



# Exploring high-pressure FeB<sub>2</sub>: Structural and electronic properties predictions



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## ABSTRACT

The high pressure (HP) structural phase of FeB<sub>2</sub> compound is investigated by using first-principles crystal structure prediction based on the CALYPSO technique. A thermodynamically stable phase of FeB<sub>2</sub> with space group *Imma* is predicted at pressure above 225 GPa, which is characterized by a layered orthorhombic structure containing puckered graphite-like boron layers. Its electronic and mechanical properties are identified and analyzed. The feature of band structures favors the occurrence of superconductivity, whereas, the calculated Pugh's ratio reveals that the HP *Imma* structure exhibits ductile mechanical property.

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## 1. Introduction

As in transition metal borides, the phase transitions of iron-boride (Fe–B) compounds have been attracted considerable attentions due to their desirable physical and chemical properties. A series of Fe–B compounds such as (FeB, FeB<sub>2</sub>, FeB<sub>4</sub>, Fe<sub>2</sub>B) have been explored theoretically and experimentally [1–12]. Recently, the high pressure phase of B-rich Fe–B compound FeB<sub>4</sub> is found at pressure above ~65.9 GPa, whose oP10-FeB<sub>4</sub> phase is confirmed to possess superconductivity and superhard properties under high pressure [1,2,6]. This report spurred the endeavors in search for new HP phase of Fe–B compounds (especially FeB<sub>2</sub>) for revealing their properties.

As is known, the superconducting MgB<sub>2</sub> crystallizes in the AlB<sub>2</sub>-type hexagonal structure, in which B atoms form in 2D layers [13,14]. If FeB<sub>2</sub> as AlB<sub>2</sub>-type compound has similar 2D boron units in its structural phases, it is expected to exhibit the same superconducting behavior at high pressure. However, the crystal structure of FeB<sub>2</sub> at normal pressure is found to be comprise with boron chains rather than boron layers, which belong to the *Pnma* space group, denoted as oP12-FeB<sub>2</sub> [2,5]. The HP structural phases of FeB<sub>2</sub>

remained unknown. This attracted our attentions to investigate the FeB<sub>2</sub> phase structures under HP, expected to find the 2D boron layers with superconductivity.

Herein, we systematically investigated the HP phase stabilities of FeB<sub>2</sub> compounds and identified its structures in large pressure range 0–300 GPa. We utilized a combination of developed computer software based on CALYPSO (crystal structure analysis by particle swarm optimization) [15–17] with a first-principles density functional total energy calculation to explore the entire configuration space. The effectiveness of the method has been demonstrated by various systems [18–22]. Here, a brand-new orthorhombic phase structure of FeB<sub>2</sub> with puckered graphite-like boron layers has successfully predicted at pressure above 225 GPa. The first-principles calculations confirmed its thermodynamical, dynamical and mechanical stability at desired pressure. Moreover, its electronic and mechanical properties are also identified and analyzed.

## 2. Methods

The most significant progressing in computational power and materials theory is crystal structures prediction methods as implemented in the CALYPSO computer code. The structural prediction of FeB<sub>2</sub> is preformed by using CALYPSO code interfaced with Vienna *ab initio* simulation package VASP code [23] for local

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structure optimization within the (PAW) potential and Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) [24]. The electron projector-augmented wave (PAW) method was adopted with PAW potentials, where  $3d^7 4s^1$  and  $2s^2 2p^1$  for Fe and B respectively were treated as valence electrons. In the underlying *ab initio* electronic structure calculations and geometry relaxations, the cutoff energy of 700 eV and appropriate Monkhorst-Pack [25] k-meshes were chosen to ensure that all the enthalpy calculations are well converged to less than 1 meV/atom. The phonon calculations were carried out by using a finite displacement approach through the PHONOPY code [26]. Elastic constants were calculated by the strain-stress method and the bulk modulus and shear modulus were thus derived from the Voigt-Reuss-Hill averaging scheme [27,28].

### 3. Results and discussions

#### 3.1. Structure prediction

Pressure is one of the fundamental thermodynamic factors, which has a direct influence on atomic bond by modifying the bonding patterns of the material. Therefore, HP causes in the occurrence of the structural transition phase with unusual physical and chemical properties [16]. By using the widely applied structures prediction code CALYPSO, the structures predictions for  $\text{FeB}_2$  were performed with the simulation cells containing 1–4 formula units (f.u.) at the pressure range 0–300 GPa. Several hundreds predicted structures were successfully generated and the lowest enthalpy structures were obtained, where the free energy reduces to the enthalpy at  $T = 0$  K [17]. At low pressure range, the oP12- $\text{FeB}_2$  which predicted by A.N. Kolmogorov et al. [2] is successfully found. At high pressure range, an orthorhombic *Imma* structure (denoted as oI18- $\text{FeB}_2$ ) was predicted at pressure of 250 GPa (4f.u./cell) to have the lowest enthalpy. Enthalpy curves as a function of pressure for the predicted  $\text{FeB}_2$  structures relative to the oP12- $\text{FeB}_2$  phase are presented in Fig. 1. It can be clearly seen that the oI18- $\text{FeB}_2$  phase is more stable than the oP12- $\text{FeB}_2$  phase above 225.5 GPa. In order to examine the dynamical stabilities of the new structure, the phonon dispersions were calculated for oI18- $\text{FeB}_2$  at 250 GPa (Fig. 2.). No imaginary frequency was found for the structure in the whole Brillouin zone, which indicated that it is dynamically stable.

