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# Revealing phase relations between $\text{Fe}_2\text{B}_7$ and $\text{FeB}_4$ and hypothetical $\text{Fe}_2\text{B}_7$ -type $\text{Ru}_2\text{B}_7$ and $\text{Os}_2\text{B}_7$ : 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  $\text{FeB}_4$  and  $\text{Fe}_2\text{B}_7$  in the experiment are compared by their enthalpy and structural features. The closely similar enthalpy of  $\text{Fe}_2\text{B}_7 + \text{B}$  and  $\text{Fe}_2\text{B}_8$  ( $\text{FeB}_4$ ) may explain the coexistence and tight mutual intergrowth of these two phases. The hypothetical  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  are also suggested by the stability evaluations. The stable  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  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.

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## 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.<sup>1–4</sup> 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.*  $\text{OsB}_2$ ,<sup>5</sup>  $\text{RuB}_2$ ,<sup>2</sup>  $\text{ReB}_2$ ,<sup>2,6–10</sup>  $\text{WB}_4$ ,<sup>2,11–13</sup> and  $\text{CrB}_4$ ,<sup>14,15</sup> 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 stoichiometry were identified, providing a road map for exploring design and synthesis strategies for new osmium, ruthenium and tungsten borides.<sup>16,17</sup> Recently,  $\text{FeB}_4$  with *Pnmm* symmetry was synthesized to be a phonon mediated superconductor.<sup>18</sup> Computational structure simulations of the energy landscape did expedite the exploration for the discovery of  $\text{FeB}_4$ .<sup>19</sup> Interestingly,  $\text{Fe}_2\text{B}_7$  was found to coexist with  $\text{FeB}_4$  in experiments. This stoichiometry was not previously identified in any 3d metal boron systems. Aided by

single-crystal X-ray diffraction, Bykova *et al.*<sup>20</sup> identified  $\text{Fe}_2\text{B}_7$  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  $\text{Fe}_2\text{B}^{21}$  and  $\text{FeB}_2$  (ref. 22) in the Fe–B system have been theoretically reported. Moreover, an experimental determination of the phase stability of  $\text{Fe}_2\text{B}_7$  and  $\text{FeB}_4$  has not been characterized. Furthermore,  $\text{FeB}_4$  is found to exhibit great incompressibility along the *b* axis.<sup>18</sup> Due to the intergrowth of  $\text{Fe}_2\text{B}_7$  and  $\text{FeB}_4$ ,  $\text{Fe}_2\text{B}_7$  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.<sup>23</sup>  $\text{OsB}_2$  and  $\text{RuB}_2$  crystallize in the orthorhombic *Pmnm* structure.<sup>24,25</sup> Furthermore,  $\text{OsN}_2$  and  $\text{RuN}_2$  are also formed in the same marcasite structure.<sup>26,27</sup> In addition,  $\text{IrN}_2$  was predicted to have the *IrP}\_2*-type structure by Wang *et al.*<sup>28</sup> It is thus reasonable to expect the existence of  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  with the same crystal symmetry of  $\text{Fe}_2\text{B}_7$ . Inspired by the potential of investigating the rich phase space of metal borides, we carried out a systematic study of  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  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.<sup>29</sup> Exchange and correlation functional was treated by the generalized gradient approximation with Perdew–Burke–Ernzerhof (GGA-PBE).<sup>30</sup> An energy cutoff of 500 eV and dense *k*-point grids within the Monkhorst–Pack scheme<sup>31</sup> 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.<sup>32</sup> The theoretical Vickers hardness was estimated using Chen's empirical model,<sup>33</sup>  $H_v = 2.0(k^2G)^{0.585} - 3.0$ , and Tian's empirical model,<sup>34</sup>  $H_v = 0.92k^{1.137}G^{0.708}$ , 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:

