First-Principles Study on the Stability, Site Preference, Electronic Structure and Magnetism of Alloyed Fe$_3$B with Ni$_3$P-Type Structure

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1. Introduction

Magnetic materials play a major role in improving the performance of devices in the field of energy applications, data storage, refrigeration technologies, etc. [1]. Metastable Fe$_3$B is an attractive magnetic compound due to its large saturation magnetization and reasonably strong magnetic anisotropy. In particular, it appears in various important magnetic materials, such as nanocomposite permanent magnets (e.g., Fe$_3$B/Nd$_2$Fe$_{14}$B) [2–5] and Fe-B-based amorphous and nanocrystalline soft magnetic alloys [6–9]. For the nanocomposite permanent magnets, Fe$_3$B, as the main phase and providing large saturation magnetization, interacts with hard magnetic phase (e.g., Nd$_2$Fe$_{14}$B) by exchange-coupling interaction, achieving large energy production. Whereas, in the latter case, nanocrystalline Fe$_3$B precipitated from liquid phase or amorphous precursor is generally undesirable, mainly because it is magnetically harder than Fe-based solid solution such as $\alpha$-(Fe, Si) and $\alpha$-(Fe, Co, Ni). Further, to improve the magnetic properties, alloying has been widely investigated and used [4,7,10–27]. It was found that three effects can be achieved by alloying elements to affect the magnetic properties of these materials, as follows: (1) partitioning into phases and directly modifying their magnetic properties; (2) changing phase stability further to affect crystallization behaviors, and consequently influencing the size, distribution, content, and type of phases and (3) accelerating nucleation and/or suppressing the growth of phases by segregation. Numerous experimental studies have been conducted. Results
show that Cr [4,10], Co [11], Mn [12], V [13], W [14] and Mo [15,16] are closely related to the former two cases, whereas Cu [17–19], Nb [7,20,21] and Zr [20] more easily generate segregation due to their lower solubility. It has been reported that the partial substitution of Fe by Cr probably improves the stability of Fe$_3$B [10], while Cr reduces its magnetic moments [23,24,26]. Yang et al. [11] suggested that Co suppresses the crystallization of Fe$_3$B, but the effect of Co on its hyperfine field (HF) in three inequivalent Fe sites is negligible. Rajasekhar et al. [12] pointed out that when Mn incorporates into Fe$_3$B by replacing partial Fe, the HF values in all three Fe sites decrease linearly with increasing Mn concentration, implying that site preference is negligible for the occupation of Mn among these sites. Although alloyed Fe$_3$B has significant impacts on the magnetic properties of those materials, previous research [10,13,15,22–27] mainly focused on the effects of alloying elements on crystallization behaviors, microstructures and macroscopic magnetic properties. As mentioned above, only a few works have been done involving the stability and magnetism of alloyed Fe$_3$B because of the limitation of experiments. On the other hand, to the best of our knowledge, theoretical study—an effective way to predict the stability and magnetism of compounds—is missing in terms of alloyed Fe$_3$B.

Fe$_3$B has three isomers, namely, the Ni$_3$P-type Fe$_3$B with body-centered-tetragonal structure (space group: I-4), the Ti$_3$P-type Fe$_3$B with body-centered-tetragonal structure (space group: P4$_2$/n) and the Fe$_3$C-type Fe$_3$B with orthorhombic structure (space group: Pnma). According to the available literature, it can be concluded that (1) pure Ni$_3$P-type Fe$_3$B [28,29] and Fe$_3$C-type Fe$_3$B [28–34] have been investigated by theoretical calculations, whereas the study of Ti$_3$P-type Fe$_3$B is missing due to the lack of atomic positional parameters; (2) theoretical [32] and experimental [35] results confirmed that the Fe$_3$C-type Fe$_3$B is thermodynamically more stable than the Ni$_3$P-type Fe$_3$B, but the relative thermodynamic stability of three Fe$_3$B is still unknown because Ni$_3$P-type Fe$_3$B and Ti$_3$P-type Fe$_3$B generally are not distinguished clearly by experiments [36] and (3) their formation greatly depends on the composition of alloys [10,11,13,14,16,20,23,37]. Therefore, it is meaningful to continuously focus on these topics in order to improve our understanding of the properties of Fe$_3$B and alloyed Fe$_3$B, and to efficiently guide the composition design and performance optimization of Fe$_3$B-containing magnetic materials. The aim of this work is to explore the site preference of alloying elements, as well as the effect of alloying elements on stability, electronic structure and magnetism of alloyed Fe$_3$B with Ni$_3$P-type structure at 0 K via first-principles calculations.

