate their electrons to boron and thereby induce a planar B structure. The same trend is observed when calculating the electron transfer between the 4d metals and the borons. It was found that the metals in the preferred planar structures would donate more than one electron to two neighboring boron atoms. The metal atoms within the MB_2 structures with preferred puckered B skeletons will, on the other hand, donate less than one electron to the neighboring B atoms. Two donated electrons per metal atom (or very close to) will result in the most stable AlB_2 structure.

It has furthermore been observed that strong M–M antibonding (i.e., negative electron bond population) is obtained for the puckered structures, while nonbonding interactions have been observed for the energetically favored planar structures (zero electron bond populations). The electron bond populations for the other bond types do not seem to be of any importance for either of the structures. A major conclusion that can be drawn from these observations is that charge transfer is important for

the planar structures whereas M–M repulsions are important for the puckered structures to form.

As can be seen from the trend of radius values, the size of the metal atoms also seems to be correlated to the energetically most preferred structure. The energetically most preferred planar structures have a radius above 1.60, and the energetically most preferred puckered structures have a radius around 1.50. The radius and charge transfer/bond populations do not contradict each other since small metallic radii (i.e., small radius) are generally expected to result in orbital overlap (i.e., for these systems causing M–M antibonding).

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