# First-principles modeling of hardness in transition-metal diborides

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Based on recent experiments, the diborides $OsB_2$ and $ReB_2$ were proposed to be ultraincompressible and superhard materials. By application of an *ab initio* density-functional theory approach we investigate the elastic and cleavage fracture properties of the borides $MB_2$ ($M=$ Hf, Ta, W, Re, Os, and Ir). We derive a direct correlation between the lowest calculated critical cleavage stress and the experimental (micro)hardness. By calculating the critical shear stress and estimating the possibility of dislocation emission we can justify the prediction that $ReB_2$ is indeed a superhard material.

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The search for superhard materials is motivated by the technological need of robust and chemically stable materials for, e.g., cutting tools and wear resistant coatings. Although diamond and cubic boron-nitride are well known to be intrinsically superhard materials, their technological applicability is limited.[1] Therefore, for the purpose of finding new superhard materials with desired properties it is crucial to understand and predict the occurrence of superhardness.

Recently, a new promising material, $ReB_2$, has been synthesized. It is proposed to be superhard because a tip of this material could leave scratches on a (100) diamond surface and a hardness of 48 GPa was claimed experimentally.[2] Very recently, single crystals of $ReB_2$ have been prepared and Vickers microhardness and nanoindentation testing have indicated hardness $H=40.5$ and 36.4 GPa, respectively.[3] $ReB_2$ also exhibits anisotropic incompressibility along the $c$ axis with a magnitude comparable to that of diamond.[2,4] Because $ReB_2$ is so far the only known bulk superhard material which is metallic (known superhard materials such as diamond and boron nitride are insulators), it has attracted a large scientific and technological interest and stimulated further investigations on the structural, electronic, and elastic properties of other 5*d*-transition-metal diborides, $OsB_2$,[5–9] $RuB_2$,[7] $ReB_2$,[10,11] $WB_2$,[10] and $TcB_2$.[11]

In this Brief Report, we study the ideal mechanical properties (the critical cleavage and shear stresses) on a fully *ab initio* basis. We do not refer to any model which involves nearest-neighbor bonds and/or (semi)empirical parameters. We rather directly exploit results of parameter free density-functional theory (DFT) calculations. We assume that at the very onset of an indentation the hardness of an intrinsically brittle material is related to the *minimum* critical stress for brittle cleavage $\sigma_{c,\min}$: when an indenter enters a brittle material, it breaks bonds between planes of orientation $[hkl]_{\min}$ for which the critical stress has its lowest value. Following this concept we derive values for the hardness $H$ which are in good agreement with experiment and we also predict superhardness for $ReB_2$ (see Fig. 3) without the need for any empirical parameter. Such an approach enables us also to investigate the trend in cleavage stresses of $M$ diborides ($M=$Hf, Ta, W, Re, Os, and Ir) and consequently search for superhardness.

The DFT calculations have been performed by application of the Vienna *ab initio* simulation package VASP.[14] We used the projector augmented wave method with the generalized gradient approximation according to the parametrization of Perdew and Wang.[15,16] Convergency of the total energies with respect to basis size and number of **k** points for the Brillouin zone integration was carefully checked. For modeling the cleavage interfaces, we constructed unit cells with 12 atomic layers, which ensured suitable precision.

Brittle cleavage formation has been modeled by a repeated slab construction as described in detail in Refs. 17 and 18: along a given direction $[hkl]$ a material is cleaved between two planes by a rigid opening $x$, i.e., no relaxations of atomic positions are allowed. Then the decohesive energy for ideal brittle cleavage $E_b$ can be expressed by the so-called universal binding energy relation (UBER),[19]

$$E_b(x) = G_b\left[1 - \left(1 + \frac{x}{l_b}\right)\exp\left(-\frac{x}{l_b}\right)\right]. \quad (1)$$

The material and direction-dependent parameters are the cleavage energy $G_b$ and the critical length $l_b$ at which the stress $\sigma(x)=dE_b/dx$ reaches its maximum, $\sigma_c=\max[\sigma(x)]=G_b/el_b$.