$$\Delta H = [H(TM_2B_7) - 2H(TM) - 7H(B)]/(2 + 7) \quad (1)$$

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  $FeB_4$  and  $Fe_2B_7$  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  $Fe_2B_7 + B$  and  $Fe_2B_8$  ( $FeB_4$ ) are found to be favored with respect to element Fe and B phases. Moreover, the enthalpy of  $Fe_2B_7 + B$  is very similar to that of  $Fe_2B_8$  ( $FeB_4$ ) in the entire pressure range considered (the enthalpy difference is 9–14 meV per atom), which confirms the coexistence of  $Fe_2B_7$  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  $Fe_2B_2 + 6B$  ( $FeB + B$ ) is also shown for comparison. In the entire pressure range, the enthalpy of  $Fe_2B_2 + 6B$  ( $FeB + B$ ) is lower than that of  $2Fe + 8B$ , but higher

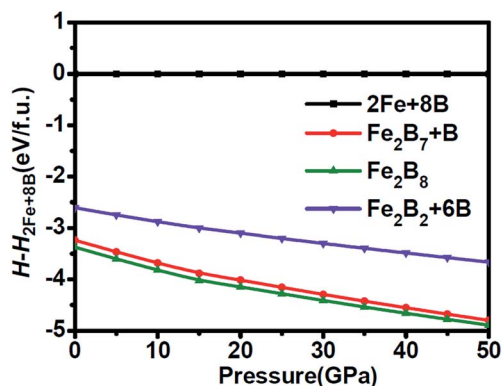


Fig. 1 Relative enthalpy of  $Fe_2B_7 + B$ ,  $Fe_2B_8$  and  $Fe_2B_2 + 6B$  with respect to  $2Fe + 8B$  as a function of pressure.

than that of  $Fe_2B_7 + B$  and  $Fe_2B_8$  ( $FeB_4$ ). The larger enthalpy difference between  $Fe_2B_2 + 6B$  ( $FeB + B$ ) and  $Fe_2B_8$  ( $FeB_4$ ) may explain why they are not in tight mutual intergrowth.

The structural characteristic of  $Fe_2B_7$  with  $FeB_4$  may give the clue of the phase competition of  $Fe_2B_7$  and  $FeB_4$  during

