RSC Advances

PAPER

Cite this: RSC Adv., 2017, 7, 44860

Revealing phase relations between $Fe₂B₇$ and $FeB₄$ and hypothetical $Fe₂B₇$ -type $Ru₂B₇$ and $Os₂B₇$: firstprinciples 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 FeB₄ and $Fe₂B₇$ in the experiment are compared by their enthalpy and structural features. The closely similar enthalpy of Fe₂B₇ + B and Fe₂B₈ (FeB₄) may explain the coexistence and tight mutual intergrowth of these two phases. The hypothetical Ru₂B₇ and Os₂B₇ are also suggested by the stability evaluations. The stable Ru_2B_7 and Os_2B_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. **PAPER**
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Received 24th July 2017 Accepted 6th September 2017

DOI: 10.1039/c7ra08134k

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1 Introduction

Over the decades, transition metal (TM) borides have attracted much attention due to their great promise for hard, wearresistant, chemically inert coatings' applications.¹–⁴ 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 ,⁵ RuB_2 ,² ReB_2 ,^{2,6-10} $\mathrm{WB}_{4},^{2,11-13}$ and $\mathrm{CrB}_{4},^{14,15}$ 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.^{16,17} Recently, FeB₄ with Pnnm symmetry was synthesized to be a phonon mediated superconductor.¹⁸ Computational structure simulations of the energy landscape did expedite the exploration for the discovery of FeB₄.¹⁹ Interestingly, Fe₂B₇ was found to coexist with FeB₄ in experiments. This stoichiometry was not previously identified in any 3d metal boron systems. Aided by

single-crystal X-ray diffraction, Bykova et al.²⁰ identified Fe₂B₇ 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 $Fe₂B²¹$ and $FeB₂$ (ref. 22) in the Fe–B system have been theoretically reported. Moreover, an experimental determination of the phase stability of $Fe₂B₇$ and $FeB₄$ has not been characterized. Furthermore, $FeB₄$ is found to exhibit great incompressibility along the b axis.¹⁸ Due to the intergrowth of $Fe₂B₇$ and $FeB₄$, $Fe₂B₇$ 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.

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It is found that chemically related compounds usually share similar crystallographic structure.²³ OsB₂ and RuB₂ crystallize in the orthorhombic *Pmmn* structure.^{24,25} Furthermore, OsN₂ and $RuN₂$ are also formed in the same marcasite structure.^{26,27} In addition, IrN₂ was predicted to have the IrP₂-type structure by Wang et $al.^{28}$ It is thus reasonable to expect the existence of $Ru₂B₇$ and $Os₂B₇$ with the same crystal symmetry of Fe₂B₇. Inspired by the potential of investigating the rich phase space of metal borides, we carried out a systematic study of $Fe₂B₇$, $Ru₂B₇$ and $Os₂B₇$ 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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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra08134k

2 Computational details and methods

The structural optimizations were performed within CASTEP code.²⁹ Exchange and correlation functional was treated by the generalized gradient approximation with Perdew–Burke–Ernzerhof (GGA-PBE).³⁰ An energy cutoff of 500 eV and dense k -point grids within the Monkhorst-Pack scheme³¹ 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_{ii} , bulk modulus, B , and shear modulus, G, were obtained using the Voight–Reuss–Hill (VRH) approximation.³² The theoretical Vickers hardness was estimated using Chen's empirical model,³³ $H_v = 2.0(k^2 G)^{0.585} - 3.0$, and Tian's empirical model,³⁴ $H_v = 0.92k^{1.137}G^{0.708}$, where $k = G/B$. In the enthalpy calculations, α -B and γ -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:

$$
\Delta H = [H(TM_2B_7) - 2H(TM) - 7H(B)]/(2 + 7)
$$
 (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 $FeB₄$ and $Fe₂B₇$ 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 $Fe₂B₇ + B$ and $Fe₂B₈$ (FeB₄) are found to be favored with respect to element Fe and B phases. Moreover, the enthalpy of $Fe₂B₇ + B$ is very similar to that of $Fe₂B₈$ (FeB₄) in the entire pressure range considered (the enthalpy difference is 9–14 meV per atom), which confirms the coexistence of $Fe₂B₇$ and $FeB₄$ during the synthesis process. Orthorhombic FeB was also obtained independent of pressure in their high-pressure experiments, and hence the relative enthalpy of $Fe₂B₂ + 6B (FeB + B)$ is also shown for comparison. In the entire pressure range, the enthalpy of $Fe₂B₂ + 6B (FeB + B)$ is lower than that of 2Fe + 8B, but higher

Fig. 1 Relative enthalpy of $Fe₂B₇ + B$, $Fe₂B₈$ and $Fe₂B₂ + 6B$ with respect to 2Fe + 8B as a function of pressure.

than that of Fe₂B₇ + B and Fe₂B₈ (FeB₄). The larger enthalpy difference between $Fe_2B_2 + 6B$ (FeB + B) and Fe_2B_8 (FeB₄) may explain why they are not in tight mutual intergrowth.

