Revealing phase relations between Fe$_2$B$_7$ and FeB$_4$ and hypothetical Fe$_2$B$_7$-type Ru$_2$B$_7$ and Os$_2$B$_7$: first-principles calculations†

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Investigation of new materials recovered using high pressure can foresee the unobservable structures and bonding of crystals. Employing first-principles calculations, we aim to provide an atomic understanding of the origin of multiple phases and mutual intergrowth for metastable iron borides. The competing FeB$_4$ and Fe$_2$B$_7$ in the experiment are compared by their enthalpy and structural features. The closely similar enthalpy of Fe$_2$B$_7$ + B and Fe$_2$B$_6$ (FeB$_4$) may explain the coexistence and tight mutual intergrowth of these two phases. The hypothetical Ru$_2$B$_7$ and Os$_2$B$_7$ are also suggested by the stability evaluations. The stable Ru$_2$B$_7$ and Os$_2$B$_7$ show an interesting metallic property and a great mechanical property due to the hybridization of metal-d and B-p orbitals and B$-$B covalent bonding.

1 Introduction

Over the decades, transition metal (TM) borides have attracted much attention due to their great promise for hard, wear-resistant, chemically inert coatings’ applications. Extensive experimental and theoretical studies have been performed with a focus on the synthesis and physical property characterizations of transition metal borides. Thus far, a variety of transition metal borides, e.g. OsB$_2$, RuB$_2$, ReB$_2$, WB$_4$, and CrB$_3$ have been successfully synthesized in experiments, enabling the discovery of structural complexity, unique chemical bonding and exotic properties. Subsequently, the Os–B, Ru–B and W–B systems were investigated by first-principles calculations and the stable phases with different stoichiometries were identified, providing a road map for exploring design and synthesis strategies for new osmium, ruthenium and tungsten borides. Recently, FeB$_4$ with Pnmm symmetry was synthesized to be a phonon mediated superconductor. Computational structure simulations of the energy landscape did expedite the exploration for the discovery of FeB$_4$. Interestingly, Fe$_2$B$_7$ was found to coexist with FeB$_4$ in experiments. This stoichiometry was not previously identified in any 3d metal boron systems. Aided by single-crystal X-ray diffraction, Bykova et al. identified Fe$_2$B$_7$ to have an orthorhombic symmetry of Pbam, with lattice parameters of $a = 16.9699(15)$ Å, $b = 10.6520(9)$ Å, and $c = 2.8938(3)$ Å. However, the understanding of this compound is lacking to date, although Fe$_2$B$_7$ and FeB$_4$ (ref. 22) in the Fe–B system have been theoretically reported. Moreover, an experimental determination of the phase stability of Fe$_2$B$_7$ and FeB$_4$ has not been characterized. Furthermore, FeB$_4$ is found to exhibit great incompressibility along the $b$ axis. Due to the intergrowth of Fe$_2$B$_7$ and FeB$_4$, Fe$_2$B$_7$ may exhibit interesting physical properties. In view of the similarity of these two borides, there is a lack of understanding of the mechanical and electronic properties of this phase. Knowledge about these properties is essential to the understanding of the fundamental phase behaviors of this compound and offers the potential to discover new phases in transition metal borides.

It is found that chemically related compounds usually share similar crystallographic structure. OsB$_2$ and RuB$_2$ crystallize in the orthorhombic Pnmm structure. Furthermore, OsN$_2$ and RuN$_2$ are also formed in the same marcasite structure. In addition, IrN$_2$ was predicted to have the IrP$_2$-type structure by Wang et al. It is thus reasonable to expect the existence of RuxB$_7$ and Os$_x$B$_7$ with the same crystal symmetry of Fe$_2$B$_7$. Inspired by the potential of investigating the rich phase space of metal borides, we carried out a systematic study of Fe$_2$B$_7$, Ru$_2$B$_7$ and Os$_2$B$_7$ based on first-principles density functional calculations. We elucidated their phase relations and discussed their thermodynamic stability and mechanical and electronic properties. The results may provide guidance for further experimental and theoretical studies of these phases.

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2 Computational details and methods

The structural optimizations were performed within CASTEP code. Exchange and correlation functional was treated by the generalized gradient approximation with Perdew–Burke–Ernzerhof (GGA-PBE). An energy cutoff of 500 eV and dense k-point grids within the Monkhorst–Pack scheme were adopted for the Brillouin zone sampling, yielding excellent convergence for total energies (within 1 meV per atom). By calculating the individual elastic constants of crystals, \( C_{ij} \), bulk modulus, \( B \), and shear modulus, \( G \), were obtained using the Voight–Reuss–Hill (VRH) approximation. The theoretical Vickers hardness was estimated using Chen’s empirical model, \( H_v = 2.0(\kappa^2G)^{0.585} - 3.0 \), and Tian’s empirical model, \( H_v = 0.92k^{1.137}G^{0.708} \), where \( k = G/B \). In the enthalpy calculations, \( \alpha \)-B and \( \gamma \)-B are adopted as the reference structure below 20 GPa and 20–50 GPa for boron, respectively.

