

# Effect of spin polarization on the structural properties and bond hardness of $\text{Fe}_x\text{B}$ ( $x = 1, 2, 3$ ) compounds first-principles study

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**Abstract.** In this paper, spin and non-spin polarization (SP, NSP) are performed to study structural properties and bond hardness of  $\text{Fe}_x\text{B}$  ( $x = 1, 2, 3$ ) compounds using density functional theory (DFT) within generalized gradient approximation (GGA) to evaluate the effect of spin polarization on these properties. The non-spin-polarization results show that the non-magnetic state (NM) is less stable thermodynamically for  $\text{Fe}_x\text{B}$  compounds than spin-polarization by the calculated cohesive energy and formation enthalpy. Spin-polarization calculations show that ferromagnetic state (FM) is stable for  $\text{Fe}_x\text{B}$  structures and carry magnetic moment of 1.12, 1.83 and 2.03  $\mu\text{B}$  in  $\text{FeB}$ ,  $\text{Fe}_2\text{B}$  and  $\text{Fe}_3\text{B}$ , respectively. The calculated lattice parameters, bulk modulus and magnetic moments agree well with experimental and other theoretical results. Significant differences in volume and in bulk modulus were found between the ferromagnetic and non-magnetic cases, i.e., 6.8, 32.8%, respectively. We predict the critical pressure between ferromagnetic and non-magnetic phases. The model for hardness calculation using Mulliken population coupled to semi-empirical hardness theory proved effective in hardness prediction for the metal borides which agree well with the experimental values. These results would help to gain insight into the spin-polarized effect on the structural and bond hardness.

**Keywords.** Iron boride; DFT; spin polarized; critical pressure; Mulliken population; bond hardness.

## 1. Introduction

The physical properties of metal borides such as hardness, high melting point, wear resistance, corrosion resistance and ferromagnetism are important for both basic research and technological applications [1–3]. Boride steel alloys form a single phase  $\text{Fe}_2\text{B}$  or a double phase  $\text{Fe}_2\text{B} + \text{FeB}$  layers with definite compositions. In the formation of  $\text{Fe}_2\text{B}$ ,  $\text{Fe}_3\text{B}$  appears as a metastable phase. The phase diagram B-Fe was drawn [4].  $\text{Fe}_2\text{B}$  can also be prepared as bulk single crystals.  $\text{FeB}$  was prepared as nanoparticles by the chemical reduction method for the improvement of the cycle stability of the PuNi3-type hydrogen storage electrode. The properties such as structural, hardness, Young modulus and fracture toughness of iron boride layer depend on process time and temperature [5,6]. Their notable mechanical properties are due to the B–B covalent bonding associated to hybrid metal–nonmetal bonding. Iron borides are metallic in nature and exhibit ferromagnetism. The saturation magnetization decreases with increasing boronizing time. This decrease was attributed to the increase of  $\text{FeB}$  and  $\text{Fe}_2\text{B}$  thicknesses [7].

The relationship between the structure parameters and bond hardness in  $\text{M}_2\text{B}$  ( $M = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Mo}, \text{W}$ ) was investigated by calculating hardness of X–B and B–B bonds using a semi-empirical hardness theory [8,9].

Recently, Meneses-Amador *et al* [5] used indentation for the mechanical characterization of the  $\text{Fe}_2\text{B}$  layer and found that layer hardness ranged from 9 to 14.2 GPa depending on boriding temperature and time. Furthermore, the mechanical properties of  $\text{FeB}$  and  $\text{Fe}_2\text{B}$  layers were estimated by Berkovich Nano indentation on tool borided steels. These measurements showed that hardness ranged between 14.5 and 19 GPa for  $\text{FeB}$  and from 13 to 16.3 GPa for  $\text{Fe}_2\text{B}$  depending on temperature and boriding time [6].

