Elastic properties of Mg$_x$Ti$_{1-x}$B$_2$ (0 ≤ x ≤ 1) studied by first-principles calculations

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The elastic properties, including elastic constants, bulk, and shear moduli, and anisotropic index of hexagonal Mg$_x$Ti$_{1-x}$B$_2$ (0 ≤ x ≤ 1) are obtained using a first-principles density-functional-theory method. A difference in chemical bonding occurs between Ti-rich and Mg-rich diborides, leading to significantly different elastic properties: a small elastic anisotropy with relatively large bulk and shear moduli for Ti-rich diborides with x < 0.25, and a large elastic anisotropy and relatively small bulk and shear moduli for Mg-rich diborides with x > 0.25. The calculated results reveal a dominant role of the interplanar metal-metal bonds in predicting the extent of shear elastic anisotropy in Mg$_x$Ti$_{1-x}$B$_2$ (0 ≤ x ≤ 1).

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I. INTRODUCTION

Titanium diboride, TiB$_2$, is well known to be an ultrahigh-strength, highly ductile, and highly deformable material. The physical and chemical properties of TiB$_2$ have been extensively studied by experimental and theoretical methods. Due to its high hardness, extreme melting point, and chemical inertness, TiB$_2$ is a candidate for a number of applications. Specifically, it is found to have large shear strength under high pressure with a shear modulus value of 265 GPa. The combination of high hardness and shear strength make it attractive for ballistic armor, but its relatively high density (4.50 gm/cm$^3$) (Ref. 2) makes it less attractive for this purpose than some other ceramics. One can consider a combination of magnesium (Mg) and TiB$_2$ as potentially bringing optimal materials characteristics in terms of its mechanical properties while at the same time making the resulting material system much lighter. Isomorphic MgB$_2$ is a light-weight material with a density of (2.66 gm/cm$^3$), but lacks shear strength compared to TiB$_2$. In the present study, we consider Mg$_x$Ti$_{1-x}$B$_2$ (0 ≤ x ≤ 1), investigating its elastic properties using a first-principles density-functional theory (DFT) method. Specifically we calculate the variation of the structural and elastic properties of Mg$_x$Ti$_{1-x}$B$_2$ with the dopant (Mg) concentration in the host (TiB$_2$) lattice. The composition of the ordered mixed system was chosen in such a way that the doping of Mg atoms maintained the hexagonal symmetry of the host TiB$_2$ requiring relatively modest computational resources for calculations. It is expected that such a fundamental understanding of the elastic properties of Mg$_x$Ti$_{1-x}$B$_2$ will aid in determining its stability and shear strength for use as a lightweight impact-resistant material. It is also noted that there have been experimental efforts to incorporate Ti in MgB$_2$—a bulk superconductor—to improve its mechanical and superconducting properties.

II. COMPUTATIONAL METHOD

A. Modeling of structure

Quantum-mechanical calculations based on DFT were performed using the CRYSTAL09 program. A linear combination of Gaussian-type orbitals (GTO) is used to construct a localized atomic basis from which Bloch functions are constructed by a further linear combination with phase factors. The exchange and correlation effects were treated with the B3LYP functional form (i.e., Becke’s three-parameter hybrid exchange functional and the Lee, Yang, and Parr correlation functional), which has been found to yield band gaps consistent with measured values for semiconducting and ionic materials.

All-electron basis sets employed in the present study are the split-valence GTO basis sets consisting of three- and two p-type shells for B (i.e., a 6-21G set), five s-, four p-, and one d-type shell for Ti (i.e., an 8-511G set), and four s- and three p-type shells (i.e., an 8-511G set) for Mg. The chosen level of basis sets has been demonstrated to be very good in providing accurate and reliable predictions of structural properties for a wide variety of materials, including Si, BN, GaN, GeC, PbF$_2$, Ga$_2$O$_3$, and boron. Several higher levels of basis sets with polarization were also studied for boron yielding very similar structural properties for Mg$_4$Ti$_4$B$_{16}$ including lattice and elastic constants. The integral overlap tolerances were 10$^{-7}$ Hz and energy tolerance was 10$^{-6}$ Hz in the iterative solution of the Kohn-Sham equations. The Brillouin zone was sampled with a 12 × 12 × 12 Monkhorst grid for integrations in reciprocal space.

