Brittle to Ductile Transition Dependence upon the Transition Pressure of \( \text{MB}_2 \) (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) Compounds

T. Chihi, M. Reffas, M. Fatmi, A. Bouhemadou, B. Ghebouli, and M. A. Ghebouli

1Research Unit on Emerging Materials (RUEN), Setif 1 University, Setif 19000, Algeria
2Department of Physics Faculty of Science, Setif 1 University, Setif 19000, Algeria
3Laboratory of studies of Surfaces and Interfaces of Solids Materials, Setif 1 University, Setif 19000, Algeria

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First principles calculations were performed to investigate the electronic and elastic properties of the group IV to group VI transition metal borides. As a result, the electronic bands and the density of states (DOS) at the Fermi level were obtained, also the independent elastic constants \((C_{ij})\) of hexagonal \( \text{MB}_2 \) (M= Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) at zero pressure, the bulk moduli \((B)\), the shear moduli \((G)\), and the \(B/G\) ratio were also obtained. The brittle/ductile behavior of the group IV to group VI transition metal borides were evaluated and analyzed in comparison with the available data. The Debye temperature for ZrB\(_2\) was calculated from the average elastic wave velocity obtained from the shear and bulk moduli. The calculated elastic properties are found to be in good agreement with the experimental values. The volume expansion coefficient \(\beta\) versus temperature and pressure for ZrB\(_2\) are discussed. The dependencies of the bulk, shear, Young’s modulus, Poisson’s ratio, and sound velocities \(V_s, V_l\) on the pressure \(P\) for ZrB\(_2\) were also analyzed.

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I. INTRODUCTION

A material is considered to be hard if it resists plastic deformation. Searching for intrinsic hard or superhard materials is of great practical significance. Hard materials can be divided into three groups dependent on the chemical bonding character. We have the metallic hard materials (borides, carbides, and nitrides of the transition metals), covalent hard materials (borides, carbides, and nitrides of Al, Si, and B as well as diamond) and ionic (ceramic) hard materials (oxides of Al, Zr, Ti, and Be) [1].

Most of the research effort on binary transition-metal (TM) borides has been focused so far on alloys composed of group IV-VI metals, in which the B atoms tend to occupy interstitial sites. The intercalation of small atoms such as boron into transition metals is a well-established strategy for designing materials with high hardness and melting point. Sung et al. [2] studied the correlation between hardness and the bulk modulus, then Haines et al. [3] observed a strong correlation between the hardness and the shear modulus.

Electronic address: fatmimessaoud@yahoo.fr

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Chung et al. successfully synthesized the hard material ReB$_2$ under ambient conditions [4], with the incorporation of B into the interstitial sites of Re to form ReB$_2$. They concluded that ReB$_2$ is an ultra-incompressible material with a bulk modulus of (360 GPa) as well as a hard (30.1–55.5 GPa) material [4], rivaling that of the diamond (442 GPa) [5].

Proceeding from group IV-VI transition metal borides, the diborides of the group IV-VI ceramics have received great attention, and as candidate materials for extreme environments, owing to their outstanding mechanical and chemical stability, they are widely used in many technological applications, for example as protective coatings for components as hard material [6, 7]. However, the group IV (V and VI) transition metals present a hexagonal crystal structure (cubic crystal structure) with a space group P6$_3$/mmc, $N^\circ 194$ (Im-3m $N^\circ 229$), with the incorporation of light atoms B inserted into the interstitial sites among the transition metal atoms to form MB$_2$ ($M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W$), the crystal structure undergoes a distortion to a hexagonal crystal structure of AlB$_2$-type with a space group P6/mmm, $N^\circ 191$, the Pearson symbol is hP3.

In this work, we performed density functional calculations to study the structural, elastic, and electronic properties of some compounds. The equilibrium structural parameters, bulk modulus, and elastic constants were calculated and compared with the experimental results, and the elastic anisotropy was discussed.

The density of states (DOS) of MB$_2$ ($M = Zr, Nb$) and TaB$_2$ were also calculated in order to investigate the electronic properties. The thermodynamic properties were also calculated.

II. METHODS AND MODELS

The density functional calculations on the structural, elastic, and electronic properties of MB$_2$ were performed using the CASTEP code [8].