Accordingly, the relationships between structures and magnetic on one hand and hardness on the other hand will be simultaneously discussed to better understand the effect of spin polarization of the intermetallic iron borides  $\text{Fe}_x\text{B}$  ( $x = 1, 2, 3$ ). In this paper, spin and non-spin polarization have been studied to calculate cohesive energy and formation enthalpy. We also used for the first time to our knowledge, *ab-initio* density functional theory (DFT) method and Mulliken population analysis [10] for the calculation of the hardness of  $\text{FeB}$ ,  $\text{Fe}_2\text{B}$  and  $\text{Fe}_3\text{B}$  compounds. At the end of results presentation, we show the effect of the magnetic moment on all calculated parameters (see figure 1) by the

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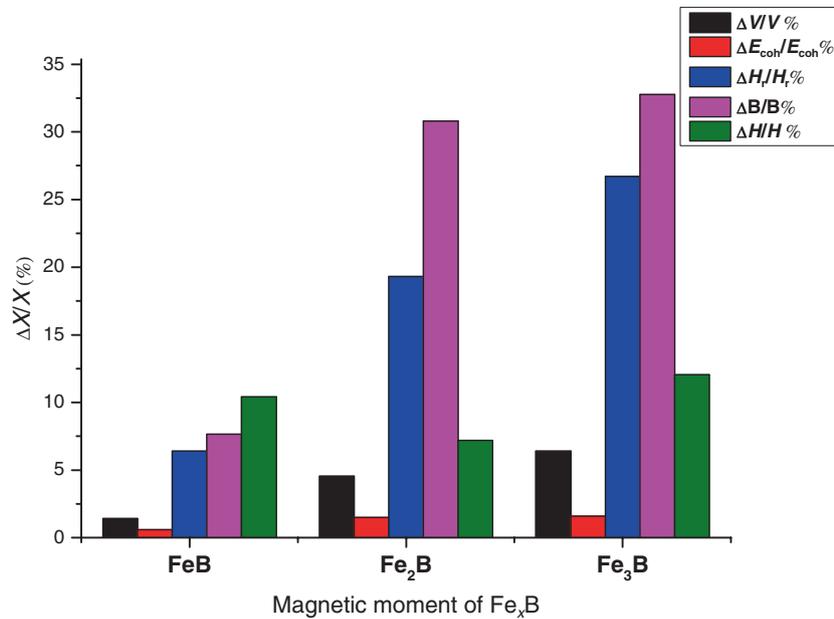


Figure 1. The calculated percent relative change of parameters.

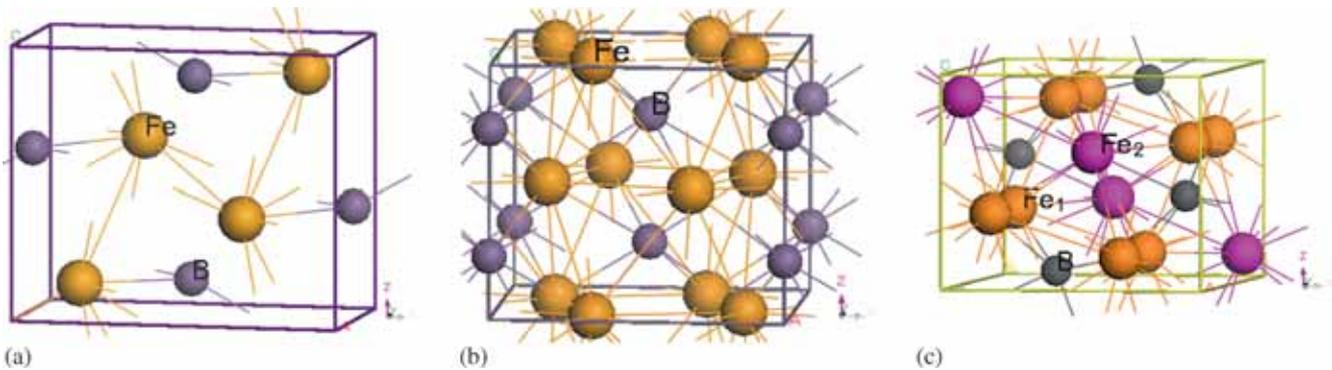


Figure 2. Crystal structure of (a) FeB, (b) Fe<sub>2</sub>B and (c) Fe<sub>3</sub>B illustrated by ball and stick model.