Formation enthalpy was calculated by the following formula:

\[
\Delta H = \left[ H(\text{TM}_2\text{B}_7) - 2H(\text{TM}) - 7H(\text{B}) \right] / (2 + 7)
\]  

where TM represents transition-metal Ru and Os, and \( H \) is the enthalpy of a constituent element.

3 Results and discussion

Motivated by the tight mutual intergrowth of FeB and FeB\(_4\) in the experiment, we initially examined the structural stability by calculating the relative enthalpy as a function of pressure, shown in Fig. 1. In the pressure range from 0 to 50 GPa, both \( \text{Fe}_2\text{B}_7 + \text{B} \) and \( \text{Fe}_2\text{B}_8 \) (FeB\(_4\)) are found to be favored with respect to element Fe and B phases. Moreover, the enthalpy of \( \text{Fe}_2\text{B}_7 + \text{B} \) is very similar to that of \( \text{Fe}_2\text{B}_8 \) (FeB\(_4\)) in the entire pressure range considered (the enthalpy difference is 9–14 meV per atom), which confirms the coexistence of \( \text{Fe}_2\text{B}_7 \) and FeB\(_4\) during the synthesis process. Orthorhombic FeB was also obtained independent of pressure in their high-pressure experiments, and hence the relative enthalpy of \( \text{Fe}_2\text{B}_2 + 6\text{B} \) (FeB + B) is also shown for comparison. In the entire pressure range, the enthalpy of \( \text{Fe}_2\text{B}_2 + 6\text{B} \) (FeB + B) is lower than that of \( 2\text{Fe} + 8\text{B} \), but higher than that of \( \text{Fe}_2\text{B}_7 + \text{B} \) and \( \text{Fe}_2\text{B}_8 \) (FeB\(_4\)). The larger enthalpy difference between \( \text{Fe}_2\text{B}_2 + 6\text{B} \) (FeB + B) and \( \text{Fe}_2\text{B}_8 \) (FeB\(_4\)) may explain why they are not in tight mutual intergrowth.

The structural characteristic of \( \text{Fe}_2\text{B}_7 \) with FeB\(_4\) may give the clue of the phase competition of \( \text{Fe}_2\text{B}_7 \) and FeB\(_4\) during synthesis.
synthesis. As shown in Fig. 2a, the structure of Fe$_2$B$_7$ consists of B12, B10 and B8 units (see Fig. 2d–f), with Fe atoms situated among or inside these units. Therefore, each unit cell of Fe$_2$B$_7$ can be viewed as eight small distorted cells (see Fig. 2b). Compared with Fe$_2$B$_7$, Fe$_4$ (see Fig. 2c) consists of only B12 units (see Fig. 2g) with Fe atoms located inside. In Fe$_2$B$_7$, the length of B–B bonds is 1.616–2.028 Å in the B12 units, 1.666–1.771 Å in the B10 units, and 1.669–1.896 Å in the B8 units. For Fe$_4$, the length of B–B bonds is between 1.694 and 1.880 Å in the B12 units, which is close to the lengths of B–B bonds in B12, B10 and B8 units in Fe$_2$B$_7$. Between the two structures, moreover, we can find some close correlation that the size of the unit cell of Fe$_2$B$_7$ is closely similar to the size of the 4 × 2 × 1 supercell of Fe$_2$B$_7$. Therefore, we can speculate that the small cells with B12 units in Fe$_2$B$_7$ may transform to a unit cell of Fe$_2$B$_7$ through compression, and on adding more B in the experiment, the small cells with B10 and B8 units in Fe$_2$B$_7$ may also transform to Fe$_2$B$_7$ through diffusion and deformation (high pressure and temperature may be needed). Hence, it is reasonable to consider that Fe$_2$B$_7$ may be synthesized by reacting Fe$_2$B$_7$ and B under certain conditions.

It is known that RuB$_2$ and OsB$_2$ crystallize in the same orthorhombic structure. Similarly, RuN$_2$ and OsN$_2$ in experiment adopt an identical marcasite-type structure. In addition, IrP$_3$, IrAs$_3$, IrSb$_3$, CoP$_3$, and RhP$_3$ [ref. 35] with cubic skutterudite CoAs$_2$-type structure were synthesized in experiments. Corresponding nitrides IrN$_3$, CoN$_3$ [ref. 38] and RhN$_3$ [ref. 38] with the same type structure were also suggested by first-principles calculations. Thus, it is expected that Ru$_2$B$_7$ and Os$_2$B$_7$ adopt a similar crystallographic structure to Pb$_{3}$Fe$_6$B$_7$. The lattice parameters of Fe$_2$B$_7$, Ru$_2$B$_7$, and Os$_2$B$_7$ obtained from geometric optimization are listed in Table 1 in comparison with available experiment data. The calculated lattice parameters of Pb$_{3}$Fe$_6$B$_7$ are in good agreement with the experimental data within a maximum error of 1.4%, which confirms the reliability of our calculations.