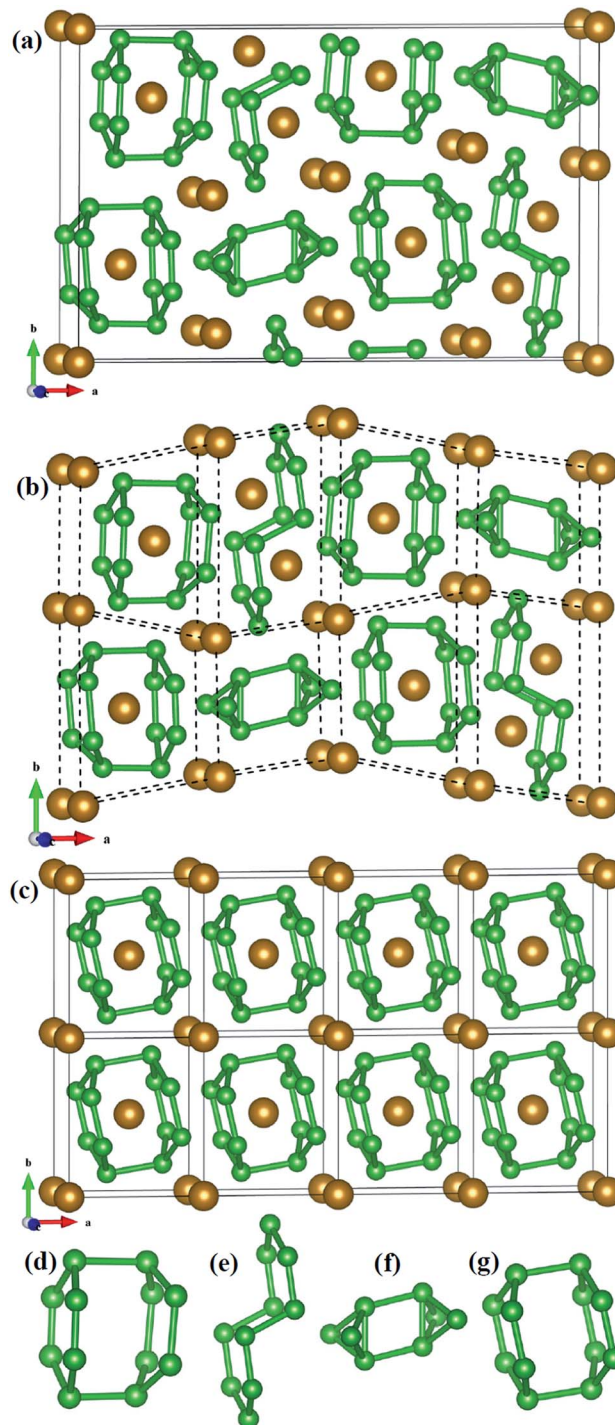


Fig. 2 (a) The unit cell of  $Fe_2B_7$ , (b) the unit cell of  $Fe_2B_7$  can be seen as eight small cells, (c)  $4 \times 2 \times 1$  supercell of  $FeB_4$ , (d–f) B12, B10 and B8 units in  $Fe_2B_7$ , respectively, (g) B12 units in  $FeB_4$ . The brown and green spheres represent Fe and B atoms, respectively.



synthesis. As shown in Fig. 2a, the structure of  $\text{Fe}_2\text{B}_7$  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  $\text{Fe}_2\text{B}_7$  can be viewed as eight small distorted cells (see Fig. 2b). Compared with  $\text{Fe}_2\text{B}_7$ ,  $\text{FeB}_4$  (see Fig. 2c) consists of only B12 units (see Fig. 2g) with Fe atoms located inside. In  $\text{Fe}_2\text{B}_7$ , 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  $\text{FeB}_4$ , 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  $\text{Fe}_2\text{B}_7$ . Between the two structures, moreover, we can find some close correlation that the size of the unit cell of  $\text{Fe}_2\text{B}_7$  is closely similar to the size of the  $4 \times 2 \times 1$  supercell of  $\text{FeB}_4$ . Therefore, we can speculate that the small cells with B12 units in  $\text{Fe}_2\text{B}_7$  may transform to a unit cell of  $\text{FeB}_4$  through compression, and on adding more B in the experiment, the small cells with B10 and B8 units in  $\text{Fe}_2\text{B}_7$  may also transform to  $\text{FeB}_4$  through diffusion and deformation (high pressure and temperature may be needed). Hence, it is reasonable to consider that  $\text{FeB}_4$  may be synthesized by reacting  $\text{Fe}_2\text{B}_7$  and B under certain conditions.

It is known that  $\text{RuB}_2$  and  $\text{OsB}_2$  crystallize in the same orthorhombic structure.<sup>24,25</sup> Similarly,  $\text{RuN}_2$  and  $\text{OsN}_2$  in experiment adopt an identical marcasite-type structure.<sup>26,27</sup> In addition,  $\text{IrP}_3$ ,<sup>35</sup>  $\text{IrAs}_3$ ,<sup>36</sup>  $\text{IrSb}_3$ ,<sup>36</sup>  $\text{CoP}_3$ ,<sup>35</sup> and  $\text{RhP}_3$  (ref. 35) with cubic skutterudite  $\text{CoAs}_3$ -type structure were synthesized in experiments. Corresponding nitrides  $\text{IrN}_3$ ,<sup>37</sup>  $\text{CoN}_3$  (ref. 38) and  $\text{RhN}_3$  (ref. 38) with the same type structure were also suggested by first-principles calculations. Thus, it is expected that  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  adopt a similar crystallographic structure to *Pbam*- $\text{Fe}_2\text{B}_7$ . The lattice parameters of  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  obtained from geometric optimization are listed in Table 1 in comparison with available experiment data. The calculated lattice parameters of *Pbam*- $\text{Fe}_2\text{B}_7$  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  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$ , we calculated the formation enthalpy of the two phases. The computed formation enthalpy is  $-0.071$  eV per atom for  $\text{Ru}_2\text{B}_7$  and  $0.058$  eV per atom for  $\text{Os}_2\text{B}_7$ . However, at a pressure of 100 GPa, the formation enthalpy for  $\text{Os}_2\text{B}_7$  becomes negative, with the value of  $-0.027$  eV. The negative formation enthalpy indicates that  $\text{Ru}_2\text{B}_7$  may exist at ambient pressure, while  $\text{Os}_2\text{B}_7$  should be favored with high pressure.