relative change of these parameters between the ferromagnetic and nonmagnetic state (equation (1)):

$$\frac{\Delta X}{X} = \left| \frac{X_{FM} - X_{NM}}{X_{FM}} \right|, \quad X = V, B, H, E_{coh}, \Delta H_I. \quad (1)$$

We dedicate the last section to the most important conclusions of this work.

## 2. Structure aspects and calculation methods

FeB and Fe<sub>3</sub>B belong to the orthorhombic space group *Pnma* [11–14]. Both structures contain four formulae per unit cell, figure 2. In Fe<sub>3</sub>B, an isotype of Fe<sub>3</sub>C, iron atoms are distributed over two distinct lattice sites: the general Fe(I) sites (Wyckoff position *8d*) and the special Fe(II) sites (Wyckoff position *4c*). On the other hand, Fe<sub>2</sub>B belongs to the body-centred tetragonal Bravais lattice with *I4/mcm* space group, where the unit cell contains four equivalent Fe atoms in the positions of point group *mm* and two equivalent B atoms in

the positions of point group *42* [14]. The B atoms in Fe<sub>2</sub>B are located between two layers of Fe atoms in a distorted closely-packed arrangement, as shown in figure 2b.

The total energy calculations were performed within DFT [15–18]. Cambridge serial total energy package (CASTEP) code was used for the whole study, which uses the plane wave expansion method in reciprocal space [19,20]. The ultra-soft Vanderbilt pseudo-potentials were employed to represent the electrostatic interactions between valence electrons and ionic cores [21], which were used with the following valence electronic configurations: Fe: 3d<sup>6</sup>4s<sup>2</sup> and B: 2s<sup>2</sup>2p<sup>1</sup>. Generalized gradient approximation Perdew-Burke-Ernzerhof-GGA (PBE-GGA) was used for exchange-correlation energy calculations [22]. The kinetic energy cut-off value was selected as 500 eV, which was sufficient to obtain the reliable results.

The total energies were evaluated in the first irreducible Brillouin zone with the following Monkhorst-Pack grids [23]: (8 × 10 × 8) for FeB, (10 × 10 × 10) for Fe<sub>2</sub>B and (10 × 12 × 8) for Fe<sub>3</sub>B. It is known that the ground states of several Fe<sub>x</sub>B compounds are ferromagnetic [24,25].

Mechanical and thermodynamic properties were calculated for the ferromagnetic (FM) and non-magnetic (NM) configurations for our three compounds. The convergence criteria of total energy and structure optimization were set to fine quality with the energy tolerance of  $10^{-6}$  eV atom<sup>-1</sup>. BFGS (Broyden–Fletcher–Goldfarbe–Shanno) optimization method was performed to obtain the equilibrium crystal structures of  $Fe_xB$  with maximum atom displacement and force set to 0.002 Å and 0.001 eV Å<sup>-1</sup>, respectively.

The cohesive energy ( $E_{\text{coh}}$ ) of a material is a measure of the relative binding forces, is a useful fundamental property. The stability of our compounds can be evaluated by calculating two energy parameters, cohesive energy,  $E_{\text{coh}}$  and formation enthalpy,  $\Delta H_f$ , defined as follows:

$$E_{\text{coh}}(Fe_xB) = \frac{E_{\text{total}}(Fe_xB, \text{Cell}) - xnE_{\text{iso}}(\text{Fe}) - nE_{\text{iso}}(\text{B})}{n}, \quad (2)$$

$$\Delta H_f(Fe_xB) = E_{\text{coh}}(Fe_xB) - xE_{\text{coh}}(\text{Fe}) - E_{\text{coh}}(\text{B}), \quad (3)$$

where  $E_{\text{coh}}(Fe_xB)$  is the cohesive energy of  $Fe_xB$  per unit formula;  $\Delta H_f(Fe_xB)$  the formation enthalpy;  $E_{\text{coh}}(\text{Fe})$  the cohesive energy of iron element per atom;  $E_{\text{total}}(Fe_xB, \text{Cell})$  the total calculated energy of  $Fe_xB$  per conventional unit cell;  $E_{\text{iso}}(\text{Fe})$  the total energy of an isolated Fe atom and  $n$