The structural characteristic of $Fe₂B₇$ with $FeB₄$ may give the clue of the phase competition of $Fe₂B₇$ and $FeB₄$ during

Fig. 2 (a) The unit cell of Fe₂B₇, (b) the unit cell of Fe₂B₇ can be seen as eight small cells, (c) $4 \times 2 \times 1$ supercell of FeB₄, (d-f) B12, B10 and B8 units in Fe₂B₇, respectively, (g) B12 units in FeB₄. The brown and green spheres represent Fe and B atoms, respectively.

synthesis. As shown in Fig. 2a, the structure of $Fe₂B₇$ 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 $Fe₂B₇$ can be viewed as eight small distorted cells (see Fig. 2b). Compared with $Fe₂B₇$, FeB₄ (see Fig. 2c) consists of only B12 units (see Fig. 2g) with Fe atoms located inside. In $Fe₂B₇$, 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 $FeB₄$, the length of B-B bonds is between 1.694 and 1.880 \AA in the B12 units, which is close to the lengths of B-B bonds in B12, B10 and B8 units in $Fe₂B₇$. Between the two structures, moreover, we can find some close correlation that the size of the unit cell of $Fe₂B₇$ is closely similar to the size of the $4 \times 2 \times 1$ supercell of FeB₄. Therefore, we can speculate that the small cells with B12 units in $Fe₂B₇$ may transform to a unit cell of $FeB₄$ through compression, and on adding more B in the experiment, the small cells with B10 and B8 units in $Fe₂B₇$ may also transform to $FeB₄$ through diffusion and deformation (high pressure and temperature may be needed). Hence, it is reasonable to consider that $FeB₄$ may be synthesized by reacting $Fe₂B₇$ and B under certain conditions.

It is known that $RuB₂$ and $OsB₂$ crystallize in the same orthorhombic structure.^{24,25} Similarly, RuN_2 and OsN_2 in experiment adopt an identical marcasite-type structure.^{26,27} In addition, IrP_3 ,³⁵ $IrAs_3$,³⁶ $IrSb_3$,³⁶ CoP_3 ,³⁵ and RhP_3 (ref. 35) with cubic skutterudite CoAs₃-type structure were synthesized in experiments. Corresponding nitrides IrN_3 ,³⁷ CoN₃ (ref. 38) and $RhN₃$ (ref. 38) with the same type structure were also suggested by first-principles calculations. Thus, it is expected that $Ru₂B₇$ and $Os₂B₇$ adopt a similar crystallographic structure to *Pbam*-Fe₂B₇. The lattice parameters of Fe₂B₇, Ru₂B₇ and Os₂B₇ obtained from geometric optimization are listed in Table 1 in comparison with available experiment data. The calculated lattice parameters of $Pbam\text{-Fe}_2B_7$ 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 $Ru₂B₇$ and $Os₂B₇$, we calculated the formation enthalpy of the two phases. The computed formation enthalpy is -0.071 eV per atom for $Ru₂B₇$ and 0.058 eV per atom for $Os₂B₇$. However, at a pressure of 100 GPa, the formation enthalpy for $Os₂B₇$ becomes negative, with the value of -0.027 eV. The negative formation enthalpy indicates that $Ru₂B₇$ may exist at ambient pressure, while $Os₂B₇$ should be favored with high pressure.

The mechanical stability of the proposed Ru_2B_7 and Os_2B_7 is checked by calculating their individual elastic constants, as listed in Table 2. The calculated elastic constants fully satisfy

Table 1 Calculated equilibrium lattice parameters a , b , and c (Å) of $Fe₂B₇$, Ru₂B₇ and Os₂B₇, compared to available experiment data

	a	h	C	Ref.
Fe ₂ B ₇	16.732	10.538	2.893	20
	16.9699	10.6520	2.8938	
Ru ₂ B ₇	17.965	11.061	2.984	
Os_2B_7	18.322	11.101	2.989	

