Bond deformation paths and electronic instabilities of ultraincompressible transition metal diborides: Case study of OsB$_2$ and IrB$_2$

R. F. Zhang,$^{1,2,3}$ D. Legut,$^4$ X. D. Wen,$^{2,5}$ S. Veprek,$^6$ K. Rajan,$^3$ T. Lookman,$^2$ H. K. Mao,$^{7,8}$ and Y. S. Zhao$^9$

$^1$School of Materials Science and Engineering, and International Research Institute for Multidisciplinary Science, Beihang University, Beijing 100191, P. R. China
$^2$Theoretical division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
$^3$Department of Materials Science and Engineering, Iowa State University, Ames, IA50010, USA
$^4$Nanotechnology Centre, VSB-Technical University of Ostrava, CZ-708 33 Ostrava, Czech Republic
$^5$State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, P.O. Box 165, Taiyuan, Shanxi 030001, P. R. China & Synfuels China, Beijing 100195, P. R. China
$^6$Department of Chemistry, Technical University Munich, Lichtenbergstr. 4, D-85747 Garching, Germany
$^7$Geophysical Laboratory, Carnegie Institution of Washington, NW Washington, DC 20015, USA
$^8$Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, P. R. China
$^9$HiPSEC, Department of Physics and Astronomy, University of Nevada, Las Vegas, NV 89154, USA

The ultraincompressibility ($B > 250$ GPa) and possible superhardness ($H_v > 40$ GPa) of transition metal (TM) borides has stimulated tremendous interest in theoretical and experimental investigations of their properties [1–5]. The ultraincompressibility of borides of 5$d$ transition metals, such as OsB$_2$ [4], ReB$_2$ [5], WB$_2$ [6], IrB$_2$ [7], and WB$_3$ [8] and others, is widely accepted, but the experimentally determined load-invariant hardnesses are typically below 30 GPa, i.e., these materials are not superhard. Osmium diboride possesses high elastic moduli but a low hardness due to the presence of Os-Os weak metallic bonds [9]. Rhenium diboride was believed to be superhard [5], but its load-invariant hardness is also less than 30 GPa because of electronic instabilities of 5$d$ orbitals under finite shear strain resulting in transformation to phases with lower plastic resistance [10]. Tungsten diboride was originally proposed as another superhard material with “predicted” hardness of 46 GPa [6], but the experiment yields only 30 GPa [11]. Iridium diboride received much attention because of the Vickers hardness of 49.8–18.2 GPa reported for IrB$_2$ at loads of 0.49 and 9.81 N, respectively [12]. However, as discussed in [13], only the low value of 18.2 GPa measured at high load is the correctly measured load-invariant hardness. The energetically favored orthorhombic structure of IrB$_2$ is isostructural to OsB$_2$ [7], in which Os-Os metal double layers in the easiest slip system limit its anisotropic shear strength to about 9 GPa [7,9].

The presence of metal double layers in diborides of 5$d$ transition metals is believed to be the origin of their low hardness. However, studies of bond deformation paths and electronic instabilities under shear deformation, which have been shown to be critical in several ultraincompressible materials [10,14], are lacking. In many papers the conclusions are mostly based on the development of atomic structure and bond topology under shear, but the related electronic instabilities of 5$d$ orbitals remain unexplored. Taking OsB$_2$ and IrB$_2$ as examples, we show for the first time that, although easily sliding metal double layers exist in both diborides, their shear deformation paths are substantially different. In addition, in spite of a significant weakening between the Os-Os layers in OsB$_2$, the hardness of OsB$_2$ of almost 30 GPa is significantly higher than the shear strength of the easy slip system, because, under the conditions of plastic flow, all slip systems must shear to meet the compatibility condition (constant volume). Thus it is interesting to investigate the origin of the weakening of Os-Os layers and the shear resistance of the Os-B and B-B layers.