To calculate the structural and elastic properties of Mg$_x$Ti$_{1-x}$B$_2$, we began with a supercell of Ti$_8$B$_{16}$ representing the host, TiB$_2$. The cases of x = 0, 0.125, 0.25, 0.5, 0.75, and 1 can then be represented by Ti$_8$B$_{16}$, Mg$_1$Ti$_7$B$_{16}$, Mg$_2$Ti$_6$B$_{16}$, Mg$_4$Ti$_4$B$_{16}$, Mg$_6$Ti$_2$B$_{16}$, Mg$_7$Ti$_{16}$, and Mg$_8$B$_{16}$, respectively. Considering the fact that both TiB$_2$ and MgB$_2$ crystalize in the hexagonal AlB$_2$ structures, Mg$_x$Ti$_{1-x}$B$_2$ (0 ≤ x ≤ 1) are assumed to be in the AlB$_2$-type structures (Fig. 1) in the present study. We emphasize that the reliability and accuracy of the chosen computational model was successfully tested on the well-studied TiB$_2$ system, closely reproducing its observed structural properties, as we discuss in the following section.

B. Calculation of elastic constants

The calculated variation of the total energy with the strain applied to induce deformation in the lattice is used to

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V olume per unit cell (˚A³)² 5
Binding energy
(˚A³)c
Density (gm/cm³)
Cohesive energy
MgB₂, the experimental values of
for the crystal,
the neighborhood of the minimum of the calculated energy
ε
are applied strains, and the variations are evaluated in
where Voigt’s notation is employed (Cαβ
strain, which then yields the second-order elastic constants,
mine the change in energy of the crystal as a function of
matrix,
of its space group, and these are used to generate a strain
variations (derivatives) of the equilibrium energy with respect
to applied strains via the relation

\[ C_{αβ} = \frac{1}{V} \frac{∂²E}{∂ε_α∂ε_β}, \]  

(1)
where Voigt’s notation is employed (α,β = 1,2, . . . ,6), the ε are applied strains, and the variations are evaluated in
the neighborhood of the minimum of the calculated energy
for the crystal.\(^5\)

In the equilibrium configuration of a given system, allowed
deformations of the system are determined from the analysis
of its space group, and these are used to generate a strain
matrix, ε. Several numerical routines are employed to determine
the change in energy of the crystal as a function of
strain, which then yields the second-order elastic constants,
Cαβ. Note that the atomic coordinates were fully optimized in
these calculations.

III. RESULTS AND DISCUSSION

A. Structural properties

TiB₂ crystallizes in a hexagonal AlB₂ structure at ambient
conditions with the space group of 191 (i.e., P6/mmm).
The boron atoms are arrayed in graphene-type layers. Each
layer of boron atoms is separated by a hexagonal layer
of Ti atoms. Each atom in the Ti-layer lies above and below
the center of an open hexagonal space in the graphene-type
boron layer (Fig. 1). Twelve equidistant boron atoms are near
neighbors for each Ti atom, whereas the near neighbors of
each boron atom are three boron atoms at a short distance and
six titanium atoms at a longer distance.\(^2\) The experimental
values of the lattice parameters a and c are 3.028 and
3.228 ˚A (Ref. 51) [or 3.0236 and 3.2204 ˚A (Ref. 2),
respectively.