The critical stress $\sigma_c$ represents the tensile stress needed to cut the bonds between given cleavage planes. For modeling intrinsic (micro)hardness we assume that an indenter penetrating the surface of the sample preferably breaks the weakest bonds according to the lowest value of $\sigma_c$. In general, all cleavage properties depend on the material, the orientation of the actual cleavage plane, and between which planes the materials is cleaved. The model parameters $G_b$ and $l_b$ of Eq. (1) are obtained by fitting UBER to DFT calculations.

For our study of brittle cleavage we consider cleavage between the low-index planes for which the effect of breaking the bonds is expected to be the strongest. According to Fig. 1, for $MB_2$ compounds with the $ReB_2$-type crystal structure, (0001) cleavage results in two different cleavage planes: the (0001)-S1 plane, which involves breaking of boron-boron bonds, and the (0001)-S2 planes for which metal-boron bonds are broken. By symmetry, $(11\bar{2}0)$ cleavage results in only one cleavage interface denoted by $(11\bar{2}0)$-S3, for which boron-boron as well as metal-boron bonds are broken in the cleavage process. For $HfB_2$ and $TaB_2$ with the $AlB_2$-type crystal structure, we construct the three cleavage planes (0001), (1100), and $(11\bar{2}0)$, respectively. Because boron atoms form a graphite layer structure,

 

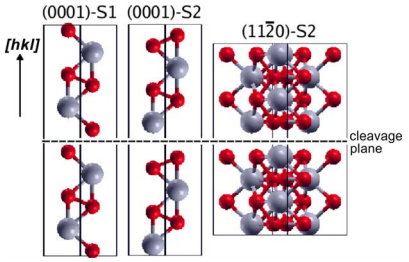


FIG. 1. (Color online) Orientation-dependent cleavage of an $MB_2$ compound with the hexagonal $ReB_2$-type crystal structure. The material is cleaved perpendicular to the indicated cleavage plane.

the (0001) interface again involves breaking of metal-boron bonds, but for the (1100) and (11$\bar{2}$0) planes strong covalent boron-boron bonds have to be broken.

Figure 2 shows that the DFT results for $ReB_2$ (upper panel) and $HfB_2$ (lower panel) fit the UBER model very well and similar fits are obtained also for the isostructural compounds $OsB_2$, $WB_2$, $IrB_2$, and $TaB_2$. The results are summarized in Table I. For the W, Re, and Os diborides, the direction dependency of the cleavage properties has the same trend: the cleavage energies are lowest for (0001)-S2 cleavage indicating that this is the preferred cleavage plane. In addition and most important for hardness, this cleavage orientation provides the lowest critical stresses. For (11$\bar{2}$0)-S3 cleavage, the values of $G_b$ are largest and a very high stress is needed for spontaneous cleavage. Finally, for (0001)-S1 cleavage, the cleavage energies are intermediate due to the fact that only boron-boron covalent bonds are broken.

We find that the critical stresses, in particular for $ReB_2$, are very large in comparison to common hard intermetallic compounds and ceramics.[17] For $ReB_2$, the experimentally claimed superhard material, our DFT results agree well with the experimental data,[2] namely, that the (0001) planes and (11$\bar{2}$0) planes support the weakest and strongest stresses, respectively. For $HfB_2$ and $TaB_2$ of the $AlB_2$ structure type (cf. Fig. 2 and Table I), the lowest cleavage energies and critical stresses were calculated for (0001) cleavage, which breaks metal-boron bonds. The other two cleavage orientations (1100) and (11$\bar{2}$0) exhibit considerably higher stresses similar to those of the studied W, Re, and Os diborides.

