DFT calculation for stability and strength of iron borides

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ABSTRACT

The structural stability and mechanical properties of FeB_x have been investigated by first principles methods with semiempirical model. With the analysis of the mechanical properties in both elastic and plastic regions, it is found that the hardness of FeB_x becomes higher by following the increase of B content up to FeB_2. From the stress-strain curves with the semiempirical model about hardness, the hardness of FeB_2 is about 31 GPa and similar to that of FeB_4. It is expected that these results can give some light on the applications of FeB_x with high B content, such as the boronizing of iron surface.

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1. Introduction

Superhard materials are of tremendous interest in both technological applications and fundamental science. Due to the superior mechanical and physical property, they can be used in a variety of industrial applications such as cutting tools, hard coatings, and abrasives and are synthesized by the design [1–4]. Among the superhard materials, the borides are expected to have the excellent properties [5,6]. For example, boron can combine with other light elements, such as C and N to form the superhard alloys BC_5 [7–9], BC_3 [10–12], BC_2N [13–15], and so on. These materials with the strong covalent bond network have fine mechanical properties. However, their preparation condition is harsh and the increased production costs prevent them from being used in industry [6]. Recently, another category of borides with the combination of boron and transition metals, such as Cr, Re, W, Os, Fe, etc were found to have the ultra-incompressible and expected to have good mechanical properties [6,16–24]. For example, ReB_2 was synthesized under ambient pressure and with a hardness of 48 GPa [16], which was comparable to that of cubic BN [25]. OsB_2 was shown to have an ultra-incompressible hard behavior [6]. The strength of WB_4 was reported to reach up to 46 GPa [17,18]. In addition to high hardness, these borides also possibly exhibit superior electronic properties, such as the typical superconductive MgB_2 with a T_c of 39 K [19].

With the structure search, iron-based borides FeB_4 (op10-FeB_4) were considered to thermodynamically stable and predicted to have the phonon-mediated superconducting characteristic, recently [26]. Subsequently, the route for the FeB_4 synthesis with pressure was suggested [27] and it was synthesized experimentally at a pressure above 8 GPa and high temperature by Gou et al. [28] The results of magnetic susceptibility and heat capacity demonstrated the superconductivity below 2.9 K. In addition, it was found that the new phase FeB_4 had the highly incompressible with a nanoindentation hardness of about 62 GPa [28]. The reported anomalous high hardness more than 60 GPa is considered to be a strong deviation from that of the well-known transition metal borides. The stability of FeB_4 with different crystal structure was studied [29] and the hardness derived by the semiempirical method was shown to be lower than the experimental result, not exceeding the superhard threshold of 40 GPa. Moreover, Li et al. [30] investigated the ideal strength of FeB_4 using first principles methods to analyze the contribution of the stress response. The stress-strain relations under different loading conditions showed the indentation strength of FeB_4 was about 17 GPa [30] and its Vickers hardness was estimated to be about 25 GPa [31]. As we know, the detailed understanding of the stability and mechanical properties of Fe-B alloy system is still limited, though that of FeB_4 may be analyzed well [32–36].

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In this work, we investigated the structural stability and mechanical properties of Fe-B alloy by considering the different phases including Fe_2B and FeB from the previous Fe-B phase diagram, and both FeB_2 and FeB_4 from the structural research with first-principles methods. By following the change of B content, the relative stability of these structures under pressure was analyzed by considering the formation enthalpy. With the calculations of elastic constants and the analysis of shear stress-strain relations, the mechanical properties of FeB_x with different B contents were explored. The charge distribution in real space was analyzed in order to get a deep insight into the tendency in mechanical strength with the content of boron in the Fe-B compounds.

2. Computational method

We carried out the first-principle calculations with the accurate frozen-core full-potential projector augmented wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP) [37,38]. The calculations performed were based on density functional theory with the exchange and correlation effects described by the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [39]. A place wave basis with an energy cutoff of 500 eV was used. The Monkhorst-Pack grid [40] with a k-point spacing of 0.02 Å were chosen in the Brillouin zone for the total energy convergence at the 1 meV/atom level. The energy convergence criterion was 10^{-6} eV and the Hellmann-Feynman forces were relaxed to below 0.01 eV Å^{-1}. The spin-polarization effect is considered due to the partial occupations of 3d-orbitals of Fe. In addition, to consider the strong correlations from 3d_Fe, the GGA + U was tested and the Hubbard parameter U didn't result in the obvious effect on mechanical properties of Fe_xB.

From the structural research about binary alloy FeB_x [26], there are four possible single-phases for the different contents of B including x = 0.5, 1, 2 and 4. For the four phases Fe_2B, FeB, FeB_2 and FeB_4 (op10-FeB_4), the corresponding possible stable structures are with space groups $I4/mcm$, $Pnma$, $Pnma$, and $Pnnm$ [26], respectively. In addition, the energy-favorable structure (tp10-FeB_4) of FeB_4 under high pressure is found to be with $P4_2/nmc$. These structures are plotted in Fig. 1.