2. Computational Details

The Ni$_3$P-type Fe$_3$B has a body-centered-tetragonal structure with a space group of I-4. Each unit cell contains 24 Fe atoms and 8 B atoms; that is, each cell consists of 8 Fe$_3$B formula units. B atoms only have one Wyckoff site 8g (0.078 0.111 0.491), whereas Fe atoms have three different Wyckoff sites, which are Fe1 (8g (0.078 0.111 0.244)), Fe2 (8g (0.364 0.031 0.988)) and Fe3 (8g (0.166 0.220 0.751)), respectively, with equal quantities. The crystal structure of Ni$_3$P-type Fe$_3$B is shown in Figure 1. To obtain alloyed Fe$_3$B, in the unit cell one Fe atom (Fe1 or Fe2 or Fe3) was replaced by alloying elements M (M = Ti, V, Cr, Mn, Co, Ni, Cu, Mo, W or Nb) to generate alloyed borides Fe$_{23}$M$_1$B$_8$, namely, (Fe$_{2.875}$M$_{0.125}$)B. All calculations were carried out by Vienna ab initio simulation package (VASP) based on density functional theory (DFT) [38]. The interactions between valence electrons and ionic cores were treated by projector-augmented wave (PAW) pseudopotential [39], where for B a standard version of PAW pseudopotential was used, and an extended M$_{pv}$ version was applied for all alloying elements M. The generalized gradient approximation (GGA) method in the scheme of Perdew–Burke–Ernzerhof (PBE) was used to deal with exchange-correlation potentials [40]. The Monkhorst–Pack method was used to generate a k-points mesh in the first irreducible Brillouin zone (BZ). After extensive convergence tests, a cutoff energy of 550 eV and a 5 × 5 × 11 k-points mesh were determined for all calculations. The convergence criteria were as follows: for electronic relaxation, the maximum energy change was set to 1 × 10$^{-7}$ eV/atom, and for ion relaxation, the maximum force acting...
on each atom was set to 0.001 eV/Å. In addition, spin polarization was considered for all the calculations.

Figure 1. Crystal structure of Ni$_3$P-type Fe$_3$B.

### 3. Results and Discussion

#### 3.1. Geometry Optimization

The equilibrium cell parameters of Ni$_3$P-type Fe$_3$B and its alloyed counterparts, together with some available experimental and calculated results, are presented in Table 1. The data of Fe$_3$B show that the maximum deviations of lattice constants and cell volume between the calculated values and the previous results [28,41,42] are less than 2% and 4%, respectively, suggesting that our calculation method is credible. Note that small lattice distortion was triggered by alloying elements in all alloyed Fe$_3$B, which is related to the differences of atomic radius and electronegativity between alloying elements and Fe. Figure 2 shows the atomic radius of alloying elements and the cell volume of all studied compounds. As can be seen, the variation trends of cell volume are almost identical to that of the atomic radius of alloying elements, implying that the difference of atomic radius dominates the lattice distortion. In addition, it can be found from Figure 2 that the cell volumes of the compounds are different from each other when the alloying elements occupy a different Fe site. This is mainly attributed to the different neighboring environments of different Fe sites. Previous research [29] reported that the Fe$_1$, Fe$_2$ and Fe$_3$ have 12, 10 and 10 iron neighbors, respectively, and have 2, 4 and 3 boron neighbors, respectively. However, the present results demonstrate that the Fe$_3$ has 11 iron neighbors and 2 boron neighbors. It is well known that Fe$_3$B is a metastable phase, and thus it is relatively difficult to produce it, and further to obtain high-quality polycrystalline X-ray diffraction (XRD) data. The existing XRD data on Fe$_3$B, PDF#39-1316, is marked with “?”*, implying its lower reliability. Therefore, we simulated the XRD data of Fe$_3$B based on the optimized crystal structure, and the pattern is given in Figure 3a. It can be found that the pattern of PDF#39-1316 is roughly consistent with the simulated one, especially at lower angles. Figure 3b shows the three patterns of Fe$_2$B from the experiment [43], high-quality PDF card data and the simulation based on optimized crystal structure. They are in good agreement with each other, indicating that the simulated result is reliable. Thus, it can be inferred that the simulated XRD data of Fe$_3$B is probably more credible than that of PDF#39-1316.