Both lattices were optimized to get the equilibrium structure for MB$_2$. The exchange-correlation function was treated by the generalized gradient approximation (GGA-PBE) [9]. Also, the pseudopotentials were constructed using the ab initio norm conserving scheme to describe the valence electron interaction with the atomic core, in which the $M_{IV}$ transition metal $M_{IV}$ (nd$^2$(n+1)s$^2$) $n = 3–5$, M$_V$ (nd$^3$(n+1)s$^2$) $n = 3, 5$, Nb(4d$^5$s$^1$), and B(2s$^2$ 2p$^1$) orbitals are treated as valence electrons. The cut-off energy for the plane-wave expansion was set at 700 eV and the Brillouin zone sampling was carried out using the $10 \times 10 \times 8$ set of Monkhorst-Pack mesh [10]. The structures where optimized, using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique. This technique provides a fast way of finding out the lowest energy structure out of all the converged structures, with the following thresholds: energy change less than $2 \times 10^{-5}$ eV/atom, residual force less than 0.05 eV/Å, displacement of atoms during the geometry optimization less than 0.002 Å, and maximum stress within 0.1 GPa. The crystal structures and phase temperature range ($^\circ$C) are reported (Table I).
TABLE I: Calculated M1B₂, M2B₂, and M3B₂ structures: lattice parameters in Å and phase temperature range (°C) and compared with experimental data.

<table>
<thead>
<tr>
<th>MB₂</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>a⁺ (Å)</th>
<th>c⁺ (Å)</th>
<th>c/a⁺</th>
<th>Phase temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1B₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiB₂</td>
<td>3.0277</td>
<td>3.2180</td>
<td>1.0628</td>
<td>3.038</td>
<td>3.239</td>
<td>1.066ações</td>
<td>&lt; 3225</td>
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<tr>
<td>VB₂</td>
<td>3.0020</td>
<td>3.0387</td>
<td>1.0122</td>
<td>2.997</td>
<td>3.056</td>
<td>1.019ações</td>
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<tr>
<td>CrB₂</td>
<td>3.0005</td>
<td>2.9386</td>
<td>0.9793</td>
<td>2.969</td>
<td>3.066</td>
<td>1.032ações</td>
<td>&lt; 2200</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.973</td>
<td>3.072</td>
<td>1.033ações</td>
<td></td>
</tr>
<tr>
<td>M2B₂</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>ZrB₂</td>
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<td>3.5624</td>
<td>1.1208</td>
<td>3.170</td>
<td>3.532</td>
<td>1.114ações</td>
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<td></td>
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<td>3.165</td>
<td>3.547</td>
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<td></td>
<td>3.130</td>
<td>3.533</td>
<td>1.129ações</td>
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<td>NbB₂</td>
<td>3.1270</td>
<td>3.3122</td>
<td>1.0592</td>
<td>3.116</td>
<td>3.264</td>
<td>1.060ações</td>
<td>&lt; 3036</td>
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<tr>
<td>MoB₂</td>
<td>3.0444</td>
<td>3.3613</td>
<td>1.104</td>
<td>3.041</td>
<td>3.066</td>
<td>1.008ações</td>
<td>—</td>
</tr>
<tr>
<td>M3B₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>HfB₂</td>
<td>3.0986</td>
<td>3.3627</td>
<td>1.0852</td>
<td>3.082</td>
<td>3.243</td>
<td>1.0522ações</td>
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<tr>
<td>TaB₂</td>
<td>3.0674</td>
<td>3.1803</td>
<td>1.0368</td>
<td>3.098</td>
<td>3.224</td>
<td>1.0407ações</td>
<td>&lt; 3037</td>
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<td></td>
<td>3.097</td>
<td>3.225</td>
<td>1.041ações</td>
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<tr>
<td>WB₂</td>
<td>3.0249</td>
<td>3.3162</td>
<td>1.0963</td>
<td></td>
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</table>


III. RESULTS AND DISCUSSION

III-1. Structural properties

The unit cell is shown in Fig. 1. The considered MB₂ adopts the hexagonal structure with an AlB2-like structural type and space group P6/mmm (N°. 191). In the unit cell, one transition metal TM atom was placed in (0, 0, 0) and two B atoms in (1/3, 2/3, 1/2); (2/3, 1/3, 1/2).

The results for the lattice parameters a, c, and c/a are reported in Table I and compared with the experimental values and the previous theoretical calculations. Our
calculated value for the lattice parameters of the MB$_2$ compounds are in excellent agreement with the experimental and previous theoretical data [11–15].

III-2. Elastic Properties

Elastic constants determine the response of the crystal to the applied forces and play an important role in describing the mechanical properties of a solid material. Also, they give important information concerning the nature of the forces operating in the considered solids. In particular, they allow for determining the corresponding stability and stiffness. It is well known that the first-order and second-order derivatives of the potential give the forces and elastic constants, respectively.

