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Structural Variety beyond Appearance: High-pressure Phases of CrB₄ in comparison with FeB₄

Yunkun Zhang,a Lailei Wu,*a Biao Wan,a Yan Zhao,a Rui Gao,b Zhiping Li,b Jingwu Zhang,**a Huiyang Gou*cd and Ho-kwang Mao cd

Employing Particle Swarm Optimization (PSO) combined with first-principles calculations, we systemically studied high-pressure behaviors of hard CrB₄. Our predictions reveal a distinct structural evolution under pressure for CrB₄ despite having the same initial structure with FeB₄. CrB₄ is found to adopt a new P2/m structure above 196 GPa, another Pm structure at a pressure range of 261-294 GPa and then a Pmna structure beyond 294 GPa. Instead of puckering boron sheets in initial structure, the high-pressure phases have the planar boron sheets with different motifs upon compression. Comparatively, FeB₄ prefers an I4/acd structure over 48 GPa with terahedron B₄ units and a P2₁3 structure above 231 GPa having equilateral triangle B₃ units. Significantly, CrB₄ exhibits the persistent metallic behaviors in contrast with the semiconducting features of FeB₄ upon compression. The varied pressure response of hard tetraborides studied here is of importance for understanding boron-rich compounds and designing new materials with superlative properties.

I. Introduction

Transition metal (TM) borides have continued to attract much attention over decades because of great potentials for the development of next generation hard/superhard materials.¹⁻⁷ The synthesis of 5d noble metal borides, e.g. OsB₄ and ReB₄, was expected to yield superhard materials due to the strong covalent interactions between TM-B and B-B. Although great efforts have been made to obtain the high bulk modulus in these borides, however, this incompressibility did not guarantee the better mechanical properties,⁷ e.g. hardness. The continuing searching for possible superhard materials is thus focusing on the more boron-rich compounds.⁸⁻¹¹ Once more boron atoms are introduced into the metal lattices, the mechanical properties are expected to be enhanced due to the presence of three-dimensional (3D) boron networks, e.g. nominal WB₄.¹²⁻¹⁴ In comparison with 5d metal borides, the weak bonding between metal and boron in 3d metal borides makes them less attractive for potentially hard materials. Nevertheless, the studies of 3d transition metal tetraborides (TMB₄), CrB₄⁸,¹⁵,¹⁶, FeB₄⁹,¹⁷ and MnB₄¹⁰,¹¹,¹⁸, have become one of the exciting topics because of the possible higher hardness, together with intriguing physical properties, such as superconductivity, semiconductivity and magnetism. For example, Pnnm type FeB₄ was predicted and experimentally confirmed to be phonon mediated superconductor.⁹,¹⁵ MnB₄ opens a band gap at Fermi level due to the Peierls distortion of Mn chains in the monoclinic symmetry.¹⁰,¹¹,¹⁸ Additionally, they also show the incompressible behavior due to the presence of short boron-boron bonds in the boron networks, comparable to 5d metal borides. The unique features of 3d TMB₄ are inspiring for a variety of engineering applications.
Studies of material behaviors under pressure are of great importance for both planetary physics and materials science. Application of pressure greatly stimulated the discovery of the unexpected structural materials, e.g. NaCl$_3$ and Na$_3$Cl, and physical phenomena, e.g. metal-insulator transitions in Li$_2$O and Na$_2$O. In these studies, structural prediction strategies have showed the great ability to assist and even guide the material discovery in experiments.

The improvement of density functional theory-based methods and the development of computational resources predict complex configurations given only the composition, leading to identification of exotic high-pressure (HP) phases. Recently, Kotmool et al. theoretically proposed a structure change of FeB$_4$ from superconductor to semiconductor above 53.7 GPa. This phase is found to be stable up to 300 GPa. Under further compression, another phase transition above 695 GPa was reported by Jiang et al. This new cubic $Im3m$ phase was predicted to be stable up to 1TPa. As we know, the neighboring CrB$_4$ have similar structural and metallic features at ambient condition. However, there is little information about high-pressure behaviors of CrB$_4$. Here we comparatively explored the HP phases of CrB$_4$ and FeB$_4$ within structure search methodology. Furthermore, we have studied their structures, mechanical and electronic features through the first-principles calculations. Our predictions are expected to greatly stimulate future experiments to synthesize these phases.