The cleavage anisotropy is due to the peculiar bonding properties of the studied borides: covalent boron-boron bonds are significantly stronger than the covalent metal-boron bonds.[4] Consequently, the critical stress is lowest for the (0001)-S2 cleavage in compounds with the $ReB_2$-type structure and for the (0001) cleavage of compounds with the $AlB_2$ structure because only weak metal-boron bonds are broken. For all other cleavage directions strong boron-boron bonds are cut, resulting in higher cleavage energies and critical stresses. Therefore, strong diborides will crack between atomic layers of metal and boron of (0001) direction, and therefore these planes are also the easiest location for stress release.[2] In light of these facts it is surprising that the most incompressible direction of the materials is ⟨0001⟩. Our results clearly demonstrate that ultraincompressibility (which is based on elastic properties) does not necessarily impose

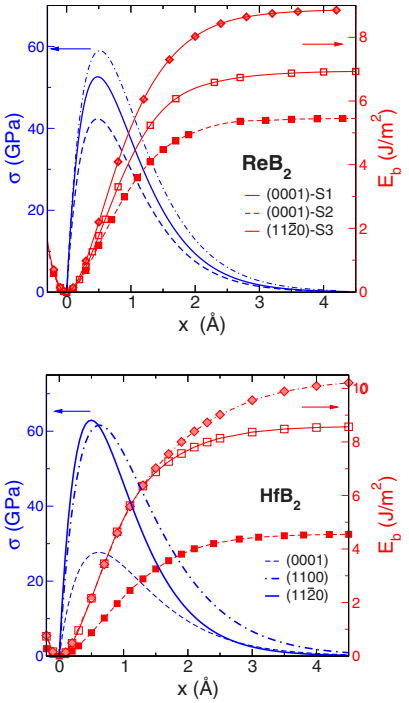


FIG. 2. (Color online) DFT results for brittle cleavage. Cleavage energy $E_b(x)$ and stress $\sigma_b$ vs cleavage opening $x$ for hexagonal $ReB_2$ (upper panel) and orthorhombic $HfB_2$ (lower panel).

high resistance against cleavage or fracture. However, a high elastic modulus is often being correlated with high hardness, even though the underlying deformations are fundamentally different and no clear relationship exists. The elastic moduli describe response of a material under small load, whereas cleavage properties and hardness correspond to a material response to much larger loads. If a material undergoes large elastic changes under small loads (i.e., it has a low elastic modulus), it often tends to respond to larger loads by plastic deformation (which means low hardness).[20] Transition-metal diborides, however, clearly do not belong to this class of materials.

According to our model of hardness for an ideal brittle material, we define the DFT derived hardness $H_{\mathrm{DFT}}$ as

$$H_{\mathrm{DFT}} = \min\{\sigma_c(S,[hkl])\}, \tag{2}$$

being equal to the lowest of all cleavage stresses as a function of the orientation $[hkl]$ and possible different cleavage planes $S$ for the same direction. This assumption is of course only valid for the very onset of an indentation because we assume that an indenter breaks bonds in surface layers when it penetrates a sample.

The most important result is that $H_{\mathrm{DFT}}$ describes the experimental hardness very well (see Fig. 3). It is lowest for $HfB_2$, increases with increasing covalency of the neighboring diborides, and it reaches its maximum for $ReB_2$, which is superhard also according to our DFT calculation. The agreement concerns not only the trend but $H_{\mathrm{DFT}}$ for $HfB_2$ is also in quantitative agreement with the experimental values of 29 GPa (Ref. 21) and 31.5 GPa.[22] Furthermore, for $TaB_2$ the $H_{\mathrm{DFT}}$ agrees well with the highest experimental value of 33.7 GPa (Ref. 23). (It should be noted that there is some scatter-

TABLE I. Results of DFT calculations for ideal brittle cleavage for compounds structure type hex. (prototype: hexagonal $ReB_2$) and structure type orth. (prototype: orthorhombic $AlB_2$): direction-dependent cleavage energy per surface area $G_b/A$ in $J/m^2$, critical length $l_b$ in Å, and critical stress per area $\sigma_c/A$ in GPa.

