Ab Initio Computations of Electronic, Mechanical, and Thermal Properties of ZrB$_2$ and HfB$_2$

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A comprehensive ab initio analysis of the ultra high temperature ceramics ZrB$_2$ and HfB$_2$ is presented. Density functional theory (DFT) computations were performed for the electronic, mechanical, thermal, and point defect properties of these materials. Lattice constants and elastic constants were determined. Computations of the electronic density of states, band structure, electron localization function, etc. show the diverse bonding types that exist in these materials. They also suggest the connection between the electronic structure and the superior mechanical properties. Lattice dynamical effects were considered, including phonon dispersions, vibrational densities of states, and specific heat curves. Point defect (vacancies and antisites) structures and energetics are also presented.

I. Introduction

The materials often referred to as ultra-high temperature ceramics (UHTC) are characterized by high melting point, high strength, and good chemical stability. The relatively good oxidation resistance of the diboride class of materials, in particular ZrB$_2$ and HfB$_2$, has attracted special attention, both as pure materials and as constituents in composites.$^{1,2,3,4}$ They are candidates for applications which require high temperature materials that can operate above 3000 K with little or no oxidation. These include the extreme environments experienced during hypersonic flight, atmospheric re-entry, and rocket propulsion. Aerospace applications include sharp leading edges and nose caps for hypersonic reentry vehicles. Sharp leading edges will enable greater maneuverability and cross range during reentry. The high temperatures generated at sharp leading edges, however, will require new materials with properties beyond the current state of the art.

Despite the thermal and chemical stability of UHTCs, many scientific challenges related to processing, characterization, and performance under operating conditions remain. As a result, these materials are not currently widely used. Basic research is needed to understand microstructural evolution, property improvement, and response to high temperature reactive environments seen in atmospheric reentry. The refractory nature of these materials means they must be processed at high temperature and pressure, although efforts to use pressureless sintering is ongoing.$^5$ Oxidation resistance has been improved through the use of additives; however, it remains an issue especially in high temperature reactive environments. These materials also display low fracture toughness which must be addressed as well.

Many of these challenges could benefit from computational modeling. In this article, ab initio modeling of the UHTC materials ZrB$_2$ and HfB$_2$ is performed. Ab initio, first principles methods are the most accurate modeling approaches available and represent a parameter free description of the material based on the quantum mechanical equations. In particular, we employed density functional theory (DFT) where the fundamental quantity is the electron density. In general, ab initio approaches can be computationally demanding. However, for single crystals with relatively small unit cells, the high symmetry of these systems can make a full ab initio treatment tractable. Using these methods, we obtained many of the intrinsic properties of these materials. In this article, we present results on structural quantities (lattice constants, bond lengths, etc.), electronic structure (band motifs, densities of states, band structure, etc.), thermal quantities (phonon spectra, phonon densities of states, specific heat), as well as information about point defects such as vacancy and antisite formation energies.

II. Method

All calculations were performed using DFT as developed by Perdew, Burke, and Ernzerhof (PBE).$^6$ These methods give very good results for calculations on solids. We used the plane wave DFT codes VASP$^{7,8,9}$ and ABINIT.$^{10,11}$ These codes have significant overlap, but also have a number of distinct features. Using different codes with differing methodologies also allows us to cross-check our results. With VASP, the projected augmented wave (PAW) potentials were used while with ABINIT, Fritz Haber Institute (FHI) pseudopotentials which are of the Troulliers–Martin form (Tr–Ma)$^{12}$ were employed. In general, the PAW potentials are expected to be slightly more accurate, and computationally more efficient, than those of Tr–Ma. However, in our computations, we found largely similar results. All quantities were converged individually with respect to k-point sampling and the plane wave energy cutoff. Dense k-point meshes were typically used, sometimes up to 40 × 40 × 40 grids, along with a plane wave cutoff energy of 400 eV. The method of Methfessel and Paxton was used with a smearing parameter of 0.1 eV.

III. Atomic Structure

The materials, ZrB$_2$, and HfB$_2$, are an interesting mix of atomic species. Boron, which these two materials have in common, is a relatively small atom with an atomic radius of 0.9 Å and an atomic weight of 10.8 g/mol. Boron’s electronic configuration is [He]2s$^2$2p$^3$, giving it one less valence electron than Carbon. This electron “deficiency” has a significant impact on the properties of pure Boron whose ground state
structure is still unresolved. In pure materials, Boron is known to form strong covalent bonds.