II. Methods

Structure searches at high pressure (50, 100, 200 and 300 GPa) of CrB$_4$ and FeB$_4$ within six formula units were performed by the particle swarm optimization methodology as implemented in the CALYPSO code. CASTEP code was used for the structural optimizations and energy calculations for various structures. Exchange and correlation functional was treated by generalized gradient approximation with Perdew-Burke-Ernzerhof (GGA-PBE). An energy cut-off of 500 eV for the plane-wave basis, and a dense $k$-point grid in the Monkhorst-Pack scheme for integration in Brillouin zone were tested to ensure the convergence of the total energy to within 1 meV per formula unit. By calculating the elastic constants of crystals, $C_{ij}$, bulk modulus, $B$, and shear modulus, $G$, of each structure were obtained using the Voight-Reuss-Hill (VRH) approximation. The phonon spectrums of HP phases of CrB$_4$ and FeB$_4$ have been calculated by finite displacement methods to examine their dynamical stabilities. The structures were visualized by VESTA.

III. Results and discussion

The structure searches produced a large variety of candidates for high pressure phases, and the enthalpy difference under compression for CrB$_4$ and FeB$_4$ are summarized in Fig. 1. To make a complete comparison, the previously proposed $Im3m$ phase was also added for
FeB$_4$. The total energy as a function of unit volume (per f.u.) curves for CrB$_4$ and FeB$_4$ are shown in Fig. S1 of the Supplementary Information (SI).

As shown in Fig.1 and S1, the structure searches confirmed the orthorhombic $Pnnm$ structure for CrB$_4$ and FeB$_4$ at ground state (Space group (SG) No. 58, denoted as $op10-\alpha$-CrB$_4$ and $op10$-FeB$_4$ later). In the orthorhombic structure (Fig. 2), the boron atoms are connected by the buckling layers with six-member rings in $yz$ crystallographic plane, the neighboring boron layers are linked together by B$_4$ rhomboid units to form a 3D boron network. The metal Cr (Fe) atoms are situated in the boron channels with uniform bond distance of 4.714 Å (4.476 Å for FeB$_4$) in [100] direction, and 2.848 Å (3.015 Å for FeB$_4$) in [001] direction. Upon compression, a tetragonal $I4_1/acd$ type FeB$_4$ (SG No. 142, denoted as $tI40$-FeB$_4$ shown in Fig. 3(a)) is energetically preferable above 48 GPa (Fig. 1(b)), in agreement with previous predictions, 53.7 GPa by Kotmool et al. and 55.0 GPa by Jiang et al. Intriguingly, a B$_4$ tetrahedron appeared in $tI40$-FeB$_4$ differs from the planar rhomboid B$_4$ arrangement in $op10$-FeB$_4$. In this configuration, a diverse 3D boron network is found with varied bond distances, four B-B bonds with a distance of 1.818 Å and two B-B bonds with a distance of 1.842 Å, all of the tetrahedrons are closely connected with vertexes with a distance of 1.818 Å and two B-B bonds with a distance of 1.842 Å. This journal is © The Royal Society of Chemistry 20xx