The 30 GPa hardness of OsB$_2$ can be understood in terms of complex deformation beneath the indenter upon the measurement, as described by slip-line fields [15,16]. Accordingly, the material upon indentation displays a complex flow where many slip systems, including the strong ones, are activated. Moreover, correctly measured, load-invariant hardness describes the mechanical behavior of strongly deformed material with a large density of flaws. Therefore the recent “theories of hardness” [17–19] describe only the elastic stiffness of an ideal crystal but not real hardness [20].

Our calculations of phonon dispersion of OsB$_2$ and IrB$_2$ show that whereas OsB$_2$ is dynamically stable in its lowest energy structure, IrB$_2$ is unstable. This result contradicts the previous results by Wang et al. [21], who suggested that IrB$_2$ is dynamically stable. Furthermore, we show that although both OsB$_2$ and IrB$_2$ have the same equilibrium structure, their bond deformation paths are substantially different due to different electronic instabilities under shear.
We first show that oP6[59] structure (expressed by Pearson symbol and space group number in bracket) of IrB2 and OsB2 is energetically favorable. We use the VASP code [22] to perform first-principles density functional theory (DFT) calculations of the formation energy of OsB2 and IrB2 in more than 30 commonly observed Tm-B, Tm-C, Tm-N, Tm-Al, and Tm-Si ICSD structure types [23] and in the diboride structures by means of the “high-throughput” evolutionary search method [21,24,25]. (See the Supplemental Materials [26] for details of the OsB2 and IrB2 structures.) All studied structures were relaxed with respect to both lattice parameters and atomic positions. Based on the reaction $\text{Tm} + 2\text{B} = \text{TmB}_2$, the formation energy was calculated as $\Delta E = \frac{1}{2}(E(\text{TmB}_2) - E(\text{Tm}) - 2E(\text{B}))$, with $\alpha = \text{B}$ and $\text{Tm}$ in their ground states. Figure 1(a) summarizes the calculated formation energies vs volume at 0 K. The stable and metastable structures with formation energy close to zero are shown in the inset of Fig. 1(a). Obviously, oP6[59] has the lowest formation energy for both OsB2 and IrB2.

We next study the dynamical properties of both OsB2 and IrB2 in five selected structures reported in [23], using the direct method [27] as employed by the PHONOPY code [28]. The boron layers in these structures are flat in hP3[191], armchair in oP6[59], zigzag in hP6[194], alternately flat and zigzag in hP12[194], and nonequal zigzag in hR6[166]. The resulting phonon dispersion and density of states (PDOS) were the same as those using the $2 \times 2 \times 2$ supercell method. Figures 1(b) and 1(c) show the dispersion relations of OsB2 in oP6[59], indicating a dynamic stability for OsB2, as there are no modes with imaginary frequencies, but dynamic instability of IrB2, as there are imaginary frequencies at the high-symmetry $S$ point [0.5 0.5 0.0]. The partial PDOS of IrB2 and OsB2 indicate that the lower frequencies of the total PDOS are dominated by lattice dynamics of heavy Ir (Os) atoms and higher frequencies by light B atoms. Imaginary frequencies found for IrB2 with oP6[59] structure are given exclusively by the atomic vibrations of Ir atoms. There is a gap in phonon frequencies between ca. 6.8 (7.2) and 10.9 (11.6) THz in IrB2 (OsB2) that entirely separates higher and lower frequencies. For the high-energy structures we found that OsB2 is dynamically unstable in several important directions in hP3[191], hP12[194], and hR6[166] but is stable in the hP6[194] structure. In contrast, the IrB2 is dynamically instable in all these structures.