Zirconium and Hafnium, on the other hand, are relatively large transition metal (TM) atoms. Zirconium has an atomic radius of 1.6 Å and an atomic weight of 91.2 g/mol while Hafnium has an atomic radius of 1.59 Å and an atomic weight of 178 g/mol. The electronic configuration for these elements is very similar: [Kr]4d55s2 for Zr and [Xe]4f145d56s2 for Hf. Thus, both species have two “s” and two “d” valence electrons to donate to the electronic structure of the material.

Because of the very similar electronic configurations and atomic radii of Zr and Hf, we expect ZrB2 and HfB2 to have very similar bonding motifs and electronic structure. At the atomic level, the principal difference between Zr and Hf is their atomic weights. This difference will show up most prominently in the vibrational properties.

The crystal structure of both ZrB2 and HfB2 is the AlB2-type TM diboride designated as C32 with space group symmetry P6/mmm. The structure is shown in Fig. 1. These materials are layered with alternating planes of pure TM and pure B. In the TM planes, the atoms have a closed packed hexagonal structure where each atom has six neighbors. The TM planes have a graphitic structure with six membered rings and a coordination number of three. The TM and B planes have a graphitic structure with six membered rings and a coordination number of three. The TM and B planes are situated such that the TM atoms lie above (and below) the center of Boron rings in the neighboring planes. Thus, each metal atom has 12 Boron atoms as the nearest neighbors. The primitive cell of these structures contains one formula unit (one TM and two Borons) and the crystal has simple hexagonal symmetry (Dh). Primitive vectors can be chosen to position the metal at (0,0,0) and the two Borons at (1/3,2/3,1/2) and (2/3,1/3,1/2) inside the unit cell. Thus, the hexagonal lattice constant “a” gives the metal–metal atom distance within a plane and the “c” lattice constants give the metal–metal atom distance in alternate planes. The reciprocal space Brilloouin zone is also hexagonal.

The first step in our computations is the determination of the lattice constants. This is accomplished in a straightforward way by minimizing the total energy with respect to these parameters. These constants are largely determined by bonding and the atomic sizes. Our results are presented in Table I. As expected, ZrB2 and HfB2 have very similar lattice constants. Agreement with experiment is excellent.

With the optimized lattice structure, we obtain the cohesive energy of the crystal from the sum of the total energies of the isolated atomic constituents. These numbers are also given in Table I. Uncorrected atomic energies from the FHI potentials are known to be unreliable. We therefore obtained them using results from reference materials for pure Zr, Hf, and B.

Detailed bonding information can be obtained from the electron localization function (ELF). The ELF measures the probability of finding an electron near a reference electron located at a given point and with the same spin. Physically, this measures the spatial localization of the reference electron and thus provides information about the electron pair distribution. As such, it is useful for identifying covalent bonds. This is in contrast to the electron density which gives the single particle distribution only. For ZrB2 in Fig. 2, we show slices of the full, three dimensional ELF. The first pane shows the ELF in the plane of the Zirconium atoms; the second pane shows the Boron plane; and the third pane shows a diagonal slice through a Zr atom and four of its neighboring B atoms. These numbers are also given in Table I. Uncorrected atomic energies from the FHI potentials are known to be unreliable. We therefore obtained them using results from reference materials for pure Zr, Hf, and B.

Table I. Structural and Mechanical Constants. Quantities in Parenthesis are Unrelaxed. Units are Å, eV/cell, and GPa. Experimental Results are from Reference 2 and 19