**Table 1.** Total and cohesive energies of Fe and B.

Energy	Fe	B
$E_{\text{iso}}$ (eV)	-859.821 (-855.913) <sup>a</sup>	-70.501 (-70.492) <sup>a</sup>
$E_{\text{total}}$ (eV)	-865.315 (865.335) <sup>a</sup>	-76.953 (-76.875) <sup>a</sup>
$E_{\text{coh}}$ (eV)	-5.494 (-4.28) <sup>exp</sup> (-9.422) <sup>a</sup>	-6.452 (-6.383) <sup>a</sup>
$V$ of unit cell (Å <sup>3</sup> )	11.775 (11.82) <sup>exp</sup>	

<sup>exp</sup>Ref. [29], <sup>a</sup>Ref. [9].

refers to the number of unit formulas of  $Fe_xB$  in the conventional cell. The calculation method for  $E_{\text{coh}}(Fe_xB)$  can also be used to evaluate the cohesive energy of pure elements B and Fe. Equations (2) and (3) require negative values of  $E_{\text{coh}}(Fe_xB)$  and  $\Delta H_f(Fe_xB)$  to refer to a thermodynamically stable structure. The crystal structures of  $Fe_xB$  studied in this paper were built based on experimental results.

### 3. Results and discussion

#### 3.1 Stability and structural properties

The calculated total energy, lattice parameters, unit cell volumes, bulk modulus, cohesive energy and the formation enthalpy for  $Fe_xB$  along with the available experimental and previous theoretical data for comparison are shown in tables 1–4, furthermore, the predict critical pressure is also shown. These results show that the total energy in FM case of the three compounds are less than the NM case, which indicate that the magnetic structures for all iron borides are in the ground state. The calculated structure parameters in FM structures are in good agreement with the experimental counterparts than those calculated in NM configurations. All calculated lattice parameters in NM case are smaller than the FM case except for  $c$  parameter in  $Fe_2B$  compound. This lead to a volume expansion of 1.4, 4.7 and 6.8% for FeB,  $Fe_2B$  and  $Fe_3B$ , respectively, in FM, which reduce the bulk modulus of our compounds by 7.7, 30.8 and 32.8%. This result indicates that the calculated setting is appropriate and the computed results for these borides are credible and in accordance with Stoner model [26].

The calculated magnetic moments of our compounds are in good agreement with theoretical and experimental values [12,27,28] and range from 2.0  $\mu_B$  for  $Fe_3B$  to 1.12  $\mu_B$  for FeB. These moments are smaller than the magnetic moments of pure ferromagnetic iron (2.22  $\mu_B$ ) [29]. Actually, when B atoms are distributed in Fe crystals, the volume concentration of metallic Fe–Fe bonds are decreased, but a higher

**Table 2.** Total, cohesive and formation energies, structural parameters, bulk modulus and magnetic moment of FeB.

Parameters	NM	FM
$E_{\text{total}}$ (eV)	-3773.59	-3773.900
$(a, b, c)$ (Å)	5.124, 3.096, 3.865	5.317, 2.950, 3.964 (5.495, 2.946, 4.053) <sup>b</sup>
Fe $(x, y, z)$	0.183, 0.25, 0.122	0.178, 0.25, 0.122
B $(x, y, z)$	0.0395, 0.25, 0.623	0.0348, 0.25, 0.620
$V$ of unit cell (Å <sup>3</sup> )	61.303	62.178
$B$ (GPa)	330.91	305.58, (287.5) <sup>a</sup>
$\mu_B$ atom <sup>-1</sup>	0	1.126 (1.12) <sup>exp1</sup> , (1.20) <sup>b</sup> , (0.95) <sup>exp2</sup>
$E_{\text{coh}}$ (eV)	-13.076	-13.153
$\Delta H_f$ (eV)	-1.13	-1.207
$P_c$ (Kbar)		576.63

<sup>exp1</sup>Ref. [27], <sup>b</sup>Ref. [30], <sup>exp2</sup>Ref. [12], <sup>a</sup>Ref. [31].