The calculated structural properties of TiB₂ (or Ti₈B₁₆)
at the B3LYP-DFT level of theory are in excellent agree-
ment with the corresponding experimental values. For ex-
ample, the calculated lattice parameters a and c are 3.0328
and 3.2254 ˚A, respectively, giving a unit-cell volume of
25.54 ˚A³. The experimental value for the unit-cell volume
is 25.5 ˚A³, whereas previously reported first-principles cal-
culations find the unit-cell volume of TiB₂ to be 25.1–
25.7 ˚A³.\(^26,28,31\) A recent ultrasoft pseudopotential-generalized
gradient approximation to DFT calculation reported the
lattice constants a and c to be 3.0315 and 3.238 ˚A,
respectively.\(^34\)

Table I collects the optimized lattice parameters, unit-cell
volume, density, and cohesive energy associated with the
equilibrium configurations of MgₓTi₁₋ₓB₂ (0 ≤ x ≤ 1)
obtained at the B3LYP-DFT level of theory. A gradual increase
in the lattice parameters together with the equilibrium volume
and density is predicted as the concentration of Mg increases
in the TiB₂ lattice except in the case of a for Mg₁Ti₇B₁₆, which
contracts slightly (∼0.2%) relative to that of the host Ti₈B₁₆.
The variation of lattice parameters versus the concentration of
Mg is shown in Fig. 2. In going from Ti₈B₁₆ to Mg₈B₁₆, the
increase in a is ≈1.3% whereas the increase in c is ≈4.5%.
The slight increase in a is also reflected in the variation of
the intraplanar distance, R_B−B, as expected. The calculated
lattice parameters for Mg₈B₁₆ are in very good agreement
with previously reported experimental\(^52–56\) and theoretical
studies.\(^30,57–60\) Note that the values of the bulk modulus and
its pressure derivative obtained using the calculated energy
surface (i.e., total energy versus volume) numerically fitted to
the static equation of state (EOS) are given as supplementary
information.\(^61\)

The calculated cohesive energy with respect to atomic
constituents comes out to be 10.36 eV for Ti₈B₁₆ gradually
decreasing to 9.16 eV for Mg₈B₁₆. Considering that only a
small change occurs for a, the expansion in c in going from
Ti₈B₁₆ to Mg₈B₁₆ can mainly be attributed to the weakening of

TABLE I. Structural properties of MgₓTi₁₋ₓB₂. For TiB₂, the experimental values of a and c are 3.028 and 3.228 Å, respectively.\(^55\) For
MgB₂, the experimental values of a and c are 3.086 and 3.521 Å, respectively.\(^53\)

<table>
<thead>
<tr>
<th></th>
<th>Ti₈B₁₆</th>
<th>Mg₁Ti₇B₁₆</th>
<th>Mg₂Ti₆B₁₆</th>
<th>Mg₄Ti₄B₁₆</th>
<th>Mg₆Ti₂B₁₆</th>
<th>Mg₇Ti₁B₁₆</th>
<th>Mg₈B₁₆</th>
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<td>a (Å)</td>
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<td>3.0192</td>
<td>3.0279</td>
<td>3.0329</td>
<td>3.0457</td>
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<td>3.0638</td>
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<tr>
<td>c (Å)</td>
<td>3.2254</td>
<td>3.2666</td>
<td>3.2872</td>
<td>3.3312</td>
<td>3.3611</td>
<td>3.3694</td>
<td>3.3720</td>
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<tr>
<td>Volume per unit cell (Å³)</td>
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<td>25.79</td>
<td>26.10</td>
<td>26.54</td>
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<td>27.19</td>
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<tr>
<td>Density (gm/cm³)</td>
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<td>4.31</td>
<td>4.07</td>
<td>3.63</td>
<td>3.20</td>
<td>2.99</td>
<td>2.79</td>
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<tr>
<td>Bond distance [R_B−B (Å)]</td>
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<td>1.743</td>
<td>1.748</td>
<td>1.751</td>
<td>1.758</td>
<td>1.757</td>
<td>1.769</td>
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<tr>
<td>Cohesive energy/atom (eV)</td>
<td>10.36</td>
<td>10.18</td>
<td>10.01</td>
<td>9.72</td>
<td>9.43</td>
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<td>0.039</td>
<td>0.037</td>
<td>0.037</td>
<td>0.032</td>
<td>0.016</td>
<td></td>
</tr>
</tbody>
</table>

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the intraplanar bonds along the c direction yielding a lower cohesive energy for Mg₈B₁₆ relative to Ti₈B₁₆. Table I also shows the binding energy of the mixed system with respect to its constituent, suggesting Mg₈Ti₁₋ₓB₂ to be stable for all values of x.