Figure 2. Cell volume of Fe$_3$B and alloyed Fe$_3$B and atomic radius of Fe and alloying elements.
Figure 3. (a) Polycrystalline XRD patterns of (a) Fe$_3$B and (b) Fe$_2$B.

Table 1. Cell parameters of Ni$_3$P-type Fe$_3$B and its alloyed counterparts.

| Model | a (Å)  | b (Å)  | c (Å)  | α (°)  | β (°)  | γ (°)  | Volume (Å$^3$) |
|-------|--------|--------|--------|--------|--------|--------|----------------|
| Fe$_3$B in this work | 8.5538 | 8.5538 | 4.2106 | 90.0000 | 90.0000 | 90.0000 | 308.0780 |
| Exp. in Ref. [35] | 8.6470 | 8.6470 | 4.2820 | 90.0000 | 90.0000 | 90.0000 | 320.1677 |
| Exp. in Ref. [37] | 8.6300 | 8.6300 | 4.2900 | 90.0000 | 90.0000 | 90.0000 | 319.5059 |
| Cal. in Ref. [24] | 8.5510 | 8.5510 | 4.2400 | 90.0000 | 90.0000 | 90.0000 | 310.0271 |

Fe$_1$ Site

- (Fe$_{2.875}$,Ti$_{0.125}$)B
- (Fe$_{2.875}$,V$_{0.125}$)B
- (Fe$_{2.875}$,Co$_{0.125}$)B
- (Fe$_{2.875}$,Mo$_{0.125}$)B
- (Fe$_{2.875}$,Ni$_{0.125}$)B
- (Fe$_{2.875}$,Cu$_{0.125}$)B
- (Fe$_{2.875}$,W$_{0.125}$)B
- (Fe$_{2.875}$,Nb$_{0.125}$)B

Fe$_2$ Site

- (Fe$_{2.875}$,Ti$_{0.125}$)B
- (Fe$_{2.875}$,V$_{0.125}$)B
- (Fe$_{2.875}$,Co$_{0.125}$)B
- (Fe$_{2.875}$,Mo$_{0.125}$)B
- (Fe$_{2.875}$,Ni$_{0.125}$)B
- (Fe$_{2.875}$,Cu$_{0.125}$)B
- (Fe$_{2.875}$,W$_{0.125}$)B
- (Fe$_{2.875}$,Nb$_{0.125}$)B

Fe$_3$ Site

- (Fe$_{2.875}$,Ti$_{0.125}$)B
- (Fe$_{2.875}$,V$_{0.125}$)B
- (Fe$_{2.875}$,Co$_{0.125}$)B
- (Fe$_{2.875}$,Mo$_{0.125}$)B
- (Fe$_{2.875}$,Ni$_{0.125}$)B
- (Fe$_{2.875}$,Cu$_{0.125}$)B
- (Fe$_{2.875}$,W$_{0.125}$)B
- (Fe$_{2.875}$,Nb$_{0.125}$)B

α denotes the total energy of (Fe$_{1-x,M_x}$)$_3$B per unit cell. Ecry (Fe), Ecry (B) and Ecry (M) are the formation enthalpies of Fe$_3$B$_{3n}$, Fe$_3$B$_{3n+1}$ and Fe$_3$B$_{3n+2}$ respectively.
3.2. Thermodynamic Stability and Site Preference of Alloying Elements

In order to analyze the thermodynamic stability of alloyed Fe$_3$B and the site preference of alloying elements, formation enthalpy ($E_{\text{for}}$) and cohesive energy ($E_{\text{coh}}$) were calculated according to the following equations:

$$E_{\text{for}} \left((\text{Fe}_{1-x}\text{M}_x)\text{B}\right) = \left(E_{\text{total}} \left((\text{Fe}_{1-x}\text{M}_x)\text{B}\right), \text{cell} \right) - 3n(1-x)E_{\text{cry}} \text{(Fe)} - 3nE_{\text{cry}} \text{(M)} - nE_{\text{cry}} \text{(B)})/n$$