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is energetically substituted by an orthorhombic \(Pmma\) type structure (SG No. 51, denoted as \(oP10-\beta-CrB_4\) hereafter), the latter is thermodynamic stable at least up to 350 GPa. Rather than the distinctive 3D boron networks of \(FeB_4\) phases, all of high pressure structures of \(CrB_4\) are closely packed by the sequence of \(ABAB...\) along the [010] direction (see Fig. 4). A is planar boron sheet; B is metal Cr-layer inserted by boron atoms. Generally, such a planar boron network usually introduces metallic features because the \(sp\)-or \(sp^2\)-hybridized orbitals form a network of \(\sigma\) bonds, and the non-filled \(p_z\) orbital form delocalized \(\pi\) bonds (Detailed electronic analysis are presented later). The major differences among these phases stem from the motifs of planar boron sheets and varied B-B distances within Cr-B layers. For \(mP10-\alpha-CrB_4\), the planar boron sheets are composed of rhomboid \(B_6\) (or conjugated rhomboid \(B_4\)) units with interior B-B bonds of 1.728 Å - 1.785 Å. Rhomboid \(B_6\) units are vertex connected together by the B-B distances of 1.799 Å and 1.935 Å, and the interesting \(B_8\) rings are formed. Simultaneously, \(B_2\) pairs with a bond length of 1.727 Å appear within Cr-B layer, the neighboring boron pairs are separated by a distance of 3.889 Å along \(a\) direction. For \(mP10-\beta-CrB_4\), the conjugated rhomboid \(B_4\) units are separated, and the planar \(B_6\) and \(B_8\) rings are showed up. The \(B-B\) bond length in the boron sheets varies from 1.694 Å to 1.837 Å, slightly shorter than those in \(mP10-\alpha\) phase. Interestingly, boron distance in \(B_2\) pairs enlarges to 1.782 Å, and the separation between boron pairs shortens to 3.678 Å along \(a\) direction in comparison with \(mP10-\alpha\) phase. When goes to \(oP10-\beta-\)
CrB₄ phase, the rhombohedral B₄ units are replaced by vertex connected B₃ triangles with two B-B bonds of 1.724 Å and one B-B bond of 1.896 Å, the B-B bonds between the neighboring B₃ units are 1.791 Å. Additionally, the B₂ pairs in Cr layers are also separated with a uniform distance of 2.765 Å. In three HP phases, the planar boron sheets are connected by boron pairs (or isolated boron atoms) with B-B bonds of 1.788 and 1.807 Å for mP10-α-CrB₄, 1.752-1.918 Å for mP10-β-CrB₄, and 1.949 Å and 2.095 Å for oP10-β-CrB₄, respectively. As a result, hexagonal prism channels are formed in [100] direction, and hosted by zig-zag Cr chains with more uniform Cr-Cr separations 2.807 Å and 3.200 Å for CrB₄ phase, the rhomboid B₄ units are replaced by vertex connected B₃ triangles with two B-B bonds of 1.724 Å and one B-B bond of 1.896 Å, the B-B bonds between the neighboring B₃ units are 1.791 Å. Additionally, the B₂ pairs in Cr layers are also separated with a uniform distance of 2.765 Å. In three HP phases, the planar boron sheets are connected by boron pairs (or isolated boron atoms) with B-B bonds of 1.788 and 1.807 Å for mP10-α-CrB₄, 1.752-1.918 Å for mP10-β-CrB₄, and 1.949 Å and 2.095 Å for oP10-β-CrB₄, respectively. As a result, hexagonal prism channels are formed in [100] direction, and hosted by zig-zag Cr chains with more uniform Cr-Cr separations 2.807 Å and 3.200 Å for mP10-α-CrB₄, 2.955 Å and 2.965 Å for mP10-β-CrB₄, and 3.172 Å for oP10-β-CrB₄. The zig-zag motif of Cr atoms in HP phases induces more close-packed stacking than the ground-state oP10-α-CrB₄, similar arrangement has also be found in VB₄ with relatively larger vanadium atom radius.³⁴

The calculated lattice parameters for CrB₄ and FeB₄ at ambient pressure are listed in Table 1. Calculated total energy relative to \( P_{nnm} \) structure is given for comparison. Our calculated equilibrium lattice constants agree well with the previous results within the error of 2.2%.⁸,⁹,¹⁷ The dynamic stabilities of new proposed HP phases for CrB₄ and FeB₄ are validated by calculating the phonon spectra (as shown in Fig. S3). The absence of imaginary phonon frequencies throughout the Brillouin Zone, except for oP10-β-CrB₄, indicates their dynamical stability at 0 K and zero pressure. For oP10-β-CrB₄, imaginary frequency is found in the Brillouin Zone at zero pressure (see Fig. S3(c)). At pressure above 294 GPa, however, all of phonon frequencies become positive (Fig. S3(d)), indicating the dynamical stability under compression.

Elastic constants of a crystal describe its response to an applied stress or the stress required to maintain a given deformation, which is directly related to elastic stability and mechanical properties. The satisfaction of the Born-Huang stability criteria³⁵ was firstly examined by their elastic constants, showing the mechanical stability