Figure 3 shows contours of the projected valence-band charge density for Ti₈B₁₆, Mg₄Ti₄B₁₆, and Mg₈B₁₆. The planar YZ cross-sectional projection across the hexagonal axis shows the interaction between the metallic Ti planes in Ti₈B₁₆ which appears to decrease when Ti is replaced by Mg in Mg₄Ti₄B₁₆. No interaction between Mg planes is seen for Mg₈B₁₆, where the charge-density contours only show the presence of covalent-type B-B bonding features of the hexagonal boron layers.

The predicted stability of Ti-rich diborides relative to Mg-rich diborides can therefore be understood in terms of the presence of interplanar interactions along the c axis between Ti atoms in the lattice. Furthermore, the calculated total and projected densities of states (not shown here) confirm the presence of dominant Ti bands in Ti-rich diborides. There is also a finite density of states at the Fermi energy, suggesting that the nature of diborides is metallic, as also suggested by their calculated band structures (not shown here). There is a small charge transfer (= 0.2e) from Ti to B revealed by a Mulliken charge analysis of Ti-rich diborides.

**B. Elastic properties**

The calculated elastic properties, including elastic constants, bulk and shear moduli, and percentage of anisotropy of Mg₅₁₋ₓTiₓB₂, are listed in Table II and illustrated in Fig. 4. Here, B₅ is the X-axis elasticity in a system under hydrostatic pressure, K is the bulk modulus, and G is the shear modulus. The percentage of anisotropy of the elastic modulus is defined as (B₅ − B₅)/B₅ × 100% and those of K and G are (Kₕ − Kₚ)/(Kₕ + Kₚ) × 100% and (Gₕ − Gₚ)/(Gₕ + Gₚ) × 100%. The Voigt estimate is labeled as V and the Reuss estimate is labeled as R. For these calculations, we follow the methodology that is developed in Ref. 63. A² is the universal anisotropy index. 64 Note that there are six different elastic coefficients—C₁₁, C₁₂, C₁₃, C₃₃, C₄₄, and C₆₆—associated with a hexagonal crystal structure such as TiB₂, although C₆₆ can be written as (C₁₁ − C₁₂)/2.

The calculated elastic constants Cᵦᵦ show a gradual decrease in their values as we go from Ti-rich to Mg-rich diborides. We notice that the Cᵦᵦ values of Mg₈B₁₆ are about 60%–90% of Cᵦᵦ of Ti₈B₁₆, with the exception of C₄₄. A significant decrease in C₄₄ is predicted for Mg-rich diborides relative to Ti-rich borides, thus representing a higher resistance to deformation with respect to a shearing stress in the latter case. The calculated values of elastic (E), bulk (K), and shear (G) moduli of Ti₈B₁₆ are in agreement with the previously reported theoretical and experimental studies.

**FIG. 3.** (Color online) The valence-band charge-density contours for Ti₈B₁₆, Mg₄Ti₄B₁₆, and Mg₈B₁₆. The YZ cross-sectional projection across the hexagonal axis shows the Mg and Ti atoms lying above and below the horizontal graphene-type boron layers.

**FIG. 4.** Average bulk modulus (Kᵥ), average shear modulus (Gᵥ), density, and universal anisotropy (A²) vs the amount of Mg in the alloy Mg₅₁₋ₓTiₓB₂. The values for the bulk modulus, shear modulus, and density have been normalized by dividing by the corresponding value for TiB₂ for a clearer comparison.
For example, the experimental\textsuperscript{24} (calculated) values of \( E, K, \) and \( G \) are 584.7 (632), 247.5 (282), and 264.3 (285) GPa, respectively. It should be noted that due to difficulties in growing high-quality single crystals of TiB\(_2\) or MgB\(_2\), measurements on single crystals of these materials are scarce.\textsuperscript{4,17,24} Several experimental investigations were performed, however, on polycrystalline samples of these materials,\textsuperscript{2,23} leading to a large scatter of reported values in the scientific literature. Furthermore, experimenters conducting neutron-diffraction measurements at pressures up to 0.62 GPa (Ref. 55) considered MgB\(_2\) to be anisotropic in thermal expansion and compressibility with a disproportionate response along the \( c \) axis. Other experiments using x-ray powder diffraction conducted at higher pressures characterized the anisotropic behavior of MgB\(_2\) to be only small over a pressure range up to 8 GPa (Ref. 53) to moderate\textsuperscript{54} in bonding behavior between the \( a \) and \( c \) lattice parameters for pressures up to 6.15 GPa.