(1)

$$E_{\text{coh}} \left((\text{Fe}_{1-x}\text{M}_x)\text{B}\right) = \left(E_{\text{total}} \left((\text{Fe}_{1-x}\text{M}_x)\text{B}\right), \text{cell} \right) - 3n(1-x)E_{\text{iso}} \text{(Fe)} - 3nE_{\text{iso}} \text{(M)} - nE_{\text{iso}} \text{(B)})/n$$

(2)

In the equations, $n$ is the number of Fe$_2$B per unit cell, and $E_{\text{total}} \left((\text{Fe}_{1-x}\text{M}_x)\text{B}\right), \text{cell}$ denotes the total energy of (Fe$_{1-x}$M$_x$)B per unit cell. $E_{\text{cry}}$ (Fe), $E_{\text{cry}}$ (B) and $E_{\text{cry}}$ (M) are the energy of one atom for simple substance bcc Fe, α-B and M (bcc (V, Cr, Mo, W and Nb); hcp (Co and Ti) and fcc (Ni and Cu) and α-Mn, respectively. Finally, $E_{\text{iso}}$ (Fe), $E_{\text{iso}}$ (B) and $E_{\text{iso}}$ (M) are the energy of one isolated atom for Fe, B and M (Ti, V, Cr, Mn, Co, Ni, Cu, Mo, W and Nb), respectively.

The calculated formation enthalpy and cohesive energy of Ni$_{13}$P-type Fe$_3$B and its alloyed counterparts are shown in Figure 4. The results suggest that all studied compounds are thermodynamically stable, as their formation enthalpy and cohesive energy are negative. The $E_c$ value of Fe$_3$B is consistent with previously calculated results (−22.732 eV/f.u. [28] and −22.576 eV/f.u. [29]), and its $E_{\text{for}}$ value is comparable with previously theoretical values (−0.864 eV/f.u. [28] and −0.880 eV/f.u. [44]). Although the formation enthalpies of (Fe$_{2.875}$Cu$_{0.125}$)B, (Fe$_{2.875}$W$_{0.125}$)B and (Fe$_{2.875}$Nb$_{0.125}$)B are negative, Cu, W and Nb cannot easily enter the Fe$_3$B lattice to replace the Fe atom since their formation enthalpies are greater than that of Fe$_3$B. Similarly, Ni is also unable to easily substitute the Fe atom of the Fe$_2$ site. (Fe$_{2.875}$Mo$_{0.125}$)B has the lowest formation enthalpy, which means that it is easier to fabricate than the others. From the view of cohesive energy, (Fe$_{2.875}$W$_{0.125}$)B is the most stable compound among those considered. The site preference of alloying elements is also judged by formation enthalpy and cohesive energy; namely, for the (Fe$_{2.875}$Mo$_{0.125}$)B in which the M atom occupies the Fe1, Fe2 and Fe3 site, respectively, the lower energy denotes that the M atom prefers to occupy this site. Hence, Figure 4 indicates that all alloying elements prefer to occupy Fe1, Fe3 and Fe2 sites in turn except for Mn, Mo and W. Furthermore, Mn prefers to occupy Fe2, Fe3 and Fe1 sites in turn, while for Mo and W the order is Fe1, Fe2 and Fe3. It is necessary to emphasize that, apart from Mn, all the alloying elements prefer to enter the Fe1 site in the Ni$_{13}$P-type Fe$_3$B.

Figure 4. (a) Formation enthalpy and (b) cohesive energy of Fe$_3$B and alloyed Fe$_3$B.

3.3. Electronic and Magnetic Properties

To understand the bonding characteristics and magnetic properties of Fe$_3$B and alloyed Fe$_3$B, their spin-polarized total densities of states (TDOSs) and partial densities of states (PDOSs) were calculated, and the results are exhibited in Figure 5. Since Mn preferentially occupies the Fe2 site, whereas the others are more likely to occupy the Fe1 site, the DOS calculations for all alloying elements except for Mn are based on the model that the M atom resides in the Fe1 site; similarly, for Mn the calculations are based on the Mn atom.
preferentially occupying the Fe2 site. Figure 5 shows that all DOSs have a similar shape, suggesting that the compounds have similar bonding and magnetic characteristics. The absence of an energy gap at Fermi level (E_f) indicates that a metallic bond should be contained in all compounds. In addition, it is easy to see that the TDOSs are greatly dominated by the Fe-d states. From the lower energy level to the higher energy level, all TDOSs and PDOSs of Fe and B are composed of the lower valence band, the upper valence band and unoccupied conduction band, in which there is an energy gap between the lower valence band and the upper valence band. Moreover, the lower valence band of TDOSs primarily consists of Fe-s, Fe-p and B-s states, whereas the upper valence band is mostly determined by the Fe-d states; additionally, a small number of Fe-p, Fe-s, B-p and M-d states can be observed. Due to the negligible contribution from M-s and M-p states, only the M-d states are presented in Figure 5. As can be seen, for 3d transition metals, more and more M-d states appear in the upper valence band with increasing valences, which is in good accord with the case of alloyed Fe_2B \[45\]. The PDOSs reveal that there is a strong hybridization between the Fe-d states and the B-p states in the energy range of about $-6 \text{ eV}$ to $-3 \text{ eV}$, which implies that all the compounds possess strong Fe-B covalent bonds. Moreover, the large overlaps between the Fe-d states and the Fe-s, Fe-p states suggest the existence of Fe-Fe covalent bonds.