The elastic constants were obtained by calculating the stress under small special strain with first-principles methods. For tetragonal phases, the bulk modulus and shear modulus with the Voigt model can be expressed by the equation [42],

$$B_V = (1/9)[2(C_{11} + C_{12}) + C_{33} + 4C_{13}], \text{ and } G_V$$
$$= (1/30)(M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}).$$

For the Reuss model, they are expressed as,

$$B_R = C^2/M \text{ and } G_R$$
$$= 15\left\{(18B_V/C^2) + [6/(C_{11} - C_{12})] + (6/C_{44}) + (3/C_{66})\right\}^{-1}.$$

In these formulas, M and C^2 are denoted by,

$$M = C_{11} + C_{12} + 2C_{33} - 4C_{13}, \text{ and } C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2.$$

For orthorhombic phases, the bulk and shear modulus with the Voigt model can be expressed by the equation,

$$B_V = (1/9)[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})], \text{ and}$$

$$G_V = (1/15)[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})].$$

For the Reuss approximation, they are expressed as,

$$B_R = \Delta[C_{11}(C_{22} + C_{33} - 2C_{23}) + C_{22}(C_{33} - 2C_{13}) - 2C_{33}C_{12}$$
$$+ C_{12}(2C_{23} - C_{12}) + C_{13}(2C_{12} - C_{13}) + C_{23}(2C_{13} - C_{23})]^{-1}, \text{ and}$$

$$G_R = 15\{4[C_{11}(C_{22} + C_{33} + C_{23}) + C_{22}(C_{33} + C_{13}) + C_{33}C_{12}$$
$$- C_{12}(C_{23} + C_{12}) - C_{13}(C_{12} + C_{13}) - C_{23}(C_{13} + C_{23})]/\Delta$$
$$+ 3[(1/C_{44}) + (1/C_{55}) + (1/C_{66})]\}^{-1},$$

where $\Delta = C_{13}(C_{12}C_{23} - C_{13}C_{22}) + C_{23}(C_{12}C_{13} - C_{23}C_{11}) + C_{33}(C_{11}C_{22} - C_{12}^2)$.

The shear modulus and bulk modulus are derived from the Voigt-Reuss-Hill average value. In terms of the Voigt-Reuss-Hill approximations [41], the shear modulus G and bulk modulus B are expressed as, $G = (G_R + G_V)/2$ and $B = (B_R + B_V)/2$ with Young's modulus, $E = 9BG/(3B + G)$. The shear strengths are related to the plastic deformation and obtained from stress-strain curve. The stress-strain curve along a direction in some planes was obtained by straining the structure with the way of step-by-step from
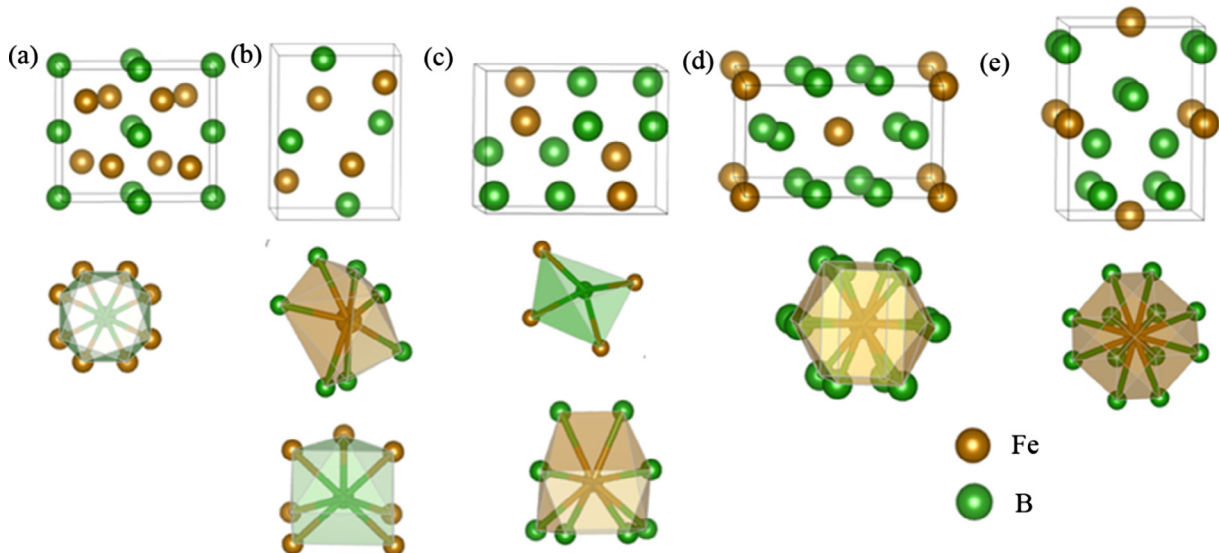

Fig. 1. Crystal structures and coordination numbers for different single-phase structures of FeB_x including Fe_2B (a), FeB (b), FeB_2 (c), ambient pressure phase FeB_4 (op10-FeB_4) (d) and high pressure phase FeB_4 (tp10-FeB_4) (e).