The mechanical stability of the proposed  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  is checked by calculating their individual elastic constants, as listed in Table 2. The calculated elastic constants fully satisfy

Born–Huang stability criteria,<sup>37</sup> suggesting their mechanical stability. For comparison, the elastic constants of  $\text{Fe}_2\text{B}_7$  are also given in Table 2, together with the bulk modulus  $B$ , shear modulus  $G$ , Young's modulus  $E$ , Poisson's ratio  $\nu$  and Vickers hardness  $H_v$ . We can see that as the atomic number of TM (TM = Fe, Ru and Os) increases, the elastic constants  $C_{11}$ ,  $C_{22}$  and  $C_{33}$  decrease. The  $C_{22}$  value for  $\text{Fe}_2\text{B}_7$  is 691 GPa, slightly lower than that of *Pnmm*- $\text{FeB}_4$  (717 GPa).<sup>39</sup> For all three compounds  $\text{TM}_2\text{B}_7$  (TM = Fe, Ru and Os),  $C_{22}$  is much larger than  $C_{11}$  and  $C_{33}$ , similar to that in  $\text{VB}_4$ ,<sup>40</sup>  $\text{CrB}_4$ ,<sup>14</sup>  $\text{FeB}_4$  (ref. 39) and  $\text{MnB}_4$ ,<sup>41</sup> as the shortest B–B bonds are almost parallel to the [010] direction. The calculated bulk modulus of  $\text{Fe}_2\text{B}_7$  is 274 GPa, which is consistent with the experiment value of 268.9 GPa,<sup>20</sup> and higher than the experiment value of *Pnmm*- $\text{FeB}_4$  (252 GPa).<sup>18</sup> Although the valence electron density of element Ru and Os is higher than that of Fe, the bulk modulus of  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  is only 264 GPa and 272 GPa, respectively, suggesting that the valence electron density is not a predominant factor accounting for the bulk moduli of  $\text{TM}_2\text{B}_7$  (TM = Fe, Ru and Os) but the boron network. Moreover,  $\text{Fe}_2\text{B}_7$  exhibits the highest shear modulus (197 GPa) and hardness (26.9 GPa), comparable to the theoretical value of *Pnmm*- $\text{FeB}_4$  (197.97 GPa/28.4 GPa). The  $G/B$  ratio, proposed by Pugh,<sup>42</sup> is correlated with the brittleness and ductility of materials ( $G/B > 0.57$  corresponds to brittle and  $G/B < 0.57$  to ductile behavior).  $\text{Fe}_2\text{B}_7$  and  $\text{Ru}_2\text{B}_7$  are brittle with  $G/B$  values of 0.72 and 0.60, while  $\text{Os}_2\text{B}_7$  is ductile with a  $G/B$  ratio of 0.50. Poisson's ratio,  $\nu$ , is an important parameter to describe the directional degree of covalent bonds in a material.<sup>43</sup> For  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$ ,  $\nu$  values are 0.21, 0.25 and 0.28, respectively, indicating their directional covalent bonding.