<table>
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<tr>
<th></th>
<th>a</th>
<th>c</th>
<th>E E</th>
<th>C11</th>
<th>C12</th>
<th>C13</th>
<th>C14</th>
<th>B</th>
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<td>PBE–Tr–Ma</td>
<td>3.17</td>
<td>3.55</td>
<td>21.41</td>
<td>553(556)</td>
<td>60(57)</td>
<td>113</td>
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<td>234</td>
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<td>PBE–PAW</td>
<td>3.17</td>
<td>3.56</td>
<td>22.23</td>
<td>563(565)</td>
<td>64(62)</td>
<td>133</td>
<td>446</td>
<td>253</td>
<td>248</td>
<td>234</td>
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<td>Exp.</td>
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<td>3.53</td>
<td>568</td>
<td>57</td>
<td>120</td>
<td>436</td>
<td>247</td>
<td>240</td>
<td>234</td>
<td>0.77</td>
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<td>HfB2</td>
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<tr>
<td>PBE–Tr–Ma</td>
<td>3.15</td>
<td>3.52</td>
<td>22.07</td>
<td>578(579)</td>
<td>71(69)</td>
<td>118</td>
<td>430</td>
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<td>3.50</td>
<td>22.47</td>
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<td>73</td>
<td>135</td>
<td>470</td>
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<td>Exp.</td>
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layers. In a plane wave basis, however, this is nontrivial, since the basis functions span the entire cell and are not localized around individual atoms as with molecular, Gaussian basis sets. One possibility is to project the electronic states onto atom-centered spherical functions and then extract the electronic populations. However, this requires defining a Reitz–Wigner radius which is difficult to do consistently in a binary system with very different atomic radii. A better method is to calculate the Bader charges. In this approach, space is divided into atomic regions where the dividing surfaces are minima of the charge density. By integrating the electron density inside these regions, the local electron charge is obtained. We performed this type of analysis and found significant charge transfer from Zr to B. The results are given in Table II. A single unit cell of ZrB₂ or HfB₂ will have one metal atom (with four valence electrons) and two Boron atoms (with three electrons each). We see that for ZrB₂, the Zr atom loses 1.43 electrons which is split between the two Borons. Similarly, for HfB₂, the Hf atom loses 1.44 electrons. This large charge transfer results in ionic bonding between the layers.

### IV. Electronic Structure

We next examine the electronic structure of these materials. The density of states (DOS) is a compact representation of the electronic structure and gives the number of states in a small interval near a given energy $E$. The DOS for both ZrB₂ and HfB₂ are presented in Fig. 3 and have similar structure. First, a low energy peak appears near $-10$ eV and this is due to localized, tightly bound $s$ electrons of Boron. These states are not expected to play a significant role in the bonding. Second, bonding states of Zr/Hf-$d$ and B-$p$ are responsible for the large peak near $-4$ eV. These states are degenerate in energy and therefore could indicate the possibility of covalent bonding between the metal atoms and Boron. However, the low ELF values as well as the significant charge transfer between layers argues for ionic rather than covalent bonding. Finally, above the Fermi level are antibonding states.

An important feature of the DOS is the existence of a pseudogap: a sharp valley around the Fermi level. A finite DOS at the Fermi level indicates some metallic behavior resulting mainly from metallic bonding between Zr/Hf ($d$ orbitals at $E_F$). This metallic behavior is responsible in part for the high thermal conductivity in these materials. On the other hand, the separation of full, bonding states, and empty antibonding states gives these materials many of the favorable cohesive properties often seen in insulators, such as high melting point and chemical stability. In fact, in other diborides, for example TaB₂ or NbB₂, the Fermi level is shifted out of this valley, resulting in a deterioration of properties. These results are consistent with X-ray photoelectron spectra and NMR results.

A more detailed representation of the electronic states can be obtained from the band structure. In our calculations, there are 10 valence electrons, and therefore, five occupied bands per $k$-point. The band diagram for ZrB₂ is shown in

| Table II. Bader Charges Per Atom Give the Amount of Charge Transfer Between the TM and Boron Atomic Layers. A Unit Cell Has 10 Electrons with One Zr/Hf (Z = 4) Atom and Two B (Z = 3) Atoms. The Large Charge Transfer Indicates the Interlayer Bonding Is Ionic |
|-----------------------------------|-------------------|
| TM atom                          | B atom            |
| ZrB₂                             | 2.57              | 3.72 |
| HfB₂                             | 2.56              | 3.72 |
Fig. 4. ZrB$_2$ band structure along high symmetry directions in reciprocal space. Results for HfB$_2$ are largely similar.

In each case, the dynamical matrix was constructed on a 6 × 6 × 6 $k$-space mesh. The phonon densities of states (pDOS) for ZrB$_2$ and HfB$_2$ are shown in Fig. 5. As can be seen, the pDOS for both materials split into a low frequency and a high frequency region which are separated by a finite gap. By plotting the partial pDOS (not shown), the low frequency, acoustic modes can be related primarily to Zr/Hf atom vibrations whereas the high frequency, optical modes are either pure Boron states or mixed TM-Boron modes. Interestingly, the Boron modes are very similar for the two materials whereas the Zr and Hf components are shifted relative to each other. This shift is easily explained by the mass difference between Zr and Hf. Thus, interestingly, while the electronic DOS for ZrB$_2$ and HfB$_2$ were almost identical due to their similar valence structure and atomic radii, the pDOS have a noticeable difference due to the atomic mass difference.