To gain insight into bonding nature, we checked the nearest-neighbor table of atoms, which was calculated on the basis of the optimized Fe_3B crystal structure. The type of bond and their bond length are summarized in Table 2, and the visualized Fe-B and Fe-Fe bonds with typical bond length are presented by charge-density plots in Figure 6. From Table 2, four Fe-B bond lengths can be found: 2.12 Å (Fe3-B bond), 2.15 Å (Fe2-B bond), 2.16 Å (Fe1-B bond and Fe2-B bond) and 2.18 Å (Fe2-B bond). Figure 6a gives a Fe2-B bond of 2.18 Å, clearly demonstrating that this bond is covalent due to the appearance of elongated contours between the Fe2 atom and the B atom. Thus, it can be concluded that all Fe-B bonds are covalent, and the Fe3-B bond has the largest bond energy because it has the shortest bond length. The Fe-Fe bonds have many more bond lengths because the quantity of Fe atoms is three times that of B atoms. Moreover, as can be seen from Figure 6, the Fe-Fe bonds with bond lengths of 2.27 Å, 2.42 Å and 2.43 Å are covalent, whereas the Fe-B bonds with bond lengths of 2.45 Å, 2.49 Å, 2.51 Å and 2.80 Å are metallic bonds. Therefore, it is reasonable to deduce that the Fe-Fe bonds are metallic bonds when their bond lengths are larger than 2.43 Å. It can thus be concluded that the Fe3B contains Fe-B covalent bonds, Fe-Fe covalent bonds and Fe-Fe metallic bonds. As mentioned above, the DOSs of alloyed Fe3B are similar to those of the Fe3B. In other words, all alloyed Fe3B is mainly composed of Fe-B covalent bonds, Fe-Fe covalent bonds and Fe-Fe metallic bonds. Additionally, due to the addition of alloying element M, M-Fe bonds and M-B bonds can also be observed in the alloyed Fe3B. Moreover, the bonding strength of the other bonds is affected by the M atoms, revealed by the nearest-neighbor table of atoms for the alloyed Fe3B. These facts mean that it is very difficult to obtain the rule of the effect of alloying elements on the bonding behaviors of Fe3B. Therefore, we did not carry out a further analysis about the bonding behaviors of alloyed Fe3B.

Table 2. Types of bond and their bond lengths in Ni3P-type Fe3B.

| Type of Bond | Fe-B | | | | | | Fe-Fe | | | | B-B |
|-------------|------|---|---|---|---|---|---|---|---|---|---|---|
| Bond length (Å) | Fe1-B | Fe2-B | Fe3-B | Fe1-Fe1 | Fe2-Fe2 | Fe3-Fe3 | Fe1-Fe3 | Fe1-Fe3 | Fe2-Fe3 | B-B |
|---------------|-------|-------|-------|--------|--------|--------|--------|--------|--------|-------|
| 2.16          | 2.15  | 2.12  | 2.16  | 2.12   | 2.62   | 2.62   | 2.18   | 2.18   | 2.67   | 2.67   |
| 2.12          | 2.72  | 2.72  | 2.16  | 2.16   | 2.72   | 2.72   | 2.43   | 2.43   | 2.51   | 2.51   |
| 2.43          | 2.43  | 2.43  | 2.43  | 2.43   | 2.43   | 2.43   | 2.42   | 2.42   | 2.45   | 2.45   |
| 2.67          | 2.67  | 2.67  | 2.67  | 2.67   | 2.67   | 2.67   | 2.80   | 2.80   |        |        |
Fe-Fe covalent bonds and Fe-Fe metallic bonds. As mentioned above, the DOSs of alloyed Fe₃B are similar to those of the Fe₃B. In other words, all alloyed Fe₃B is mainly composed of Fe-B covalent bonds, Fe-Fe covalent bonds and Fe-Fe metallic bonds. Additionally, due to the addition of alloying element M, M-Fe bonds and M-B bonds can also be observed in the alloyed Fe₃B. Moreover, the bonding strength of the other bonds is affected by the M atoms, revealed by the nearest-neighbor table of atoms for the alloyed Fe₃B. These facts mean that it is very difficult to obtain the rule of the effect of alloying elements on the bonding behaviors of Fe₃B. Therefore, we did not carry out a further analysis about the bonding behaviors of alloyed Fe₃B.