Young's modulus ( $E$ ) is an important mechanical parameter to measure of the stiffness of a solid material. To get a better understanding of the direction oriented Young's modulus, a 3D representation and corresponding two dimensional (2D) projections of Young's modulus for  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  as a function of the crystallographic direction<sup>44</sup> are calculated and presented in Fig. 3. The shape deviation from a sphere indicates the degree of anisotropy in the system. Clearly, they all exhibit a slight elastic anisotropy, and the elastic anisotropy increases as the atomic radius of TM (TM = Fe, Ru and Os) increases. For  $\text{Fe}_2\text{B}_7$ , the 2D projections of Young's modulus in the  $xy$ ,  $xz$  and  $yz$  planes have similar profiles, and the lowest Young's modulus values are along the [010] direction. For  $\text{Ru}_2\text{B}_7$ , the 2D projection of Young's modulus in the  $xy$  plane exhibits greater anisotropy than that in the  $xz$  and  $yz$  planes. For  $\text{Os}_2\text{B}_7$ , the lowest Young's modulus values are along the [100] direction, with the 2D projection of Young's modulus in the  $xy$  and  $xz$  planes showing larger anisotropy than in the  $yz$  plane.

The dynamical stability of the newly proposed  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  is checked by calculating the phonon spectra (see ESI Fig. S1†). Both compounds are dynamically stable with no imaginary frequency found throughout the Brillouin zone.

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  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$ , and the results are shown in Fig. 4. Due to the similarity of the crystal structure, the DOS profile of the three compounds

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

	$a$	$b$	$c$	Ref.
$\text{Fe}_2\text{B}_7$	16.732	10.538	2.893	20
	16.9699	10.6520	2.8938	
$\text{Ru}_2\text{B}_7$	17.965	11.061	2.984	
$\text{Os}_2\text{B}_7$	18.322	11.101	2.989	