Phonon dispersion curves are plotted in Fig. 6. The unit cells of ZrB$_2$ and HfB$_2$ contain three atoms which give a total of nine phonon branches: three acoustic and six optical branches. As mentioned, the acoustic modes result from Zr/Hf motion, whereas the upper optical modes are mainly from motion of the much lighter Boron atoms. Acoustic branches have steep slopes near $k = \Gamma$ consistent with large elastic constants. However, they show considerably less dispersion in the $z$ direction. Numerical values for the modes at $k = \Gamma$ are given in Table III. The $E_{\text{g}}$ mode is an in-plane Boron mode while the $B_{\text{g}}$ mode is an out-of-plane Boron mode. Note the degenerate in-plane modes have higher energy than the out-of-plane mode, consistent with (but not proof of) strong in-plane covalent Boron bonds. The two lower energies modes $E_{\text{g}}$ and $A_{\text{g}}$ are collective in-plane and out-of-plane motions of the Zr/Hf and both Boron atoms of the unit cell. Experimental determination of the vibrational spectra of these materials is not currently available.

From the phonon spectra, basic thermodynamic functions can be calculated within the quasiharmonic approximation to the Helmholtz free energy

$$ F_{\text{harm}} = k_B T \sum_n \ln(2 \sinh(h\omega_n/2k_B T)). $$

From this, the specific heat of ZrB$_2$ and HfB$_2$ as a function of temperature was calculated and is shown in Fig. 7. Experimental data for the ZrB$_2$ specific heat is available. Agreement between computed and experimental quantities is very good.
HfB$_2$ atoms and FHI relaxation. Results are presented in Table IV using both the PBE calculated formation energies both with and without PBE–Tr–Ma and PBE–PAW potentials, both using the PBE functional. Agreement with both potential types is very good. PAW potentials with large cores ($Z = 4$) and small cores ($Z = 12$) gave similar results. Spin polarized calculations showed that the defect configurations are spin singlets.

Vacancy formation energies for the metal vacancies are higher than those for the Boron vacancies by roughly 2.0 eV. For the three vacancies considered (Zr, Hf, and B), relaxation had only a small effect; formation energies were reduced by roughly 0.1–0.2 eV. However, the situation is very different for the antisite defects. Unrelaxed antisite formation energies for Zr/Hf are very similar to that of Boron. Upon relaxation, however, the formation energies were reduced by almost 6.0 eV for the Zr/Hf defects. This is not surprising since the Zr/Hf antisite defect requires a very large metal atom to be inserted into a lattice site normally occupied by a relatively small Boron atom. Relaxation of the considerable strain created in these configuration introduces significant distortion of the bond angles for the neighboring Borons. The left pane of Fig. 8 shows a relaxed configuration for an Zr antisite defect in a Boron plane. Conversely, insertion of a Boron into a normally metallic lattice site causes relatively little disruption as can be seen in the right pane of Fig. 8. This is also reflected in the smaller difference between relaxed and unrelaxed formation energies for the Boron antisites which is roughly 0.1–0.2 eV.

### Table IV. Point Defect Formation Energies (eV). Quantities in Parenthesis are Unrelaxed

<table>
<thead>
<tr>
<th></th>
<th>TM Vac</th>
<th>B Vac</th>
<th>TM Antisite</th>
<th>B Antisite</th>
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<td>ZrB$_2$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>PBE–Tr–Ma</td>
<td>11.20(11.38)</td>
<td>9.33(9.57)</td>
<td>11.22(16.84)</td>
<td>8.58(8.75)</td>
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<td>PBE–PAW</td>
<td>11.58(11.74)</td>
<td>9.36(9.59)</td>
<td>11.15(17.45)</td>
<td>8.84(9.01)</td>
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<tr>
<td>HfB$_2$</td>
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<td></td>
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</tr>
<tr>
<td>PBE–Tr–Ma</td>
<td>10.60(10.84)</td>
<td>9.00(9.23)</td>
<td>11.61(17.44)</td>
<td>8.40(8.58)</td>
</tr>
<tr>
<td>PBE–PAW</td>
<td>11.21(11.33)</td>
<td>9.09(9.24)</td>
<td>11.44(17.46)</td>
<td>8.99(9.08)</td>
</tr>
</tbody>
</table>

Fig. 6. ZrB$_2$ (top) and HfB$_2$ (bottom) phonon dispersions. Acoustic modes are suppressed in HfB$_2$ relative to ZrB$_2$ due to Zr/Hf mass difference.