In order to check the possibility of the existence of Ru$_2$B$_7$ and Os$_2$B$_7$, we calculated the formation enthalpy of the two phases. The computed formation enthalpy is −0.071 eV per atom for Ru$_2$B$_7$ and 0.058 eV per atom for Os$_2$B$_7$. However, at a pressure of 100 GPa, the formation enthalpy for Os$_2$B$_7$ becomes negative, with the value of −0.027 eV. The negative formation enthalpy indicates that Ru$_2$B$_7$ may exist at ambient pressure, while Os$_2$B$_7$ should be favored with high pressure.

The mechanical stability of the proposed Ru$_2$B$_7$ and Os$_2$B$_7$ is checked by calculating their individual elastic constants, as listed in Table 2. The calculated elastic constants fully satisfy Born–Huang stability criteria, suggesting their mechanical stability.

Table 1  Calculated equilibrium lattice parameters a, b, and c (Å) of Fe$_2$B$_7$, Ru$_2$B$_7$, and Os$_2$B$_7$, compared to available experiment data

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Ref.</th>
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<tr>
<td>Fe$_2$B$_7$</td>
<td>16.732</td>
<td>10.538</td>
<td>2.893</td>
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<td></td>
<td>16.9699</td>
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<td>Ru$_2$B$_7$</td>
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<td>18.322</td>
<td>11.101</td>
<td>2.989</td>
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To investigate the effect of the atomic radius of TM (TM = Fe, Ru and Os) on the electronic properties, we calculated the density of states (DOS) and band structure of Fe$_2$B$_7$, Ru$_2$B$_7$, and Os$_2$B$_7$, and the results are shown in Fig. 4. Due to the similarity of the crystal structure, the DOS profile of the three compounds...
is quite similar to each other, the valence band is dominated by B-s states at low energy part, B-p states in the middle range, and TM (TM = Fe, Ru and Os)-d states at the higher energies. We observe the gradual shift of the main peak in the DOS to a lower energy region as the atomic radius of TM (TM = Fe, Ru and Os) increases. All three compounds exhibit metallic features due to the finite values at the Fermi level ($E_F$), which is mainly contributed by TM (TM = Fe, Ru and Os)-d state. The DOSs of TM (TM = Fe, Ru and Os)-d and B-p show a similar profile from the bottom of the valence band to the Fermi level, indicating the covalent hybridization between TM (TM = Fe, Ru and Os) and B atoms. Note that a pseudogap near the Fermi level is observed for all three compounds, enhancing their structural stability. In the band structure of these compounds, the large dispersion bands cross the Fermi level, also revealing their metallic character.

### Table 2

Calculated elastic constants, $C_{ij}$ (GPa), bulk moduli, $B$ (GPa), shear moduli, $G$ (GPa), Young’s moduli, $E$ (GPa), Poisson’s ratio $\nu$ and Vicker’s hardness, $H_v$ (GPa) for Fe$_2$B$_7$, Ru$_2$B$_7$ and Os$_2$B$_7$.

<table>
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<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{22}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{55}$</th>
<th>$C_{66}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{23}$</th>
<th>$B$</th>
<th>$G$</th>
<th>$G/B$</th>
<th>$E$</th>
<th>$\nu$</th>
<th>$H_v$ (Chen)</th>
<th>$H_v$ (Tian)</th>
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<td>Fe$_2$B$_7$</td>
<td>396</td>
<td>691</td>
<td>432</td>
<td>240</td>
<td>205</td>
<td>237</td>
<td>148</td>
<td>172</td>
<td>183</td>
<td>274</td>
<td>197</td>
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<td>477</td>
<td>0.21</td>
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<tr>
<td>Ru$_2$B$_7$</td>
<td>378</td>
<td>614</td>
<td>404</td>
<td>161</td>
<td>201</td>
<td>160</td>
<td>209</td>
<td>154</td>
<td>155</td>
<td>264</td>
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<td>0.60</td>
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<td>Os$_2$B$_7$</td>
<td>359</td>
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<td>134</td>
<td>242</td>
<td>190</td>
<td>166</td>
<td>272</td>
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<td>350</td>
<td>0.28</td>
<td>12.7</td>
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</table>

Fig. 3 3D representations and 2D projections of Young’s moduli for (a) Fe$_2$B$_7$, (b) Ru$_2$B$_7$ and (c) Os$_2$B$_7$. Note that the negative sign only denotes the negative direction corresponding to the positive one.
To gain a more detailed insight into the bonding characters of these compounds, we plot the valence electron density distribution for Fe₂B₇, Ru₂B₇ and Os₂B₇ in (001) and (002) planes in Fig. 5. We can see that there is a charge density maxima located between neighboring B atoms, which correspond to strong directional nonpolar $\sigma$ covalent B–B bonding. However, between the TM (TM = Fe, Ru and Os) atom and the B atom, the valence electrons are more localized around the B atoms due to the electronegativity difference, corresponding to polar covalent bonding, which mainly originates from the hybridization between TM (TM = Fe, Ru and Os)-d and B-p orbitals.