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<th>S.G.</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( \beta )</th>
<th>( \Delta E )</th>
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Please do not adjust margins
of all proposed phases here. The calculated individual elastic constants of considered phases are listed in Table 2 and SI. Among HP phases, \( t\text{I}40-\text{FeB}_4 \) shows large \( C_{11} \) (808 GPa) and \( C_{33} \) values (831 GPa), comparable with \( C_{11} \) of c-BN (820 GPa). Nevertheless, \( C_{11}, C_{22} \) and \( C_{33} \) values of HP phases for \( \text{CrB}_4 \) are very close (varied from 477 GPa to 592 GPa) due to the similar atomic arrangements, comparable with that of \( \text{Pnma-RuB}_3 \) and \( \text{Pnma-OsB}_3 \). Especially, \( c\text{P}20-\text{FeB}_4 \) shows the ionic nature with an unusual low \( C_{44} \) value, 40 GPa, close to that of the half-Heusler insulator \( \text{LiMgP} \). The calculated bulk modulus \( (B) \), shear modulus \( (G) \), Young’s modulus \( (E) \), and Poisson’s ratio \( (\nu) \) are listed in Table 2. The largest \( B \) (308 GPa) and \( G \) (264 GPa) values for \( t\text{I}40-\text{FeB}_4 \) phase are greater than that of \( o\text{P}10-\alpha-\text{CrB}_4 \) (\( B = 290 \) GPa, \( G = 250 \) GPa) and \( o\text{P}10-\text{FeB}_4 \) (\( B = 249 \) GPa, \( G = 200 \) GPa), close to that of \( \text{WB}_4 \) (\( B = 304 \) GPa). For HP phases of \( \text{CrB}_4 \), however, all the bulk modulus are lower than that of \( o\text{P}10-\alpha-\text{CrB}_4 \), and slightly decrease from 273 GPa of \( m\text{P}10-\alpha-\text{CrB}_4 \), 259 GPa of \( m\text{P}10-\beta-\text{CrB}_4 \), to 251 GPa of \( o\text{P}10-\beta-\text{CrB}_4 \). \( G \) shows largest value for \( o\text{P}10-\beta-\text{CrB}_4 \), 202 GPa and smallest value for \( m\text{P}10-\beta-\text{CrB}_4 \), 170 GPa. Among HP phases, \( c\text{P}20-\text{FeB}_4 \) has the lowest shear modulus (55 GPa), quite close to ionic \( \text{SrO} \). Hardness is an important parameter for potentially technological application. The calculated Vicker’s hardness for \( t\text{I}40-\text{FeB}_4 \) based on empirical formulation of Chen et al. is 40.6 GPa, well consistent with previously theoretical results 47.4 GPa, indicating a potential superhard material. The estimated Vicker’s hardness of \( o\text{P}10-\alpha-\text{CrB}_4 \) is 39.5 GPa, comparable to that of the \( \text{B}_4\text{C} \) (31.3–38.9 GPa), \( \text{B}_6\text{O} \) (38 GPa) and \( \gamma-\text{B} \) (50 GPa). The estimated hardness of \( m\text{P}10-\alpha-\text{CrB}_4, m\text{P}10-\beta-\text{CrB}_4 \), \( o\text{P}10-\beta-\text{CrB}_4 \) are 25.7 GPa, 21.7 GPa, and 31.6 GPa, respectively. Poisson’s ratio, \( \nu \), is another important parameter to describe the directional degree of covalent bonds in a material. With the exception of \( c\text{P}20-\text{FeB}_4 (\nu = 0.41) \), all of proposed phases have relatively low Poisson’s ratio (0.17-0.23), indicating the possible directional covalent bonding. The ratio of \( B/G \) is correlated with the ductility of materials (the threshold is 1.75, brittle \( (B/G<1.75) \) and ductile \( (B/G>1.75) \) manners). The \( B/G \) ratio of \( c\text{P}20-\text{FeB}_4 \) is 5.4, much higher than the critical value (1.75), indicating its great ductility. The \( B/G \) values of the other phases proposed here are between 1.16 and 1.52, indicating the brittle features. Young’s modulus \( (E) \) is an important mechanical parameter to measure the stiffness of a solid material. To get a better understanding of direction oriented Young’s modulus, a 3D representation and corresponding two dimensional (2D) projections of Young’s modulus for HP \( \text{CrB}_4 \) phases are calculated as a function of the crystallographic direction and presented in Fig. 5. The shape deviation from a sphere indicates the