**Table 3.** Total, cohesive and formation energies and structural parameters, bulk modulus and magnetic moment of Fe<sub>2</sub>B.

Parameters	NM	FM
$E_{\text{total}}$ (eV)	-7235.09192	-7236.2309
$(a = b, c)$ (Å)	4.89, 4.222 (4.838, 4.208) <sup>a</sup> , (4.771, 4.121) <sup>a</sup>	5.0123, 4.209 (5.110, 4.240) <sup>exp</sup>
Fe( $x, y, z$ )	0.16632, 0.66632, 0	0.1666, 0.666, 0
B( $x, y, z$ )	0, 0, 0.25	0, 0, 0.25
$V$ of unit cell (Å <sup>3</sup> )	50.483	52.879
$B$ (GPa)	353.46	244.59, (249.7) <sup>d</sup> , (224.3) <sup>e</sup>
$\mu_{\text{B}}$ atom <sup>-1</sup>	0	1.83(1.962) <sup>b</sup> , (1.62) <sup>exp2</sup>
$E_{\text{coh}}$ (eV)	-18.63, (-30.07) <sup>a</sup> , (-26.67) <sup>a</sup>	-18.91, (-26.7014) <sup>b</sup>
$\Delta H_{\text{f}}$ (eV)	-1.19, (-1.47) <sup>a</sup> , (-0.891) <sup>a</sup>	-1.475, (-1.4749) <sup>b</sup> , (-0.85) <sup>c</sup>
$P_{\text{c}}$ (Kbar)		761.62

<sup>a</sup>Ref. [8], <sup>b</sup>Ref. [9], <sup>exp</sup>Ref. [32], <sup>exp2</sup>Ref. [12], <sup>c</sup>Ref. [33], <sup>d</sup>Ref. [31], <sup>e</sup>Ref. [34].

**Table 4.** Total energy, structural parameters, bulk modulus, magnetic moment and cohesive and formation energies of Fe<sub>3</sub>B.

Parameters	NM	FM
$E_{\text{total}}$ (eV)	-10695.7709	-10697.2989
$(a = b, c)$ (Å)	5.071, 6.556, 4.323	5.336, 6.608, 4.354 (5.397, 6.648, 4.368) <sup>b</sup>
$x, y, z$ Fe(I)	0.189, 0.057, 0.355	0.1765, 0.0560, 0.3515
Fe(II)	0.0262, 0.250, 0.863	0.0216, 0.250, 0.8776 (0.1751, 0.0556, 0.3508) <sup>b</sup> (0.0182, 0.25, 0.8832) <sup>b</sup>
$x, y, z$ B	0.881, 0.25, 0.429	0.8818, 0.25, 0.4258 (0.8812, 0.25, 0.4268) <sup>b</sup>
$V$ of unit cell (Å <sup>3</sup> )	143.74	153.56, (156.70) <sup>b</sup>
$B$ (GPa)	312.27	210, (191) <sup>a</sup>
$\mu_{\text{B}}$ atom <sup>-1</sup>	0	2.003, (2.17) <sup>b</sup> , (2.08) <sup>a</sup>
$E_{\text{coh}}$ (eV)	-23.98	-24.36
$\Delta H_{\text{f}}$ (eV)	-1.046	-1.427
$P_{\text{c}}$ (Kbar)		241.30

<sup>b</sup>Ref. [35], <sup>a</sup>Ref. [34].

concentration of B atoms influences the magnetic moment and formed new covalent bonds Fe–B and B–B, which can stabilize the Fe<sub>x</sub>B compounds and lead to the decrease of their magnetic moment.