**Figure 5.** Total density of states (TDOSs) and partial density of states (PDOSs) of (a) (Fe₂.₈₇₅,Ti₀.₁₂₅)B, (b) (Fe₂.₈₇₅,V₀.₁₂₅)B, (c) (Fe₂.₈₇₅,Cr₀.₁₂₅)B, (d) (Fe₂.₈₇₅,Mn₀.₁₂₅)B, (e) Fe₃B, (f) (Fe₂.₈₇₅,Co₀.₁₂₅)B, (g) (Fe₂.₈₇₅,Ni₀.₁₂₅)B, (h) (Fe₂.₈₇₅,Cu₀.₁₂₅)B, (i) (Fe₂.₈₇₅,Mo₀.₁₂₅)B, (j) (Fe₂.₈₇₅,W₀.₁₂₅)B and (k) (Fe₂.₈₇₅,Nb₀.₁₂₅)B.
alloying elements and their site preference on the magnetic properties of Fe3B, we cal-
is significantly affected by Fe-d states. Here, in order to quantitatively analyze the effects
electrons. In other words, all these compounds are magnetic. Moreover, their magnetism
that one of the minority-spin DOS peaks is located at the unoccupied conduction band,
fully and clearly distinguished. Thus, these experimental data will be discussed in a fol-
Figure 6. (a) Fe–B bonds with bond lengths of 2.18 Å; (b) Fe–Fe bonds with bond lengths of 2.27 Å,
2.42 Å, 2.43 Å, 2.51 Å and 2.49 Å; (c) crystal structure of Fe3B and (d) Fe–Fe bonds with bond lengths
of 2.43 Å, 2.45 Å and 2.80 Å.

Additionally, as can be seen from Figure 5, all the TDOSs are mainly composed of
two large majority-spin and minority-spin DOS peaks. Moreover, it is interesting to note
that one of the minority-spin DOS peaks is located at the unoccupied conduction band,
indicating that the majority-spin electrons are greater in number than the minority-spin
electrons. In other words, all these compounds are magnetic. Moreover, their magnetism is
significantly affected by Fe-d states. Here, in order to quantitatively analyze the effects of
alloying elements and their site preference on the magnetic properties of Fe3B, we calculated
the magnetic moments (Ms) values of unit cells, and the Ms values of different elements
and the interstices of unit cells. For the calculations, the default Wigner–Seitz radii were
employed, and only spin magnetic moments were considered because orbital Ms is very
small. The results are presented in Table 3. It can be found that for Fe3B the calculated Ms of
Fe is 1.921 μB, which is consistent with previously obtained theoretical values 2.02 μB [28]
and 1.99 μB [29]. Additionally, the Ms values of Fe1 (2.00 μB), Fe2 (1.80 μB) and Fe3 (1.97 μB)
match well with the previous results (Fe1 (2.14 μB), Fe2 (1.89 μB) and Fe3 (1.95 μB)) [29].
It is necessary to point out that although the magnetic properties of some borides, such
as Fe3B [23], (Fe0.85Cr0.15)B [23], (Fe0.85Mn0.15)B [12] and (Fe0.85Co0.15)B [11], have been
measured by experiments, the crystal structures of these borides were not carefully and
clearly distinguished. Thus, these experimental data will be discussed in a following work
about the alloyed Fe3B with Ti3P-type structure, since according to the calculated results of
the present work and the next work, their crystal structures can probably be distinguished.
From the Ms values, it can determined that Fe3B, (Fe2.875,Mn0.125)B, (Fe2.875,C0.125)B,
(Fe2.875,Ni0.125)B and (Fe2.875,Cu0.125)B are ferromagnetic compounds, whereas the others
are ferrimagnetic because the Ms values of Ti, V, Cr, Mo, W and Nb elements are negative.
In addition, the B element reduces the Ms values of unit cells for all compounds even
though its Ms value is small. Mn and Co have larger Ms values, especially when Mn
occupies the Fe2 site. Figure 7 gives the Ms values of unit cells for Fe3B and alloyed Fe3B.