For a hexagonal crystal, let us recall that the generalized elastic stability criteria [16] are:

\[ C_{11} > 0, \quad C_{33} > 0, \quad C_{14} > 0, \quad C_{66} > 0, \]
\[ C_{11} - C_{12} > 0, \quad C_{11} + C_{33} + C_{12} > 0, \quad (C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0. \]

The values of the $C_{ij}$ coefficients for the TM crystals calculated at the GGA/PBE level of theory are given in Table II, they fulfil all the mechanical stability criteria up to 300 GPa.

The $C_{11}$ and $C_{33}$ elastic constants, which correspond to the resistance to linear compression along the $x$ and $z$ crystallographic axes, are significantly larger than the other elastic constants, resulting in a pronounced elastic anisotropy in TM compounds. However the $C_{11}$ elastic constant always remains much larger than $C_{33}$, indicating that the $c$-axis is more compressible than the $a$-axis.

Furthermore the bulk and shear moduli ($B$ and $G$) are two important mechanical quantities for technological and engineering applications. The latter ($G$), which is related to bond bending, depends on the bond nature and decreases as a function of iconicity. For MB$_2$ with a hexagonal structure, the anisotropy ratio $A(C_{ij})$, is defined as $A = C_{33}/C_{11}$. The computed anisotropy ratios are listed in Table II.

For hexagonal structures, bulk modulus $B$, and shear modulus $G$ are obtained as
TABLE II: The zero pressure elastic moduli ($C_{ij}$) of hexagonal $M1B_2$, $M2B_2$, and $M3B_2$. The bulk moduli ($B$), shear moduli ($G$), $B/G$ ratio. All the elastic constants are in GPa except for the dimensionless $B/G$.

<table>
<thead>
<tr>
<th>Matter</th>
<th>$C_{11}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$B$</th>
<th>$G$</th>
<th>$B/G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M1B_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiB$_2$</td>
<td>661.96</td>
<td>458.98</td>
<td>259.61</td>
<td>64.40</td>
<td>100.10</td>
<td>251.90</td>
<td>264.82</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>660</td>
<td>432</td>
<td>260</td>
<td>48</td>
<td>93$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VB$_2$</td>
<td>665.04</td>
<td>479.11</td>
<td>204.11</td>
<td>114.75</td>
<td>108.69</td>
<td>268.54</td>
<td>235.14</td>
<td>1.14</td>
</tr>
<tr>
<td>CrB$_2$</td>
<td>518.19</td>
<td>334.03</td>
<td>148.76</td>
<td>229.84</td>
<td>203.26</td>
<td>277.31</td>
<td>137.27</td>
<td>2.02</td>
</tr>
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</table>

| $M2B_2$ |          |          |          |          |          |       |      |       |
| ZrB$_2$ | 539.82   | 421.97   | 246.71   | 56.96    | 118.40   | 231.40 | 227.49 | 0.91  |
|         | 567.8    | 436.0    | 247.5    | 56.9     | 120.5$^c$|       |      |       |
| NbB$_2$ | 581.72   | 451.95   | 211.36   | 138.36   | 184.18   | 290.33 | 202.79 | 1.43  |
| MoB$_2$ | 603.32   | 361.98   | 136.59   | 110.60   | 235.12   | 297.27 | 169.76 | 1.75  |
|         | 627.00   | 398.00   | 174.00   | 120.00   | 231.00   | 313.0$^b$| —    | —    |

| $M3B_2$ |          |          |          |          |          |       |      |       |
| HfB$_2$ | 627.08   | 485.21   | 288.65   | 74.99    | 119.15   | 276.31 | 259.61 | 0.98  |
| TaB$_2$ | 657.00   | 528.44   | 258.68   | 155.68   | 197.24   | 325.42 | 239.75 | 1.35  |
| WB$_2$  | 622.07   | 375.89   | 139.6    | 140.85   | 282.28   | 330.43 | 164.43 | 2.00  |

$^a$ [25] at 300 K.
$^b$ [26]
$^c$ [27] at 300 K.

follows:

\[
B = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}},
\]

\[
G = \frac{5}{2} \left\{ \frac{[(C_{11} + C_{12})C_{33} - 2C_{13}^2]C_{44} \left( \frac{C_{11} - C_{12}}{2} \right)}{2(C_{11} + C_{12} + \frac{C_{33} + 2C_{13}}{3})C_{44} \left( \frac{C_{11} - C_{12}}{2} \right) + [(C_{11} + C_{12})C_{33} - 2C_{13}^2] \left( C_{44} + \frac{C_{11} - C_{12}}{2} \right)} \right\}.
\]

Pugh [17] proposed the $B/G$ ratio to represent a measure of a “machinable behaviour”. A high $B/G$ value is then associated with ductility and a low value with brittleness. The critical value which separates ductile and brittle behaviours is at about 1.75. For instance, diamond has a $B/G$ of 0.80 [18], while aluminium, cobalt, rhodium, and iridium present $B/G$ ratios of 2.74, 2.43, 1.77, and 1.74, respectively [17].
We have plotted in Fig. 2 the $B/G$ Pugh ratio, and in Fig. 3 the bulk modulus for all the compounds under study as a function of the total number of valence electrons. It can be seen that our calculations show that $ZB_2$ ($Z = Cr, Mo, W$) are of a ductile character.