The values of cohesive energy of FeB, Fe<sub>2</sub>B and Fe<sub>3</sub>B in two cases NM and FM are respectively, -13.076, -18.63, -23.98 eV, and -13.13, -18.91, -24.36 eV, which are large deviations observed for 1.6% for Fe<sub>3</sub>B, which indicates that all of these Fe<sub>x</sub>B compounds are stable and the higher  $E_{\text{coh}}$  values suggests that Fe<sub>x</sub>B in NM case should have tighter atomic bonding. Furthermore, the cohesive energy decreases from FeB to Fe<sub>3</sub>B, this is mainly caused due to the increase in volume concentration of Fe atoms.

The formation enthalpy,  $\Delta H$  was calculated to check the probability of thermodynamic existence of FeB, Fe<sub>2</sub>B and Fe<sub>3</sub>B in NM case. All formation enthalpies are negative indicating that all structures in two cases FM and NM are thermodynamically stable and the values of Fe<sub>x</sub>B in FM case are less than Fe<sub>x</sub>B in NM case by 6.4, 19.3, 26.7% from FeB to Fe<sub>3</sub>B, implying that Fe<sub>x</sub>B (FM) have more thermodynamic stability. The theoretical critical (transition) pressure is estimated to be 576.63, 761.62 and 241.30 kbar for FeB, Fe<sub>2</sub>B and Fe<sub>3</sub>B, respectively. Usually, the critical pressure at which a ferromagnetic material undergoes transition to a NM state is defined as  $P_{\text{c}} = -\Delta E/\Delta V$ , where  $\Delta E$  is the difference between NM and FM equilibrium total energy by unit cell

and  $\Delta V$  is the respective difference between NM and FM equilibrium volumes.

This definition of critical pressure ( $P_c$ ) was first employed by Gilman [36] in his work on magneto-elastic anomalies in Fe–Ni Invar alloys [3] and  $NiFe_3N$  and  $PdFe_3N$  nitrides [35]. This definition is also used in the study of magnetic transition of inter-metallic bilayers and substituted iron nitrides [30,35].

### 3.2 Population analysis

Mulliken population analysis is a method for calculating partial atomic charges based on the population of linear combined atomic orbitals (LCAO) bases. This was implemented in CASTEP by Segall *et al* [20] based on the method of Sanchez Portal *et al* [37], which provided the link between methods using LCAO and those using plane waves. Owing to the difference of electro-negativity between the Fe and B atoms, the ionic bonds are formed where Fe atoms donate some electrons to B atoms and thus become slightly

positively charged. Mulliken method is applied for the overlap population and the charge calculations. We used the following equations to calculate the average bond length and the average overlap population:

$$L_{\text{moy}}(\text{AB}) = \frac{\sum_i L_i N_i}{\sum_i N_i}, \quad (4)$$

$$P^u = \bar{n}_{\text{AB}} = \frac{\sum_i n_i^{\text{AB}} N_i}{\sum_i N_i}. \quad (5)$$

Here,  $L_{\text{moy}}(\text{AB})$  and  $\bar{n}_{\text{AB}}$  represent the average bond length and the mean bond population, respectively;  $N_i$  is the total number of  $i$  bond in the cell and  $L_i$  the bond length of  $i$  type. These parameters will be used in the subsection 3.3 for the calculation of bond hardness.