Overall, the Ms values of unit cells first increase, and then decrease, and only Mn and
Co enhance the Ms of Fe3B. Regardless of which Fe site the Co occupies, the Ms values
of (Fe2.875,C0.125)B are larger those of Fe3B. However, for the (Fe2.875,Mn0.125)B, only
when Mn resides in the Fe2 site is its Ms value larger than that of Fe3B. The largest Ms values
for Fe1, Fe2 and Fe3 sites are 44.877 μB ((Fe2.875,C0.125)B), 44.948 μB ((Fe2.875,Mn0.125)B) and
44.996 μB ((Fe2.875,C0.125)B), respectively. Combined with the stability of the compounds
and the cost of production, it can be concluded that among all the studied alloying elements,
Mn is the most favorable candidate for improving the magnetic properties of Fe3B.
Table 3. Average magnetic moments of Fe atom, B atom, alloying elements M, interstitial region and unit cell for Fe$_3$B and alloyed Fe$_3$B.

| Model                     | Magnetic Moments in $\mu_B$ | Fe          | B          | M           | Interstice | Unit Cell |
|---------------------------|----------------------------|-------------|------------|-------------|------------|-----------|
| This work                 |                            | 1.921       | −0.157     | −0.123      | 44.719     |
| Cal. in Ref. [24]         |                            | 2.02        | -          | -           | -          |
| Cal. in Ref. [25]         |                            | 1.99        | -          | -           | -          |
| Fe1 Site                  |                            |             |            |             |            |           |
| (Fe$_{2.875}$,Ti$_{0.125}$)B | 1.855                     | −0.148      | −0.564     | −0.212      | 40.701     |
| (Fe$_{2.875}$,V$_{0.125}$)B | 1.873                     | −0.144      | −0.853     | −0.184      | 40.901     |
| (Fe$_{2.875}$,Cr$_{0.125}$)B | 1.899                     | −0.141      | −1.262     | −0.121      | 41.163     |
| (Fe$_{2.875}$,Mn$_{0.125}$)B | 1.894                     | −0.151      | 1.221      | −0.097      | 43.472     |
| (Fe$_{2.875}$,Co$_{0.125}$)B | 1.953                     | −0.154      | 1.319      | −0.123      | 44.877     |
| (Fe$_{2.875}$,Ni$_{0.125}$)B | 1.971                     | −0.152      | 0.571      | −0.145      | 44.554     |
| (Fe$_{2.875}$,Cu$_{0.125}$)B | 1.965                     | −0.151      | 0.129      | −0.149      | 43.971     |
| (Fe$_{2.875}$,Mo$_{0.125}$)B | 1.884                     | −0.143      | −0.461     | −0.130      | 41.595     |
| (Fe$_{2.875}$,W$_{0.125}$)B | 1.878                     | −0.142      | −0.397     | −0.159      | 41.510     |
| (Fe$_{2.875}$,Nb$_{0.125}$)B | 1.873                     | −0.146      | −0.520     | −0.161      | 41.242     |
| Fe2 Site                  |                            |             |            |             |            |           |
| (Fe$_{2.875}$,Ti$_{0.125}$)B | 1.880                     | −0.145      | −0.477     | −0.193      | 41.413     |
| (Fe$_{2.875}$,V$_{0.125}$)B | 1.874                     | −0.138      | −0.693     | −0.171      | 41.135     |
| (Fe$_{2.875}$,Cr$_{0.125}$)B | 1.898                     | −0.136      | −0.922     | −0.107      | 41.537     |
| (Fe$_{2.875}$,Mn$_{0.125}$)B | 1.938                     | −0.157      | 1.746      | −0.109      | 44.948     |
| (Fe$_{2.875}$,Co$_{0.125}$)B | 1.956                     | −0.153      | 1.065      | −0.106      | 44.726     |
| (Fe$_{2.875}$,Ni$_{0.125}$)B | 1.974                     | −0.150      | 0.420      | −0.125      | 44.484     |
| (Fe$_{2.875}$,Cu$_{0.125}$)B | 1.964                     | −0.151      | 0.069      | −0.126      | 43.914     |
| (Fe$_{2.875}$,Mo$_{0.125}$)B | 1.904                     | −0.139      | −0.309     | −0.135      | 42.247     |
| (Fe$_{2.875}$,W$_{0.125}$)B | 1.898                     | −0.136      | −0.271     | −0.154      | 42.147     |
| (Fe$_{2.875}$,Nb$_{0.125}$)B | 1.905                     | −0.142      | −0.382     | −0.158      | 42.145     |
| Fe3 Site                  |                            |             |            |             |            |           |
| (Fe$_{2.875}$,Ti$_{0.125}$)B | 1.863                     | −0.146      | −0.530     | −0.194      | 40.946     |
| (Fe$_{2.875}$,V$_{0.125}$)B | 1.871                     | −0.142      | −0.773     | −0.163      | 40.957     |
| (Fe$_{2.875}$,Cr$_{0.125}$)B | 1.897                     | −0.140      | −1.090     | −0.116      | 41.310     |
| (Fe$_{2.875}$,Mn$_{0.125}$)B | 1.895                     | −0.152      | 1.371      | −0.105      | 43.644     |
| (Fe$_{2.875}$,Co$_{0.125}$)B | 1.961                     | −0.156      | 1.268      | −0.128      | 44.996     |
| (Fe$_{2.875}$,Ni$_{0.125}$)B | 1.970                     | −0.155      | 0.508      | −0.164      | 44.405     |
| (Fe$_{2.875}$,Cu$_{0.125}$)B | 1.950                     | −0.156      | 0.097      | −0.167      | 43.542     |
| (Fe$_{2.875}$,Mo$_{0.125}$)B | 1.887                     | −0.141      | −0.391     | −0.123      | 41.752     |
| (Fe$_{2.875}$,W$_{0.125}$)B | 1.878                     | −0.140      | −0.354     | −0.149      | 41.570     |
| (Fe$_{2.875}$,Nb$_{0.125}$)B | 1.872                     | −0.144      | −0.48      | −0.149      | 41.272     |