The elastic response of a hexagonal crystal such as TiB\(_2\) is expected to show some extent of elastic anisotropy. Considering \( C_{66}/C_{44} \) to represent a degree of the shear elastic anisotropy in a hexagonal crystal, we find TiB\(_2\) to be associated with finding a low shear-mode elastic anisotropy, as also seen experimentally.\textsuperscript{24} Interestingly, the shear elastic anisotropy remains nearly the same up to 25\% Mg in Mg\(_x\)Ti\(_{1-x}\)B\(_2\). It then increases to 2.5 for Mg\(_8\)B\(_{16}\), suggesting that it exhibits a strong elastic anisotropy. Note that \( C_{66}/C_{44} = 1 \) represents the case of elastic isotropy.

Recently, Ranganathan and Ostoja-Starzewski introduced a universal elastic anisotropy index \( A^U \) whose nonzero value expresses the extent of single-crystal anisotropy accounting for both the shear and the bulk contributions.\textsuperscript{64} The calculated \( A^U \) is small for Ti-rich borides, becoming large for Mg-rich diborides. It is 1.03 for Mg\(_8\)B\(_{16}\), indicating its large elastic anisotropy.

### IV. CONCLUSIONS

In summary, we find that the elastic properties of Mg\(_x\)Ti\(_{1-x}\)B\(_2\) (0 \( \leq \) \( x \) \( \leq \) 1) can be grouped into two categories: a small elastic anisotropy with relatively large bulk and shear moduli is predicted for Ti-rich diborides with \( x < 0.25 \), whereas Mg-rich diborides are predicted to be associated with a large elastic anisotropy and relatively small bulk and shear moduli. The predicted elastic behavior is confirmed by the nature of chemical bonding in Mg\(_x\)Ti\(_{1-x}\)B\(_2\): there is a noticeable participation of interplanar metal-metal bonds in Ti-rich diborides, whereas the intraplanar B-B bonds dominate in Mg-rich diborides. The interplanar bonds in Ti-rich diborides keep boron layers from moving with respect to each other, whereas boron layers shift easily in the absence of the interplanar bonds in Mg-rich diborides, leading to a relatively large anisotropy in the shear modulus.

The calculated results, therefore, provide a guideline to design a lower-density yet isotropically hard Mg\(_x\)Ti\(_{1-x}\)B\(_2\)
alloy. Upon doping of Mg atoms into the lattice ($x \leq 0.25$), the density of the material is decreased with only a marginal decrease in elastic moduli and a slight increase in elastic anisotropy. An Mg$_x$Ti$_{1-x}$B$_2$ material with elastic properties comparable to TiB$_2$ yet lower in density is predicted. When $x > 0.25$, however, the paucity of Ti-Ti interplanar bonds is manifested in Mg$_x$Ti$_{1-x}$B$_2$ materials that exhibit more shearing behavior along boron layers. Although much less dense, these materials become highly anisotropic in their elastic behavior and would be much less favored as replacements for TiB$_2$ in technological applications.

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48All details regarding the basis sets employed in the calculations discussed in this study can be obtained from the authors (pandey@mtu.edu).
61See supplemental material at [http://link.aps.org/supplemental/10.1103/PhysRevB.83.115122] for the values of the bulk modulus and its pressure derivative obtained using the calculated energy surface (i.e., total energy versus volume) numerically fitted to the static equation of state (EOS).