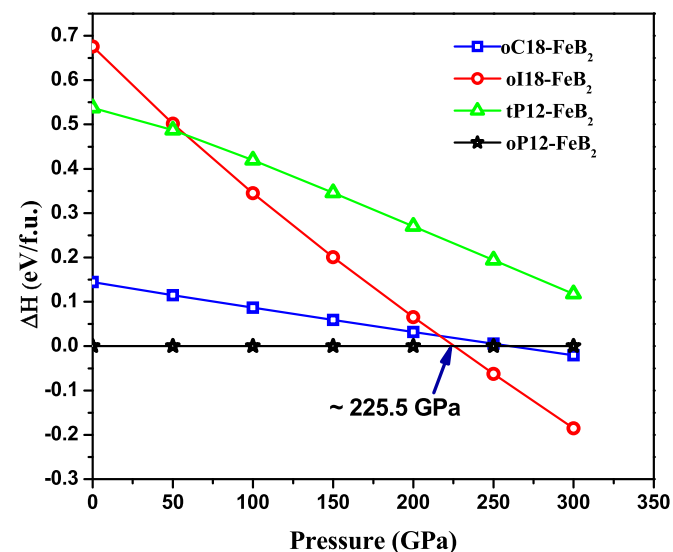


Fig. 1. Calculated enthalpies per formula units (f.u.) in  $\text{FeB}_2$  as functions of pressure between 0 and 300 GPa with respect to oP12- $\text{FeB}_2$  structure.

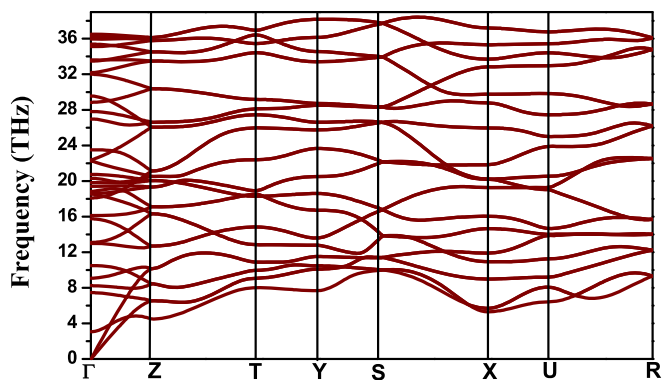


Fig. 2. Phonon dispersions curve of oI18- $\text{FeB}_2$  phase at 250 GPa.

The predicted oI18- $\text{FeB}_2$  crystal structure and the corresponding isosurface of electron localization function from the top view along  $b$  axis were shown in Fig. 3. The detail crystal structure parameters of oI18- $\text{FeB}_2$  phase were listed in Table 1. This structure forms atomic stack consisting of a polymeric 2D network B atom and Fe atom along  $b$  axis. Fe atoms on the site of 4e Wyckoff position and B atoms on the site of 8h forming a layered crystal, in which Fe atoms as well as the B atoms are arranged in alternating layers. The average bond length of Fe–B is 2.32 Å and the B–B bonds length is 1.64 Å. Due to the pressure modifying the bond lengths and bonding patterns, it isn't surprising that the 2D boron network of oI18- $\text{FeB}_2$  at high pressure is differ from the 1D puckered boron chains of oP12- $\text{FeB}_2$  phase at low pressure [2]. In order to probe the character of the B–B bonding in oI18- $\text{FeB}_2$  structure, the electron localization function (ELF) was analyzed in Fig. 3b. A strong covalent interaction between B atoms is found in ELF isosurfaces. Each B atom with  $sp^2$  hybridized orbitals form a network by the delocalized  $\pi$  bonds and  $\sigma$  bonds forming the interaction between the layers. Viewing the boron units from  $b$  axis, it seems as if puckered graphite layers (Fig. 3a). Bader charge analysis shows that one valence electron of Fe atom is transferred to B atom, which is isoelectronic to C atom. Therefore, the B lattices in the  $\text{FeB}_2$  structures are chemically comparable to the allotropes of C. The B layers in oI18- $\text{FeB}_2$  structure is thus analogous to graphite layers. Meanwhile, the graphite-like B layers in oI18- $\text{FeB}_2$  is seems similar to the B layer in  $\text{MgB}_2$  [29].

#### 3.2. Band structure and superconductivity

Similar to  $\text{MgB}_2$  with the B layer, the predicted oI18- $\text{FeB}_2$  structure is expected to have superconductivity. The electronic band structure in Fig. 4 reveals metallic characteristics of the predicted oI18- $\text{FeB}_2$  structure. The electronic bands near the Fermi level along the R-T and X-U directions are nearly flat, which gives rise to large electronic density of states near the Fermi level. The corresponding confined conduction electrons near the Fermi level possess the large effective mass with their group velocities approaching zero, while the electronic bands along the Z-T and Z- $\Gamma$  directions steeply cross the Fermi level, revealing the itinerant-like electrons with high conduction velocity. These electronic features apparently satisfy the “flat band-steep band” conditions [30,31], which have been suggested to favor the occurrence of superconductivity.

Furthermore, the electronic density of states DOS (Fig. 5) is calculated to describes the electronic states of oI18- $\text{FeB}_2$ . Clearly, it can be seen that the PDOS curves are mainly dominated by  $3d$  state of Fe and by  $2p$  state of B. At near Fermi level, the peaks of PDOS of B have strong hybridization between  $2s$  and  $2p$  states, supporting the

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