To evaluate the elastic stability [29] of both diborides, we calculated their single-crystal elastic constants using both a linear response method and efficient strain-energy method [30]. The obtained elastic constants of IrB2 ($C_{11} = 349 \text{ GPa}, C_{22} = 414 \text{ GPa}, C_{33} = 668 \text{ GPa}, C_{44} = 68 \text{ GPa}, C_{55} = 62 \text{ GPa}, C_{66} = 132 \text{ GPa}, C_{12} = 244 \text{ GPa}, C_{13} = 145 \text{ GPa}$, and $C_{23} = 167 \text{ GPa}$) and of OsB2 ($C_{11} = 565 \text{ GPa}, C_{22} = 558 \text{ GPa}$,
The shear strengths are calculated by a confined deformation scheme to restrict the Me-Me bilayer sliding.

\[ C_{33} = 763 \text{ GPa}, C_{44} = 191 \text{ GPa}, C_{55} = 73 \text{ GPa}, C_{66} = 193 \text{ GPa}, \]
\[ C_{12} = 178 \text{ GPa}, C_{11} = 185 \text{ GPa}, \text{ and } C_{23} = 130 \text{ GPa} \]
are in good agreement with the previous calculations (for IrB₂, C₁₁ = 353 GPa, C₁₂ = 416 GPa, C₃₃ = 676 GPa, C₄₄ = 69 GPa, C₅₅ = 68 GPa, C₆₆ = 140 GPa, C₁₂ = 239 GPa, C₁₃ = 138 GPa, and C₂₃ = 171 GPa [21]).

The ideal tensile (\( \sigma_{\text{min}} \)) and shear (\( \tau_{\text{min}} \)) strengths are shown in Figs. 2(c) and 2(d). Both diborides show metallic bonding because of finite value of EDOS at the Fermi level (\( E_F \)), which originate mostly from \( d \) electrons of Ir and Os and the \( p \) electrons of B. In OsB₂, the EDOS at \( E_F \) shows a pseudogap, i.e., a stronger localization of valence electrons. In IrB₂, however, the flat nature of EDOS around \( E_F \) indicates a delocalization. The strengthened B-B bonds in OsB₂ cause a denser in-plane packing of Os-Os layers, while the delocalized B-B bonds make in-plane Ir-Ir bonds even longer. The Bader charge density analysis [38] shown in Figs. 2(a) and 2(b) further confirms the positive (negative) charge transfer from Os (Ir) atoms to boron atoms, supporting further the strengthening (weakening) of boron layers by charge transfer.

This significant difference may be surprising because Os and Ir have a similar electronegativity of 2.2, the only difference being the occupation of the 5\( d \) orbital with 6 and 7 electrons in Os and Ir, respectively. This illustrates the importance of investigating the complex crystal field splitting of the 5\( d \) orbitals in the diborides [39,40], and whether the difference in the electronic structure results in different bond deformation paths.

The calculated stress- and energy-strain dependence for the easy slip system [100](001) is shown in Figs. 3(a) and 3(b). The ideal tensile (\( \sigma_{\text{min}} \)) and shear (\( \tau_{\text{min}} \)) strengths are summarized in Table I together with those of Os, Ir, Re₃N [14], ReB₂ [30], WB₃ [33], B₆O [34], c-BN [35], and diamond [34,36]. The minimum shear strengths of OsB₂ of 9.2 GPa and IrB₂ of 7.9 GPa are about 4.5 times lower than those of ReB₂, WB₃, and B₆O, and also much lower than those of Os and Ir metals of 22.2 and 18.6 GPa, respectively (Table I). Although OsB₂ and IrB₂ have a similar structure, their bond deformation paths are substantially different, as seen from the VCDD isosurfaces in Figs. 3(c) and 3(d) at shear strain of \( \gamma = 0.2899 \) (before) and \( \gamma = 0.4660 \) (after instability) for IrB₂, and \( \gamma = 0.2899 \) (before) and \( \gamma = 0.4660 \) (after instability) for OsB₂. For IrB₂, the shear slip occurs between atoms Ir₂ and Ir₃, which, after the instability, form a single Ir metal layer.
FIG. 2. (Color online) Bond structures at equilibrium for (a) IrB$_2$ and (b) OsB$_2$. The isosurface maps of the valence charge density difference (VCDD) correspond to ±0.01 electrons/bohr$^3$. Partial electronic density of states of (c) IrB$_2$ and (d) OsB$_2$. The numbers close to Ir and Os atoms are the Bader charges.