**FIG. 2:** Representing the variation of $B/G$ as a function of the e/cell ratio.

From our $B/G$ calculated ratios for the TM crystals, the main objectives of the present study are to present the effects of pressure on the $B/G$ ratio. Fig. 4 shows the effect of pressure on the brittle to ductile transition point. It is clearly seen that $B/G$ increases linearly with pressure up to 300 GPa. In this pressure range, $M1B_2$ ($M1 = Ti, V, Cr$) compounds never change character. For $M2B_2$ ($M2 = Zr, Nb, Mo$) compounds, the pressure transition is approximately of 275 GPa for $ZrB_2$ and 100 GPa for $NbB_2$, than for $TaB_2$ the pressure transition is equal to 275 GPa. For the other ($Cr, Mo, W$) compounds their $B/G$ ratio are above the considered critical value of 1.75.

Besides $B/G$, it is well known that $(C_{11} - C_{12})$ is also a very significant characteristic for the mechanical properties of materials [19]. Pointing out that $(C_{11} - C_{12})$ decreases in $M1B_2$ ($M3B_2$ ($M3 = Hf, Ta, W$)) since $TiB_2$ ($HfB_2$) until $CrB_2$ ($WB_2$), we may conclude an increase of the plasticity of $M1B_2$ ($M3B_2$) in this way.

The Debye temperature may be estimated from the average sound velocity $V_m$ [20],

$$\Theta = \frac{h}{k} \left[ \frac{3n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right]^{1/3} V_m,$$

where $h$ is Planck’s constants, $k$ is Boltzmann’s constant, $N_A$ is Avogadro’s number, $n$ is the number of atoms per formula unit, $M$ is the molecular mass per formula unit, $\rho$ is the
FIG. 3: Representing the variation of the bulk modulus $B$ as a function of the $e$/cell ratio.

FIG. 4: Pressure dependencies on the brittle to ductile transition.
density, and \( V_m \) is obtained from \([20]\)
\[
V_m = \left[ \frac{1}{3} \left( \frac{2}{V_s^3} + \frac{1}{V_l^3} \right) \right]^{-1/3},
\]
where \( V_s \) and \( V_l \) are the shear and longitudinal sound velocities, respectively.

The arithmetic average of the Voigt and the Reuss bounds is called the Voigt-Reuss-Hill (VRH) average and is commonly used to estimate the elastic moduli of polycrystals. The VRH averages for the shear modulus \( (G) \) and bulk modulus \( (B) \) are
\[
G = G_H = \frac{1}{2} (G_R + G_V), \quad B = B_H = \frac{1}{2} (B_R + B_V),
\]
where \( B_V, B_R, B_H \) are bulk modulus in Voigt, Reuss and Hill approximation and \( G_V, G_R, G_H \) are shear modulus in Voigt, Reuss and Hill approximation, respectively. Therefore, the probable values of the average shear and longitudinal sound velocities can be calculated from Navier’s equation \([21, 22]\):
\[
V_S = \sqrt{\frac{G_H}{\rho}}, \quad V_L = \sqrt{\left( \frac{B_H + \frac{4}{3}G_H}{\rho} \right)},
\]
The longitudinal, transverse, and average sound velocities and Debye temperature of ZrB\(_2\) have been calculated and are listed in the Table III.

| \( \rho \) (g/cm\(^3\)), longitudinal, transverse, and average sound velocities in (m/s) and the Debye temperature (\( \Theta \) in Kelvin) calculated from the mean-sound velocities of ZrB\(_2\). |
|---|---|---|---|---|
| ZrB\(_2\) | 6.022 | 9514.77 | 6247.83 | 6843.19 | 892.90 |

Fig. 5 shows the dependencies of the bulk, shear, Young’s modulus, and Poisson’s ratio (left panel) and sound velocities \( V_l, V_t, \) and Debye temperature (right panel) on the pressure \( P \). The calculated bulk modulus \( B_0 \) at \( T = 0 \) K is 262 GPa for ZrB\(_2\) structures, which is consistent with the calculated \( B_{\text{EOS}} \). We can see that all these physical properties increase with pressure.