Born-Huang stability criteria,³⁷ suggesting their mechanical stability. For comparison, the elastic constants of $Fe₂B₇$ are also given in Table 2, together with the bulk modulus B, shear modulus G , Young's modulus E , Poisson's ratio ν 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 Fe₂B₇ is 691 GPa, slightly lower than that of $Pnnm-FeB₄$ (717 GPa).³⁹ For all three compounds TM_2B_7 (TM = Fe, Ru and Os), C_{22} is much larger than C_{11} and C_{33} , similar to that in VB₄,⁴⁰ CrB₄,¹⁴ FeB₄ (ref. 39) and MnB₄,⁴¹ as the shortest B–B bonds are almost parallel to the [010] direction. The calculated bulk modulus of $Fe₂B₇$ is 274 GPa, which is consistent with the experiment value of 268.9 GPa,²⁰ and higher than the experiment value of $Pnnm$ -FeB₄ (252 GPa).¹⁸ Although the valence electron density of element Ru and Os is higher than that of Fe, the bulk modulus of Ru_2B_7 and Os_2B_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 TM_2B_7 (TM = Fe, Ru and Os) but the boron network. Moreover, $Fe₂B₇$ exhibits the highest shear modulus (197 GPa) and hardness (26.9 GPa), comparable to the theoretical value of Pnnm-FeB₄ (197.97 GPa/28.4 GPa). The G/B ratio, proposed by Pugh,⁴² is correlated with the brittleness and ductility of materials ($G/B > 0.57$ corresponds to brittle and $G/B < 0.57$ to ductile behavior). Fe₂B₇ and Ru₂B₇ are brittle with G/B values of 0.72 and 0.60, while Os_2B_7 is ductile with a G/B ratio of 0.50. Poisson's ratio, ν , is an important parameter to describe the directional degree of covalent bonds in a material.⁴³ For Fe₂B₇, $Ru₂B₇$ and $Os₂B₇$, ν values are 0.21, 0.25 and 0.28, respectively, indicating their directional covalent bonding. BSC Advances

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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 $Fe₂B₇$, $Ru₂B₇$ and $Os₂B₇$ as a function of the crystallographic direction⁴⁴ 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 $Fe₂B₇$, 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 Ru_2B_7 , the 2D projection of Young's modulus in the xy plane exhibits greater anisotropy than that in the xz and yz planes. For Os_2B_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 $Ru₂B₇$ and $Os₂B₇$ 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 $Fe₂B₇$, $Ru₂B₇$ and $Os₂B₇$, and the results are shown in Fig. 4. Due to the similarity of the crystal structure, the DOS profile of the three compounds

Table 2 Calculated elastic constants, C_{ij} (GPa), bulk moduli, B (GPa), shear moduli, G (GPa), Young's moduli, E (GPa), Poisson's ratio v and Vicker's hardness, H_v (GPa) for Fe₂B₇, Ru₂B₇ and Os₂B₇

	C_{11}	C_{22}	C_{33}					C_{44} C_{55} C_{66} C_{12} C_{13} C_{23} B			G	G/B	E and E and E and E and E	ν	$H_{\rm v}$ (Chen)	H_v (Tian)
Fe ₂ B ₇ Ru ₂ B ₇ Os_2B_7	396 378 359	691 614 575 377	432 -404	240 161 148	205 201	237 160 194 134 242 190	209	148 172 154	183 155 166	274 264 272	197 159 136	0.72 0.60 0.50	477 397 350	0.21 0.25 0.28	26.9 18.4 12.7	26.6 18.7 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) Fe₂B₇, (b) Ru₂B₇ and (c) Os₂B₇. 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) $Fe₂B₇$, (b) $Ru₂B₇$ and (c) $Os₂B₇$.

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 σ 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 Ru_2B_7 , and 0.83, 0.47 and 0.71 in Os_2B_7 . 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/B7–B12 bond strength decreases, with a MOP value of $0.94/0.8$ in Fe₂B₇, 0.91/ 0.67 in Ru_2B_7 , and 0.86/0.46 in Os_2B_7 . As for the B7-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. 5 Valence electron density distribution of (a) Fe₂B₇ in (002) and (d) in (001) planes, (b) Ru₂B₇ in (002) and (e) in (001) planes, (c) Os₂B₇ in (002) and (f) in (001) planes.

Table 3 Bond distances d (Å) and MOP of B-B bonds in Fe₂B₇, Ru₂B₇ and Os_2B_7

	Ru/Os-B interactions have partial covalent and partial ionic			
character.				

4 Conclusions

In conclusion, $Fe₂B₇$, $Ru₂B₇$ and $Os₂B₇$ have been studied by first-principles calculations based on density functional theory. Our calculations indicate that the enthalpy of $Fe₂B₇ + B$ is closely similar to that of $Fe₂B₈$ (FeB₄), which is responsible for the coexistence and the tight mutual intergrowth of the two phases in the experiments. $Ru₂B₇$ and $Os₂B₇$ are thermodynamically $(Os₂B₇$ at 100 GPa) and mechanically stable and can be synthesized experimentally. In addition, the bulk modulus of $Fe₂B₇$, Ru₂B₇ and Os₂B₇ is higher than that of FeB₄, and the hardness of $Fe₂B₇$ is comparable to that of $FeB₄$. The electronic structure calculations indicate that $Fe₂B₇$, Ru₂B₇ and Os₂B₇ 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/

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC) under Grants No. 51201148 and U1530402. L. Wu thanks the foundation of China Postdoctoral Science Foundation (2016M601280). Z. Li thanks Hebei Natural Science Foundation (No. B2015203096) and the Autonomic Research Project of Yanshan University under Grant No. 14LGA017.

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