Ir$_1$-Ir$_2$-Ir$_3$-Ir$_4$ [Fig. 3(d)]. In OsB$_2$, however, the shear occurs between Os1 and Os2, which form a double layer.

The decomposed EDOS of 5$d$ orbitals of both IrB$_2$ and OsB$_2$ before and after shear instability are shown in Figs. 4(a)–4(c) for IrB$_2$ and in Figs. 4(d)–4(f) for OsB$_2$ [see the arrows in Figs. 3(a) and 3(b)]. It is seen that before lattice instability, the five 5$d$ orbitals do not change their contributions at the Fermi level. The main contribution to the finite value at the Fermi level for IrB$_2$ comes from the $d_{z^2}$ orbitals, whereas $d_{x^2-y^2}$ orbitals dominate in OsB$_2$. Therefore the in-plane ($xy$ plane) Ir-Ir bonds are longer than those of the out-of-plane bonds in IrB$_2$, while in OsB$_2$ the in-plane Os-Os bond lengths are longer than the out-of-plane lengths. After lattice instability, the $d_{z^2}$ and $d_{x^2}$ orbitals dominate the EDOS in IrB$_2$ at $E_F$ [Fig. 4(c)], which corresponds to the in-plane splitting of Ir-Ir bonds and the formation of B single layers along the charge-depleting regions [see Fig. 3(d)]. In OsB$_2$, however, $d_z$ orbital shows a plateau at $E_F$, whereas the other four 5$d$ orbitals contribute either to the first peaks below $E_F$ or the first peaks above $E_F$ after the instability. These 5$d$ electronic instabilities of IrB$_2$ and OsB$_2$ resemble those for ReB$_2$ [10] and WB$_3$ [33], but the difference is that for the former cases the metallic bonds are responsible for the shear instability, while metal-boron and boron-boron bonds are the carrier of the shear instability in ReB$_2$ and WB$_3$.

In order to understand the hardness of the diborides we need to extract the bond strength of Me-B and B-B bonds. We use a “confined” stress-strain experiments by fixing the $Tm$-$Tm$ double layer bonds distance and allowing the Os-B and B-B bonds being the carrier of the shear. The results are shown in Fig. S1 in the Supplemental Material [26] for the weakest [100][001] and [010][001] slip systems. For the [100][001] system we find a high shear strength of 36.6 GPa for OsB$_2$, comparable to ReB$_2$ and WB$_3$ (Table I) and much higher than the shear strength for the unconfined case, where the sliding of the Os-Os planes is dominant. However, a lower value of 15.7 GPa is obtained for IrB$_2$ where the weaker Ir-B and B-B bonds are limiting the strength, presumably because of the presence of the 7$^\text{th}$ electron in the upper-laying $d_{z^2}$ and $d_{x^2-y^2}$ orbitals.
FIG. 4. (Color online) Orbital-decomposed electronic density of states of IrB$_2$ (a) at equilibrium (b) at strain of 0.2899, (c) at strain of 0.4660, and of OsB$_2$ (d) at equilibrium (e) at strain of 0.2899, (f) at strain of 0.4660.

In summary, we carried out first-principles calculations to evaluate the thermodynamic, mechanical, and dynamical stabilities of IrB$_2$ and OsB$_2$. In spite of its thermodynamic stability, IrB$_2$ is found to be dynamically unstable. The deformed electronic structure reveals that the low strength is due to the weak metallic bonds, but in a different manner for IrB$_2$ and OsB$_2$. The different bond deformation paths are attributed to different electronic instability modes. The high shear strength of Os-B and B-B bonds indicates that they are responsible for the high hardness, in spite of the weak Os-Os bonds. An analysis of the deformed electronic structures reveals that the electronic instability is due to $d$ orbitals of Ir or Os, and $p$ orbitals of B. The orbital-decomposed EDOS show that the $d_{z^2}$ orbitals are mostly responsible for the shear instability of IrB$_2$, whereas $d_{x^2-y^2}$ orbitals are responsible for the shear instability in OsB$_2$.

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