![Fig. 5 The 3D representations and 2D projections of Young’s moduli for (a) \( o\text{P}10-\alpha-\text{CrB}_4 \); (b) \( m\text{P}10-\alpha-\text{CrB}_4 \); (c) \( m\text{P}10-\beta-\text{CrB}_4 \); and (d) \( o\text{P}10-\beta-\text{CrB}_4 \). Note that the negative sign only denotes the direction corresponding to the positive one.](image-url)
degree of anisotropy in the system. For \(\alpha\)P10-\(\alpha\)-CrB\(_4\), the 2D projections of Young’s modulus in \(yz\) and \(xy\) planes exhibit small anisotropy, the lowest and highest Young’s modulus values are found along [001] and [010] directions, respectively. The 2D projection of Young’s modulus for \(m\)P10-\(\alpha\)-CrB\(_4\) in \(xy\) plane is almost a regular ellipse, while in \(xz\) plane, the projection exhibits distinct anisotropy. For \(m\)P10-\(\beta\)-CrB\(_4\), however, the anisotropy of Young’s modulus is similar to \(\alpha\)P10-\(\alpha\)-CrB\(_4\) with the 2D projection of Young’s modulus in \(yz\) plane showing larger anisotropy than the others. For \(\alpha\)P10-\(\beta\)-CrB\(_4\), the 2D projections of Young’s modulus in \(yz\) and \(xz\) planes are close to regular circles, while the projection exhibits slight anisotropy in \(xy\) plane.

The band structure and density of states (DOS) for \(t\)I40-FeB\(_4\) and \(c\)P20-FeB\(_4\) are presented in Fig. 6. The Fermi level of \(\alpha\)P10-FeB\(_4\) catches the edge of the antibonding peak with a \(E_F = 1.0\) states/(eV f.u.) and it was confirmed in experiment to be a superconductor.\(^9\)\(^,\)\(^17\) Intriguingly, both \(t\)I40-FeB\(_4\) and \(c\)P20-FeB\(_4\) exhibit the semiconducting feature with indirect band gap (shown in Fig. 6(a) and 6(c)). The calculated band gap of \(t\)I40-FeB\(_4\), 1.63 eV, is in good agreement with previous theoretical reports, 1.34 eV by Jiang et al.\(^28\) and 1.06 eV (at 50 GPa) by Kotmool et al.\(^27\), while \(c\)P20-FeB\(_4\) has a narrower band gap of 0.61 eV. As shown in Fig. 6(b) and 6(d), the bottom of valence band for both \(t\)I40-FeB\(_4\) and \(c\)P20-FeB\(_4\) are contributed by B-2\(s\) and B-2\(p\) states and the top of valence bands are dominated by Fe-3\(d\) states. Significantly, the overlapping of B-2\(p\) states and Fe-3\(d\) states from -4.5 eV to 0 eV are relatively strong for both \(t\)I40-FeB\(_4\) and \(c\)P20-FeB\(_4\). It should be noted that the center of Fe-3\(d\) states are showing below Fermi level, which is different from other 3\(d\) metal borides, \(\alpha\)P10-FeB\(_4\), \(\alpha\)P10-\(\alpha\)-CrB\(_4\) and MnB\(_4\),\(^11\), similar to previous studied 5\(d\) metal borides, i.e., OsB\(_2\),\(^47\) ReB\(_2\)\(^48\) and WB\(_3\)\(^49\).

Fig. 7 represents the total and partial DOS for CrB\(_4\) phases. Due to the close atomic stacking, the DOS profile of HP phases are quite close to each other, the valence band is dominated by B-2\(s\) states at low energy part, B-2\(p\) states in the middle range, and Cr-3\(d\) states at the higher energies. All CrB\(_4\) phases exhibit the metallic feature due to the finite values at the Fermi level (\(E_F\)), which is mainly contributed by Cr-3\(d\) state. For \(\alpha\)P10-\(\beta\)-CrB\(_4\), the hybridization between B-2\(s\) and B-2\(p\) orbitals is relatively strong because of the increasing overlap in comparison with \(m\)P10-\(\alpha\)-CrB\(_4\) and \(m\)P10-\(\beta\)-CrB\(_4\), which may explain the higher shear modulus, Young’s modulus and hardness (as shown in Table 2). Different from \(t\)I40-FeB\(_4\) and \(c\)P20-FeB\(_4\), Cr-3\(d\) states are more delocalized in a wide range from -8 eV to +8 eV with orbital center in the vicinity of 2 eV, indicating more Cr-Cr metallic feature and weaker Cr-B interactions.