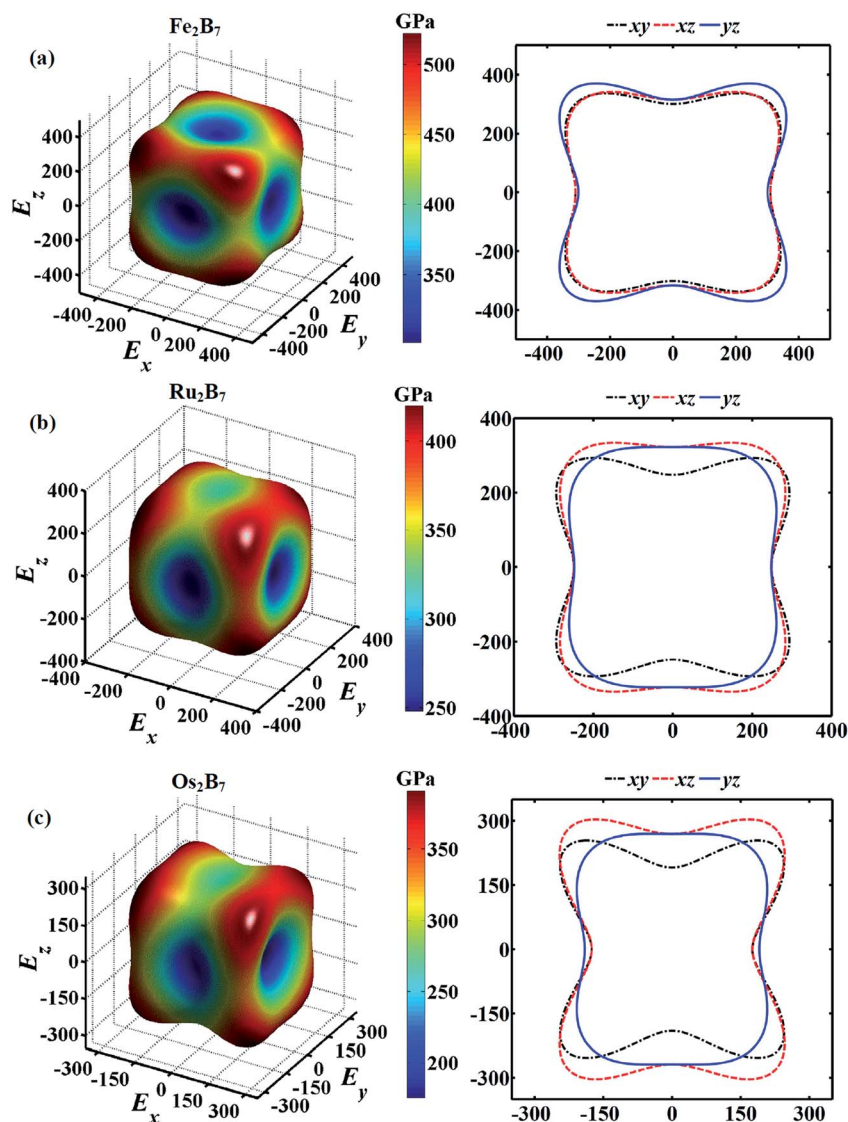


**Table 2** Calculated elastic constants,  $C_{ij}$  (GPa), bulk moduli,  $B$  (GPa), shear moduli,  $G$  (GPa), Young's moduli,  $E$  (GPa), Poisson's ratio  $\nu$  and Vicker's hardness,  $H_V$  (GPa) for  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$

	$C_{11}$	$C_{22}$	$C_{33}$	$C_{44}$	$C_{55}$	$C_{66}$	$C_{12}$	$C_{13}$	$C_{23}$	$B$	$G$	$G/B$	$E$	$\nu$	$H_V$ (Chen)	$H_V$ (Tian)
$\text{Fe}_2\text{B}_7$	396	691	432	240	205	237	148	172	183	274	197	0.72	477	0.21	26.9	26.6
$\text{Ru}_2\text{B}_7$	378	614	404	161	201	160	209	154	155	264	159	0.60	397	0.25	18.4	18.7
$\text{Os}_2\text{B}_7$	359	575	377	148	194	134	242	190	166	272	136	0.50	350	0.28	12.7	13.6

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.



**Fig. 3** 3D representations and 2D projections of Young's moduli for (a)  $\text{Fe}_2\text{B}_7$ , (b)  $\text{Ru}_2\text{B}_7$  and (c)  $\text{Os}_2\text{B}_7$ . Note that the negative sign only denotes the negative direction corresponding to the positive one.