**VII. Defects**

Finally, the structure and energetics of point defects were evaluated. We examined two types of point defects: vacancies and antisite defects. Vacancies are empty sites in the crystal lattice whereas antisite defects arise when the wrong atomic species is assigned to a given lattice site. In our computations, supercells of size $4 \times 4 \times 4$ were considered to reduce the interactions between the defects and their periodic images. Vacancy formation energies were calculated as

$$E_{\text{vac}} = [E(N) - E_{\text{atom}}] - E(N)$$  \hspace{1cm} (5)

while antisite formation energies were

$$E_{\text{anti}} = E(N) - [E(\text{sub}) - E_{\text{atom}}(\text{sub}) + E_{\text{atom}}(\text{antisub})].$$  \hspace{1cm} (6)

where $E(N)$ is the total energy for a configuration of $N$ atoms and $E_{\text{atom}}$ refers to the energy of an isolated atom. We calculated formation energies both with and without relaxation. Results are presented in Table IV using both the FHI–Tr–Ma and the PAW potentials, both using the PBE functional. Agreement with both potential types is very good. PAW potentials with large cores ($Z = 4$) and small cores ($Z = 12$) gave similar results. Spin polarized calculations showed that the defect configurations are spin singlets.

Vacancy formation energies for the metal vacancies are higher than those for the Boron vacancies by roughly 2.0 eV. For the three vacancies considered (Zr, Hf, and B), relaxation had only a small effect; formation energies were reduced by roughly 0.1–0.2 eV. However, the situation is very different for the antisite defects. Unrelaxed antisite formation energies for Zr/Hf are very similar to that of Boron. Upon relaxation, however, the formation energies were reduced by almost 6.0 eV for the Zr/Hf defects. This is not surprising since the Zr/Hf antisite defect requires a very large metal atom to be inserted into a lattice site normally occupied by a relatively small Boron atom. Relaxation of the considerable strain created in these configuration introduces significant distortion of the bond angles for the neighboring Borons. The left pane of Fig. 8 shows a relaxed configuration for an Zr antisite defect in a Boron plane. Conversely, insertion of a Boron into a normally metallic lattice site causes relatively little disruption as can be seen in the right pane of Fig. 8. This is also reflected in the smaller difference between relaxed and unrelaxed formation energies for the Boron antisites which is roughly 0.1–0.2 eV.
for the metal antisites (inserting a large metal atom into a B position, especially for the antisite defects. Large distortions are seen in these materials: covalent bonding in the Boron planes, metallic bonding in the Zr/Hf planes and ionic bonding between the planes. Electronic structure computations identify these materials as semi-metals with the Fermi level positioned in the DOS between full bonding states, and the atomic Bader charges enabled elucidation of the various bonding motifs. Interestingly, all three major bonding patterns exist in these materials: covalent bonding in the Boron planes, metallic bonding in the Zr/Hf planes and ionic bonding between the planes. Electronic structure computations identify these materials as semi-metals with the Fermi level positioned in the DOS between full bonding states, and empty, antibonding states. This pseudogap is in part responsible for the favorable mechanical properties of these materials. However, a finite DOS at the Fermi level results in metallic behavior of these materials, including high thermal conductivity. Because of the isoelectronic nature of Zr and Hf and also their comparable atomic radii, many properties of ZrB2 and HfB2 are similar. Lattice dynamical properties, however, are different, owing to the nontrivial mass difference between Zr and Hf. This affects most strongly the acoustic phonon modes. Finally, we computed the structures and formation energies for various point defects. Here, the size difference between Zr and Hf and B play a significant role especially for the antisite defects. Large distortions are seen for the metal antisites (inserting a large metal atom into a B lattice site) whereas B antisites are much less disruptive.

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References