| | Structure | Orientation | $G_b/A$ | $l_b$ | $\sigma_c/A$ |
|---|---|---|---|---|---|
| $WB_2$ | Hex. | (0001)-S1 | 7.6 | 0.49 | 57 |
| $WB_2$ | Hex. | (0001)-S2 | 4.7 | 0.49 | 35 |
| $WB_2$ | Hex. | $(11\bar{2}0)$-S3 | 8.8 | 0.51 | 64 |
| $ReB_2$ | Hex. | (0001)-S1 | 6.9 | 0.48 | 52 |
| $ReB_2$ | Hex. | (0001)-S2 | 5.5 | 0.48 | 42 |
| $ReB_2$ | Hex. | $(11\bar{2}0)$-S3 | 8.9 | 0.51 | 63 |
| $OsB_2$ | Hex. | (0001)-S1 | 5.6 | 0.48 | 43 |
| $OsB_2$ | Hex. | (0001)-S2 | 4.8 | 0.47 | 37 |
| $OsB_2$ | Hex. | $(11\bar{2}0)$-S3 | 6.9 | 0.49 | 55 |
| $HfB_2$ | Orth. | (0001) | 4.5 | 0.57 | 27 |
| $HfB_2$ | Orth. | $(11\bar{2}0)$ | 7.7 | 0.50 | 62 |
| $HfB_2$ | Orth. | (1100) | 10.2 | 0.62 | 60 |
| $TaB_2$ | Orth. | (0001) | 4.7 | 0.50 | 29 |
| $TaB_2$ | Orth. | $(11\bar{2}0)$ | 8.0 | 0.42 | 65 |
| $TaB_2$ | Orth. | (1100) | 10.3 | 0.67 | 63 |

ing of other experimental data ranging from 21 to 29.2 GPa.[24]) This trend of the hardness cannot be deduced from the elastic constants, which have rather similar values for the inspected diborides.[4]

All results for $H_{DFT}$ are in significantly better agreement with experiment than the numbers derived from the semiempirical model of Refs. 12 and 13 according to Fig. 3. The trend is well described by the semiempirical model.

The correlation between brittle cleavage stress and hardness indicates that transition-metal diborides are brittle materials. In order to justify their intrinsic brittleness and estimate the resistance against shear we calculated the slip properties of $ReB_2$, the hardest material of our study. Our modeling is based on the $\gamma$-surface concept introduced by Vitek,[25,26] which links shear energies and stresses at the atomic level to dislocation emission and mobility.[27] For the actual DFT calculations the slab is split into two halves and the upper half is shifted by a slip displacement **f** along a given direction. For each $f$ as chosen for the DFT calculation, the total energy is minimized with respect to the layer distances perpendicular to the slip plane, i.e., the layer distances are relaxed. The shear stress is then numerically derived from the derivative of the total energy. The critical shear stress is determined by the stress associated with the first point of inflexion on the total energy curve, similar to the critical cleavage stress.

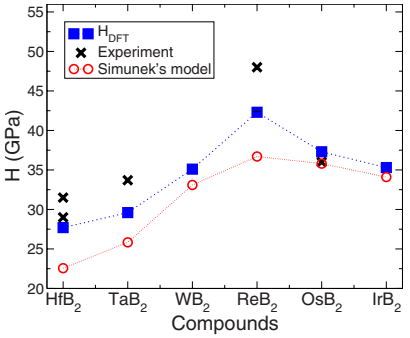


FIG. 3. (Color online) Comparison of measured and calculated hardness $H$. DFT results for lowest brittle critical cleavage stress $H_{DFT}$ (blue squares), semiempirical model of Refs. 12 and 13 (red circles), and experimental data for Vicker's hardness (black crosses).