The relative bond strength between boron atoms can be evaluated by the calculated Mulliken overlap populations (MOP). The bond distances and MOP of B–B bonds in Fe₂B₇, Ru₂B₇ and Os₂B₇ are listed in Table 3. The strongest B–B bond in all three compounds is the B₃–B₆ bond, which is located in the (001) plane with MOP values of 0.98, 1.00 and 0.94, respectively. The strong B₃–B₆ bond, nearly parallel to the b axis, is responsible for their high incompressibility along this direction. The MOP of B₆–B₉/B₃–B₉ is 0.58/0.55 in Fe₂B₇, 0.52/0.49 in Ru₂B₇, and 0.39/0.41 in Os₂B₇, indicating a decrease in the B₆–B₉/B₃–B₉ bond strength as TM (TM = Fe, Ru and Os) moves down in group from Fe to Os. A similar trend can be found in the B₂–B₂ bond, with MOP of 0.68 in Fe₂B₇, only 0.30 in Ru₂B₇, and merely 0.16 in Os₂B₇. For B₁–B₂, B₂–B₄ and B₂–B₈ bonds, MOP is found to be 0.81, 0.46 and 0.90 in Fe₂B₇, 0.87, 0.53 and 0.89 in Ru₂B₇, and 0.83, 0.47 and 0.71 in Os₂B₇. In the (002) plane, MOP for B₁₀–B₁₁, B₅–B₁₀ and B₅–B₁₁ is between 0.70 and 0.89 in Fe₂B₇, between 0.75 and 0.82 in Ru₂B₇, and between 0.71 and 0.78 in Os₂B₇. As TM (TM = Fe, Ru and Os) moves down in group from Fe to Os, the B₁₃–B₁₄/B₀–B₁₂ bond strength decreases, with a MOP value of 0.94/0.8 in Fe₂B₇, 0.91/0.67 in Ru₂B₇, and 0.86/0.46 in Os₂B₇. As for the B₁₇–B₁₄ bond, MOP is found to be 0.53, 0.61 and 0.60 in Fe₂B₇, Ru₂B₇ and Os₂B₇, respectively.

The electron transfer from TM (TM = Fe, Ru and Os) to B atoms is found to be 1.49 e for Fe₁, 1.61 e for Fe₂, 1.24 e for Fe₃ and Fe₄ in Fe₂B₇; 1.11 e for Ru₁, 1.26 e for Ru₂, 0.85 e for Ru₃, and 0.93 e for Ru₄ in Ru₂B₇; 1.02 e for Os₁, 1.09 e for Os₂, 0.76 e for Os₃, and 0.80 e for Os₄ in Os₂B₇. The valence charge transfer from TM (TM = Fe, Ru and Os) to B atoms indicates the partial ionic character of the TM–B (TM = Fe, Ru and Os) bonds.

Fig. 4 Density of states (DOS) and band structure for (a) Fe₂B₇, (b) Ru₂B₇ and (c) Os₂B₇.
In conclusion, Fe$_2$B$_7$, Ru$_2$B$_7$ and Os$_2$B$_7$ have been studied by first-principles calculations based on density functional theory. Our calculations indicate that the enthalpy of Fe$_2$B$_7$ + Bi is closely similar to that of FeB$_4$, which is responsible for the coexistence and the tight mutual intergrowth of the two phases in the experiments. Ru$_2$B$_7$ and Os$_2$B$_7$ are thermodynamically (Os$_2$B$_7$ at 100 GPa) and mechanically stable and can be synthesized experimentally. In addition, the bulk modulus of Fe$_2$B$_7$, Ru$_2$B$_7$ and Os$_2$B$_7$ is higher than that of FeB$_4$, and the hardness of Fe$_2$B$_7$ is comparable to that of FeB$_4$. The electronic structure calculations indicate that Fe$_2$B$_7$, Ru$_2$B$_7$ and Os$_2$B$_7$ are metallic, which is mainly attributed to the Fe/Ru/Os-$d$ states. The B–B bonding in the three compounds is covalent, and Fe/ Ru/Os–B interactions have partial covalent and partial ionic character.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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