According to the calculated Mulliken charges shown in tables 5 and 6, the largest positive charges are carried by Fe atoms in  $FeB$  (0.66 electrons) and B carries a negative charges in all  $Fe_xB$  compounds:  $-0.66(FeB)$ ,  $-0.63(Fe_2B)$  and  $-0.76$  electrons ( $Fe_3B$ ). Apart from Fe–Fe, the bond

**Table 5.** Milliken population analysis results of  $Fe_xB$  (NM) and (FM).

Species	NM		FM	
	Total electrons	Charge states	Total electrons	Charge states
FeB				
B	3.65	−0.65	3.66	−0.66
Fe	7.35	0.65	7.34	0.66
Fe <sub>2</sub> B				
B	3.67	−0.67	3.63	−0.63
Fe	7.67	0.33	7.68	0.32
Fe <sub>3</sub> B				
B	3.73	−0.73	3.76	−0.76
Fe <sub>1</sub>	7.75	0.25	7.74	0.26
Fe <sub>2</sub>	7.77	0.23	7.77	0.23

**Table 6.** Milliken population analysis results of FeB, B–B, Fe–B and Fe–Fe in  $Fe_xB$  (NM) and (FM) (the unit of bond length is Å).

Species	NM			FM		
	$L_{\text{moy}}(\text{AB})$	$P^u$	NB electrons	$L_{\text{moy}}(\text{AB})$	$P^u$	NB electrons
FeB						
B–B	2.302	0.65	2.60	2.322	0.725	2.9
Fe–B	2.096	0.2	3.2	2.121	0.175	2.8
Fe–Fe	2.641	−0.47	−2.8	2.674	−0.42	−2.52
Fe <sub>2</sub> B						
B–B	2.111	0.67	1.34	2.105	0.7	1.4
Fe–B	2.107	0.15	4.8	2.144	0.15	4.8
Fe–Fe	2.641	−0.098	−2.36	2.572	−0.04	−0.96
Fe <sub>3</sub> B						
B–B	2.974	−0.07	−0.14	3.076	−0.08	−0.16
Fe–B	2.078	0.321	10.28	2.124	0.32	10.24
Fe–Fe	2.511	−0.063	−3.16	2.561	−0.039	−2.06

NB electrons: net bonding electrons.

population analysis indicates that all bonds have positive overlap population except B–B bond in Fe<sub>3</sub>B, which shows a net negative population. This is due to the big separation distance between B atoms in Fe<sub>3</sub>B. The covalent B–B bonds are strong, while the covalent interactions between Fe and boron atoms are relatively weak. The compound with highest B–B bond population is FeB in two cases FM and NM (0.725, 0.65), where the number of boron and iron are equal, whereas the lowest population of Fe–B bond is found in Fe<sub>2</sub>B. Bond population results can provide more insightful information on chemical bonding. Due to the charge transfer from Fe to B atoms and strong population derived hybridization, the density of electron in B–B bonds of the boron chain is the highest.

The strongest covalent interaction is attributed to the B–B bond in FeB and Fe<sub>2</sub>B in two cases FM and NM with average calculated length of 2.322 Å (2.302 Å) and 2.105 Å (2.111 Å) of FM (NM), respectively. The population of Fe–B bond increases from 0.175 (FM) to 0.2 (NM) in FeB.

On the other hand, the calculated bond overlap populations in Fe<sub>2</sub>B kept unchanged and the value is 0.15 electrons in the two cases.

### 3.3 Bond hardness

Hardness is a measure of the resistance of materials against permanent deformations. It is usually measured by traditional techniques such as Brinell, Rockwell, Vickers or Knoop [38]. Materials with higher hardness are technologically important for cutting tools and wear resistant coatings. It has been recognized that the hardness of strongly bonded

covalent/ionic crystals are associated directly with the bond strength [36,39]. Zhang *et al* [40] showed that GGA PBE gives better values of bond hardness ( $H$ ). It was found that GGA-PBE (USP) method can be effectively used to predict the  $H$  value.