The band structure and density of states (DOS) for \(t\)I40-FeB\(_4\) and \(c\)P20-FeB\(_4\) are presented in Fig. 6. The Fermi level of \(\alpha\)P10-FeB\(_4\) catches the edge of the antibonding peak with a \(E_F = 1.0\) states/(eV f.u.) and it was confirmed in experiment to be a superconductor.\(^9\)\(^,\)\(^17\) Intriguingly, both \(t\)I40-FeB\(_4\) and \(c\)P20-FeB\(_4\) exhibit the semiconducting feature with indirect band gap (shown in Fig. 6(a) and 6(c)). The calculated band gap of \(t\)I40-FeB\(_4\), 1.63 eV, is in good agreement with previous theoretical reports, 1.34 eV by Jiang et al.\(^28\) and 1.06 eV (at 50 GPa) by Kotmool et al.\(^27\), while \(c\)P20-FeB\(_4\) has a narrower band gap of 0.61 eV. As shown in Fig. 6(b) and 6(d), the bottom of valence band for both \(t\)I40-FeB\(_4\) and \(c\)P20-FeB\(_4\) are contributed by B-2\(s\) and B-2\(p\) states and the top of valence bands are dominated by Fe-3\(d\) states. Significantly, the overlapping of B-2\(p\) states and Fe-3\(d\) states from -4.5 eV to 0 eV are relatively strong for both \(t\)I40-FeB\(_4\) and \(c\)P20-FeB\(_4\). It should be noted that the center of Fe-3\(d\) states are showing below Fermi level, which is different from other 3\(d\) metal borides, \(\alpha\)P10-FeB\(_4\), \(\alpha\)P10-\(\alpha\)-CrB\(_4\) and MnB\(_4\),\(^11\), similar to previous studied 5\(d\) metal borides, i.e., OsB\(_2\),\(^47\) ReB\(_2\)\(^48\) and WB\(_3\)\(^49\).

Fig. 7 represents the total and partial DOS for CrB\(_4\) phases. Due to the close atomic stacking, the DOS profile of HP phases are quite close to each other, the valence band is dominated by B-2\(s\) states at low energy part, B-2\(p\) states in the middle range, and Cr-3\(d\) states at the higher energies. All CrB\(_4\) phases exhibit the metallic feature due to the finite values at the Fermi level (\(E_F\)), which is mainly contributed by Cr-3\(d\) state. For \(\alpha\)P10-\(\beta\)-CrB\(_4\), the hybridization between B-2\(s\) and B-2\(p\) orbitals is relatively strong because of the increasing overlap in comparison with \(m\)P10-\(\alpha\)-CrB\(_4\) and \(m\)P10-\(\beta\)-CrB\(_4\), which may explain the higher shear modulus, Young’s modulus and hardness (as shown in Table 2). Different from \(t\)I40-FeB\(_4\) and \(c\)P20-FeB\(_4\), Cr-3\(d\) states are more delocalized in a wide range from -8 eV to +8 eV with orbital center in the vicinity of 2 eV, indicating more Cr-Cr metallic feature and weaker Cr-B interactions.
Fig. 8 and 9 represent the valence electron density distribution (VEDD), revealing the typical bonding characteristic for CrB₄ and FeB₄ phases. For CrB₄ phases, the high electron density regions are located in the middle of B atoms within planar boron sheets, indicating a strong nonpolar σ covalent bonding, furthermore, typical sp³ hybridization can be observed between B1 and B4 atoms for mP₁₀α-CrB₄ (in Fig. 8(b2)), B1 and B3 atoms for mP₁₀β-CrB₄ (in Fig. 8(c2)). However, in Cr-B layer, the valence electrons are more localized around B atoms due to the electronegativity difference, corresponding to a polar covalent bonding. The relative bond strength between boron atoms can be evaluated by the calculated Mulliken overlap populations (MOP) for CrB₄ phases. In oP₁₀α-CrB₄, MOP is found to be 0.9 for B1-B2 bond, 0.63 for B2-B3 bond. The strong B1-B2 bond, nearly parallel to b axis, is responsible for its high incompressibility along this direction. For mP₁₀α-CrB₄, MOP of the dumbbell B-B bond in Cr₂B₄ tetragon is 0.77. The strongest B-B bond is located in the B₄ rhomboid units, and MOP is 0.86 for B1-B2 and B4-B5 bonds, 0.68 for B3-B4 and B1-B6 bonds, 0.55 for B2-B3 and B5-B6 bonds, and 0.59 for B2-B5 bonds. For mP₁₀β-CrB₄, one of the two different Cr atoms and two dumbbell B atoms in Cr-B layer form CrB₂ triangle, and MOP value of the dumbbell B-B bond is 0.75. In B layer, each B₄ rhomboid is connected with the adjacent two hexatomic rings and two octatomic rings by sharing edges. The strongest B-B bond is located in the B₄ rhomboid, and MOP is 0.59 for B1-B2 bond, 0.68 for B2-B3 bond, 0.85 for B3-B4 bond, and 0.74 for B1-B4 bond. For oP₁₀β-CrB₄, Cr atoms and B atoms in Cr-B layer form zig-zag chains, and the electron density between Cr and B atoms exhibits local maximum values close to the B sites. In the B layer, each B₃ triangle is connected with the adjacent two ones by B-B bond in which the B atoms locate in the basic angle of the different triangles. The B-B bond connecting the B₃ triangles is relatively strong with a MOP of 0.85, greater than 0.78 for B1-B2 and B1-B3 bonds. The electron transfer from Cr to B atoms is found to be 1.28 e for oP₁₀α-CrB₄, 1.16 e for mP₁₀α-CrB₄, 1.11 e for Cr1 and 1.23 e for Cr2 in mP₁₀β-CrB₄, and 0.84 e in oP₁₀β-CrB₄, which is crucial for the stabilizations of boron networks in these structures.