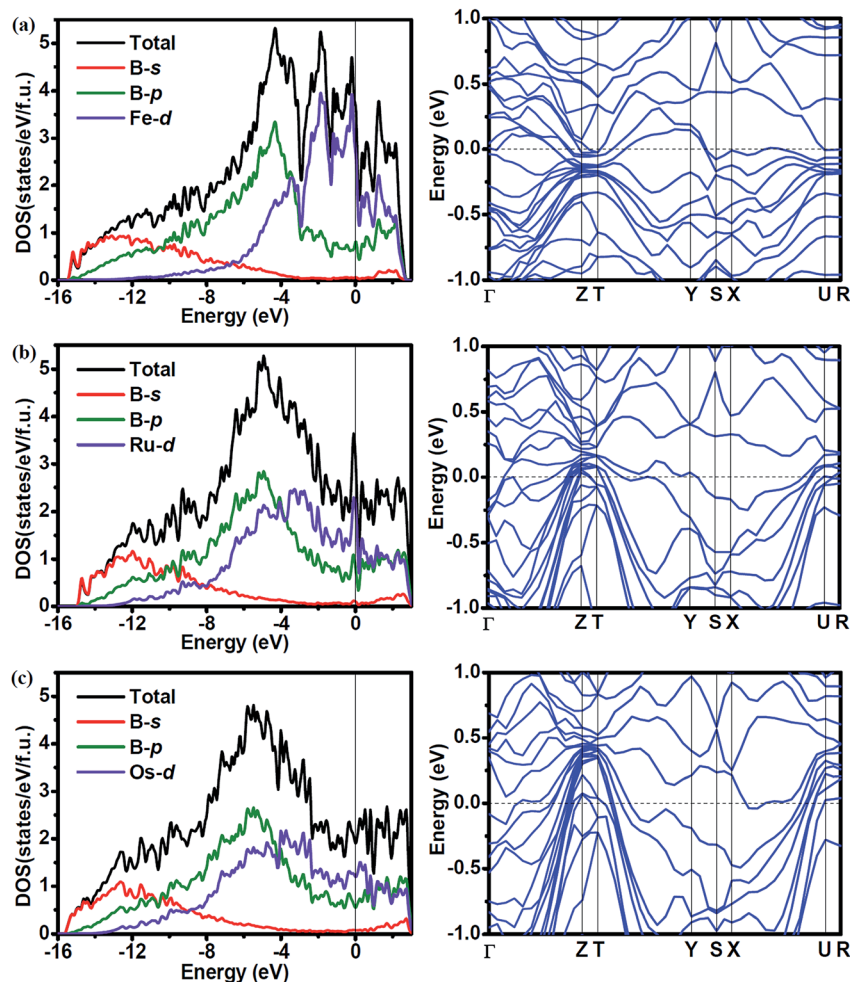


Fig. 4 Density of states (DOS) and band structure for (a)  $\text{Fe}_2\text{B}_7$ , (b)  $\text{Ru}_2\text{B}_7$  and (c)  $\text{Os}_2\text{B}_7$ .

To gain a more detailed insight into the bonding characters of these compounds, we plot the valence electron density distribution for  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  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  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  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  $\text{Fe}_2\text{B}_7$ , 0.52/0.49 in  $\text{Ru}_2\text{B}_7$ , and 0.39/0.41 in  $\text{Os}_2\text{B}_7$ , 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  $\text{Fe}_2\text{B}_7$ , only 0.30 in  $\text{Ru}_2\text{B}_7$ , and merely 0.16 in  $\text{Os}_2\text{B}_7$ . For B1–B2, B2–B4 and B2–B8 bonds, MOP is found to be 0.81, 0.46 and 0.90 in  $\text{Fe}_2\text{B}_7$ , 0.87, 0.53 and 0.89 in  $\text{Ru}_2\text{B}_7$ , and 0.83, 0.47 and 0.71 in  $\text{Os}_2\text{B}_7$ . In the (002) plane, MOP for B10–B11, B5–B10 and B5–B11 is between 0.70 and 0.89 in  $\text{Fe}_2\text{B}_7$ , between 0.75 and 0.82 in  $\text{Ru}_2\text{B}_7$ , and between 0.71 and 0.78 in  $\text{Os}_2\text{B}_7$ . As TM (TM = Fe, Ru and Os) moves down in group from Fe to Os, the B13–B14/B7–B12 bond strength decreases, with a MOP value of 0.94/0.8 in  $\text{Fe}_2\text{B}_7$ , 0.91/0.67 in  $\text{Ru}_2\text{B}_7$ , and 0.86/0.46 in  $\text{Os}_2\text{B}_7$ . As for the B7–B14 bond, MOP is found to be 0.53, 0.61 and 0.60 in  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$ , 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  $\text{Fe}_2\text{B}_7$ ; 1.11 *e* for Ru1, 1.26 *e* for Ru2, 0.85 *e* for Ru3, and 0.93 *e* for Ru4 in  $\text{Ru}_2\text{B}_7$ ; 1.02 *e* for Os1, 1.09 *e* for Os2, 0.76 *e* for Os3, and 0.80 *e* for Os4 in  $\text{Os}_2\text{B}_7$ . 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.