Figure 7. Magnetic moments of unit cells for Fe$_3$B and alloyed Fe$_3$B.
4. Conclusions

We systematically investigated the effect of alloying elements on the stability, electronic structure and magnetism of Ni$_3$P-type Fe$_3$B, as well as the site preference of alloying elements, via first-principles density functional calculations, resulting in the following conclusions.

(1) Negative formation enthalpy and cohesive energy suggest that all studied compounds are thermodynamically stable, while Cu, W and Nb do not easily enter the Fe$_3$B lattice. The lowest formation enthalpy implies that the (Fe$_{2.875}$Mo$_{0.125}$)B can be produced more easily, whereas the lowest cohesive energy means that the (Fe$_{2.875}$W$_{0.125}$)B is the most stable compound.

(2) Mn preferentially resides in the Fe2 site, whereas the others are more likely to occupy the Fe1 site. The Fe3 site is the second most popular site for most alloying elements.

(3) The DOSs of both Fe$_3$B and alloyed Fe$_3$B are dominated by Fe-d states, and the plots of charge density indicate that all the compounds mainly consist of Fe-B covalent bond, Fe-Fe covalent bond and Fe-Fe metallic bond.

(4) The Fe$_3$B, (Fe$_{2.875}$Mn$_{0.125}$)B, (Fe$_{2.875}$Co$_{0.125}$)B, (Fe$_{2.875}$Ni$_{0.125}$)B and (Fe$_{2.875}$Cu$_{0.125}$)B are ferromagnetic compounds, whereas the others are ferrimagnetic compounds since the Ms values of Ti, V, Cr, Mo, W and Nb elements are negative. Although both Mn and Co can increase the magnetic moments of Fe$_3$B, and although the maximum Ms values of (Fe$_{2.875}$Co$_{0.125}$)B are slightly larger than those of (Fe$_{2.875}$Mn$_{0.125}$)B, considering the cost of production, Mn is the more favorable candidate for improving the magnetic properties of Fe$_3$B.

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