Compared with the nonpolar σ covalent B-B bonding and polar covalent Cr-B bonding in CrB₄, the Fe-B bonding in the FeB₄ exhibits more ionic characteristics, as demonstrated by the more electron transfer from Fe to B atoms (1.35 e in tI₄₀-FeB₄ and 1.53 e in cP₂₀-FeB₄) than Cr to B in CrB₄. The ionic characteristics of the tI₄₀-FeB₄ and cP₂₀-FeB₄ may be attributed to the structure feature, resembling NaCl-type structures. For tI₄₀-FeB₄, MOP of B-B bond in B₄ tetrahedron is 0.46, MOP of the B-B bond connecting the B₄ tetrahedrons is 0.71, and thus the hybridization in the three dimensional B network is mainly sp³ hybridization. For cP₂₀-FeB₄, MOP of B1-B1 bonds in B₃ equilateral triangle is 0.56, of the B1-B2 bonds connecting the B₃ equilateral triangle is 0.65, and the sp³ type of hybridization is similar to that in tI₄₀-FeB₄, due to the similar 3D boron network.

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Fig. 8 Valence electron density distribution (a) for oP₁₀α-CrB₄ in (002) plane, (b1) for mP₁₀α-CrB₄ in (020) and (b2) in (010) planes, (c1) for mP₁₀β-CrB₄ in (010) and (c2) in (020) planes, (d1) for oP₁₀β-CrB₄ in (010) and (d2) in (020) planes.

Fig. 9 Valence electron density distribution (a) for tI₄₀-FeB₄ in (012) plane and (b) for cP₂₀-FeB₄ in (011) plane.
IV. Conclusions

In conclusion, we have extensively explored the high pressure phases of CrB₄ and FeB₄ using the particle swarm optimization technique in combination with first principles calculations. The phase transition from \( \alpha \)-CrB₄ into \( \beta \)-CrB₄ at 196 GPa, into \( \gamma \)-CrB₄ at 261 GPa and into \( \alpha \)-CrB₄ at 294 GPa, is reported here for the first time. Meanwhile, \( \alpha \)-FeB₄ transforms into \( \lambda \)-FeB₄ at 48 GPa and into \( \beta \)-FeB₄ at 231 GPa. In particular, the \( \gamma \)-FeB₄ is found to be more energetically preferable to the previously proposed \( \lambda \)-FeB₄ phase in the pressure ranges of 231 GPa to at least 700 GPa. The phonon dispersion and elastic constants calculations have demonstrated the dynamical and mechanical stabilities of the proposed high-pressure phases for CrB₄ and FeB₄. \( \lambda \)-FeB₄ and \( \beta \)-FeB₄ exhibit semiconducting feature, while \( \gamma \)-CrB₄, \( \gamma \)-CrB₄ and \( \beta \)-CrB₄ are metallic. Further, analysis of electronic structure reveals the high directional covalent bonding in these phases. Mechanical property calculations indicate that \( \lambda \)-FeB₄ is a potential superhard material and \( \gamma \)-CrB₄, \( \gamma \)-CrB₄ and \( \beta \)-CrB₄ can be classified into hard materials. Our predictions may stimulate further researches in both experiment and theory.

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References