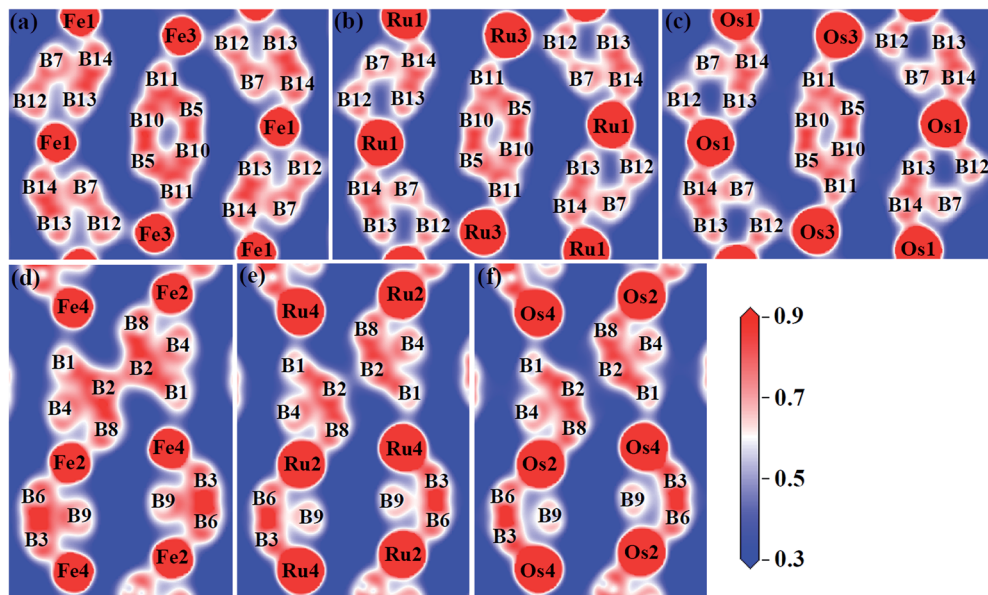


Fig. 5 Valence electron density distribution of (a)  $\text{Fe}_2\text{B}_7$  in (002) and (d) in (001) planes, (b)  $\text{Ru}_2\text{B}_7$  in (002) and (e) in (001) planes, (c)  $\text{Os}_2\text{B}_7$  in (002) and (f) in (001) planes.

Table 3 Bond distances  $d$  (Å) and MOP of B–B bonds in  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$

	$\text{Fe}_2\text{B}_7$		$\text{Ru}_2\text{B}_7$		$\text{Os}_2\text{B}_7$	
	$d$	MOP	$d$	MOP	$d$	MOP
B3–B6	1.616	0.98	1.644	1.00	1.649	0.94
B13–B14	1.691	0.94	1.733	0.91	1.726	0.86
B2–B8	1.666	0.90	1.692	0.89	1.689	0.71
B10–B11	1.728	0.89	1.800	0.82	1.792	0.78
B1–B2	1.714	0.81	1.740	0.87	1.727	0.83
B7–B12	1.773	0.8	1.884	0.67	1.991	0.46
B5–B11	1.747	0.74	1.800	0.76	1.817	0.72
B5–B10	1.669	0.70	1.682	0.75	1.687	0.71
B2–B2	1.771	0.68	2.117	0.30	2.206	0.16
B6–B9	1.834	0.58	1.991	0.52	2.101	0.39
B3–B9	1.847	0.55	1.986	0.49	2.034	0.41
B7–B14	1.859	0.53	1.884	0.61	1.880	0.60
B2–B4	1.811	0.46	1.838	0.53	1.859	0.47

## 4 Conclusions

In conclusion,  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  have been studied by first-principles calculations based on density functional theory. Our calculations indicate that the enthalpy of  $\text{Fe}_2\text{B}_7 + \text{B}$  is closely similar to that of  $\text{Fe}_2\text{B}_8$  ( $\text{FeB}_4$ ), which is responsible for the coexistence and the tight mutual intergrowth of the two phases in the experiments.  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  are thermodynamically ( $\text{Os}_2\text{B}_7$  at 100 GPa) and mechanically stable and can be synthesized experimentally. In addition, the bulk modulus of  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  is higher than that of  $\text{FeB}_4$ , and the hardness of  $\text{Fe}_2\text{B}_7$  is comparable to that of  $\text{FeB}_4$ . The electronic structure calculations indicate that  $\text{Fe}_2\text{B}_7$ ,  $\text{Ru}_2\text{B}_7$  and  $\text{Os}_2\text{B}_7$  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.

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