**III-3. Electronic Properties**

We discuss the compounds which have ductile character: MB\(_2\) (M = Zr, Nb) and TaB\(_2\) compounds. The upper panel corresponds to the pressure 50 GPa, i.e., a brittle character, and the lower panel represents a ductile character, i.e., the DOS at 280 GPa (Fig. 6, 7). Both the M-s and B-s states for all compounds and for the two characters are zero at the Fermi level and increase slightly further away on both sides of this level. In the bottom panel of the M-d cross, the Fermi level is minimum, i.e., in the ductile character the compounds become less conductive. In addition, in the area, there is a whole pseudo gap.
FIG. 5: Dependencies of the bulk, shear, Young’s modulus, and Poisson’s ratio (left panel) and sound velocities $V_i$, $V_t$, $V_m$, and Debye temperature (right panel) on pressure $P$.

FIG. 6: Electronic energy band structures of MB$_2$ ($M =$ Zr, Nb) and TaB$_2$ for the pressure 50 GPa (upper panel) and 280 GPa (lower panel), respectively.

at the Fermi level, which moves from the left in the same (column) of the periodic table, and this is due to the number of valence electrons.

In the partial $s$-, $p$-, and $d$-densities of states (DOS) at the equilibrium lattice constants of MB$_2$ ($M =$ Zr, Nb) and TaB$_2$ compounds, the valence bands starts at around 15 eV (not shown) below the Fermi level ($E_F = 0$ eV).

Below the Fermi level, the bands originate mainly from the mixed B-2$p$ and M-$d$ states. The DOS contains strongly hybridized and M-$d$, B-2$p$ states, which are responsible for the covalent M-B bonding. This strong hybridization increases with the bulk modulus
**III-4. Thermodynamic Properties**

In order to enhance the performance of heat engines, the temperature of the working fluid must be raised. This temperature is limited by the maximum working temperature of the material used in these engines. The transition metal borides have been investigated aiming at high temperature applications. Thermal expansion is one of main properties for applications. The aim of this study was the evaluation of the thermal expansion coefficients for one of the transition metals borides ZrB$_2$. This domination increases in the same period (column) of the periodic table.

The near-Fermi bands are mainly of M-$d$ type with small admixtures of the B-$2s$ and B-$2p$ states. In the vicinity of the Fermi level the M-$d$ states dominate and should contribute to the conduction properties of MB$_2$. This domination increases in the same period (column) of the periodic table.
the quasi-harmonic Debye model, we obtained the Debye temperature $\Theta = 892.90$ K at $P = 0$ GPa and $T = 0$ K for the ZrB$_2$ structures, which have almost the same values as that calculated from the elastic constants. We can see from Fig. 8 (upper panel) that, at different temperatures [pressures] and constant pressures [temperatures], the Debye temperature decreases [increases].

It may be noted that the variation of the coefficient of thermal expansion as a function of the temperature is similar as that in the specific heat at constant pressure.

It is shown that, for a given pressure [temperature], $\alpha$ increases [decreases] with temperature [pressure], especially at 0 pressure and gradually tends to a linear increase at high temperature, for ZrB$_2$ structures.

For a constant temperature, and $C_p$ varies parabolically then linearly as a function of the pressure and $C_p$ becomes more and more linear if the temperature and pressure increases.

IV. CONCLUSION

Based on the Density Functional Theory and using pseudo potential plane waves within a generalized gradient approximation, the present paper reported on a detailed study of the effect of pressure on the brittle to ductile transition point, for all compounds MB$_2$ ($M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W$). It can be seen that our calculations show
that ZB₂ (Z = Cr, Mo, W) are of ductile character.

In the pressure range, M1B₂ (M₁ = Ti, V, Cr) the compounds never change character. For M₂B₂ (M₂ = Zr, Nb, Mo) compounds, the pressure transition is approximately of 275 GPa for ZrB₂ and 100 GPa for NbB₂, while for TaB₂ the pressure transition is equal to 275 GPa. For the other (Cr, Mo, W) compounds their B/G ratios are above the considered critical value of 1.75.

Also, we studied the pressure dependence of the bulk, shear and Young’s modulus Poisson’s ratio, the sound velocities V₁, V₄, and the Debye temperature on the pressure P and temperature T for ZrB₂ structures. We can see that all these physical properties increase with pressure. The thermal expansion heat capacity Cᵥ, Cₚ, and the Debye temperature are obtained versus the temperatures and pressures for ZrB₂ structures.

References