The two slip deformation paths $\langle 12\bar{1}0\rangle$ and $\langle 10\bar{1}0\rangle$ within the weakest bonded (0001) plane are investigated. For the calculation the (0001)-S2 plane cutting metal-boron bonds was chosen, because of its cleavage energies are lower than for the S1 plane, according to Table I. Figure 4 shows the calculated stacking fault energies $\gamma$ and shear stresses $\tau$ for $ReB_2$. The values of the critical stress $\tau_c$ are 60 GPa for both slip paths are significantly higher than the corresponding brittle cleavage stress. Recently, an *ab initio* calculation of

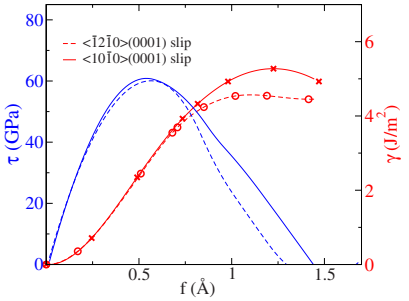


FIG. 4. (Color online) Generalized stacking fault energy $\gamma$ and shear stress $\tau$ of $ReB_2$ vs lateral shift $f$. Symbols: DFT results, lines: guide for the eyes.

shear stress-strain dependencies in $ReB_2$ derived 34.4 GPa for the lowest shear strength.[28] It should however be noted that in this work a model based on elastic deformation—different from ours—was applied. Such large values of the shear stress are very unusual because usually the critical shear strength is considerably smaller than the tensile (cleavage) stress: the ratio $\tau_c/\sigma_c$ is typically less than 1/4 for metals and close to 1 even for diamond.[29] Similarly, the maxima of the stacking fault energies along the slip paths—the so-called unstable stacking fault energies $\gamma_{us}$—are very large and act like energy barriers for dislocation emission and movement.[27] According to recent ductility/brittleness models,[30] a material is expected to be brittle if $\frac{\gamma_{us}}{\mu b} > 0.014$. Here, $\mu$ denotes the isotropic shear modulus and $\mathbf{b}$ the Burgers vector of the emitted dislocation. For hcp-$ReB_2$, we obtained the lowest $\gamma_{us}$ of 4.54 $J/m^2$. The shear modulus calculated as Voigt average is 273.5 GPa.[31] Evaluating the ratio one then gets the value of 0.05 indicating intrinsically brittle nature of $ReB_2$.

For this reason, one can expect that the amount of plastic flow involved in a common tensile test would be very small at low temperatures and $ReB_2$ would fail by cleavage of (0001) planes. Considering the similarity of bonding of the studied diborides—which is manifested, for instance, by similar direction-dependent changes of the cleavage energy—one may predict brittle failure in tensile tests also for other diborides. In indentation experiments, on the other hand, there will always occur considerable plastic deformation due to large shear stress component in the deformed zone below the indenter.

It remains an open question whether $ReB_2$ is a superhard material. It was demonstrated experimentally that $ReB_2$ can reach a superhard limit with a hardness of 48 GPa at low load.[2] However, as the load was increased the average hardness decreased to an asymptotic value of 30 GPa. This phenomenon is referred to as the indentation size effect. According to our modeling in terms of brittle cleavage our values of $H_{DFT}$ correspond to the very onset of an indentation. We compare $H_{DFT}$ with the highest values of the experimental hardness because they correspond to the lowest load and consequently also to the lowest indentation depth. Following these considerations, the calculated values for $H_{DFT}$ are very close to the highest experimental values (cf. Fig. 3). In addition, considering the very large value for the critical shear stresses of $\tau_c = 60$ GPa we conclude that $ReB_2$ is rather an ideal brittle material and at the atomic level, i.e., in situations where bond breaking processes govern hardness, is superhard.

Summarizing, the results of our DFT calculations demonstrate that the hardness of a brittle material is very well described by the lowest brittle cleavage stress. This observation is explained by the intrinsic brittleness of transition-metal diborides. Furthermore, for $ReB_2$ the critical shear stresses are significantly larger than the critical cleavage stresses, which is exceptional. Summarizing, one might expect very unusual mechanical properties of $ReB_2$, however, its intrinsic brittleness might limit its technological utilization.

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