In this paper, based on the previous works of Gao *et al* [41], the hardness of Fe–B and B–B bonds in each of our three compounds Fe<sub>x</sub>B are evaluated and compared. The proposed analytical expressions have been used to determine the hardness from first-principles theory [40]. The hardness of Fe–Fe bond, however, is not considered in this work, because for the metallic bond, the hardness is ill defined in this method. The strength of the bond per the unit volume can be characterized by average overlap populations. For complex multi-bonding compounds, the hardness of the  $u$  type bond can be calculated as follows:

$$H_v^u (\text{GPa}) = 740 P^u (v_b^u)^{(-5/3)},$$

$$v_b^u = \frac{(d^u)^3 \Omega}{\sum_v [(d^v)^3 N_b^v]},$$

$$H = ((H^{\text{Fe-B}})^{N^u} (H^{\text{B-B}})^{N^v})^{1/(N^u+N^v)}.$$

$H_v^u$  is the hardness of  $u$  type bond;  $d^u$  is the bond length;  $N_b^v$  refers to the  $v$  type bond density per cubic angstrom and the sum is over the total number of  $v$  type bonds in the cell;  $\Omega$  and  $P^u$  are the cell volume and overlap population of  $v$  type bond, respectively. The longest Fe–B bond length considered in this work was limited to 3.1 Å because the interaction between Fe atom and the next-near-neighbour B atom is assumed to be weaker than that between the near-neighbour boron atoms.

**Table 7.** The predicted hardness (FM) of B–B and Fe–B bonds and other parameters used for the calculations.

Species	Bond	$d^u$ (Å)	$P^u$	$N^u$	$\Omega$ (Å <sup>3</sup> )	$v_b^u$	$H^u$ (GPa)	$H$ (GPa)
FeB	B–B	2.322	0.725	4	62.184	3.840	56.966	26.25
	Fe–B	2.121	0.175	16		2.926	21.629	(26.28) <sup>exp1</sup> (20.4 ± 0.017) <sup>exp2</sup>
Fe <sub>2</sub> B	B–B	2.105	0.7	2	105.76	2.952	85.270	18.34
	Fe–B	2.144	0.15	32		3.121	16.658	(18.2) <sup>a</sup> (16.2 ± 0.011) <sup>exp2</sup>
Fe <sub>3</sub> B	B–B	3.076	−0.08	2	153.555	12.25	—	17.35
	Fe–B	2.124	0.32	32		4.798	17.35	

<sup>exp1</sup>Ref. [42], <sup>exp2</sup>Ref. [43], <sup>a</sup>Ref. [31].

**Table 8.** The predicted hardness (NM) of B–B and Fe–B bonds and other parameters used for the calculations.

Species	Bond	$d^u$ (Å)	$P^u$	$N^u$	$\Omega$ (Å <sup>3</sup> )	$v_b^u$	$H^u$ (GPa)	$H$ (GPa)
FeB	B–B	2.302	0.65	4	61.303	3.809	51.771	29.30
	Fe–B	2.096	0.2	16		2.878	25.416	
Fe <sub>2</sub> B	B–B	2.111	0.67	2	100.967	2.986	80.050	19.76
	Fe–B	2.107	0.15	32		2.683	21.420	
Fe <sub>3</sub> B	B–B	2.974	−0.07	2	143.738	11.132	—	19.44
	Fe–B	2.078	0.321	32		4.492	19.44	

The calculated bond length, population overlap, contribution of Fe–B and B–B bonds to the hardness  $H^v$  in FeB,  $Fe_2B$  and  $Fe_3B$  are listed in tables 7 and 8 together with material hardness of our compounds in both magnetic (nonmagnetic) cases. The hardness of B–B bond  $H^u$  is significantly larger than Fe–B bond in FeB and  $Fe_2B$  compounds because of the large bond overlap population in two cases, FM and NM. In the case of  $Fe_3B$ , the Fe–B bond is harder than B–B bond because B–B bond has the largest volume in this compound and smaller overlap population.

The calculated hardness of FeB (26.25 GPa) and  $Fe_2B$  (18.34 GPa) are in fairly good agreement with the experimental values of  $(20.4 \pm 0.017)$  GPa for  $Fe_2B$  and  $(16.2 \pm 0.011)$  GPa for FeB [43]. The disagreement can be explained by the fact that experimentally measured values of hardness of materials are very sensitive to many parameters including loading and unloading speed, applied load, anisotropy of materials, defects in the sample, method of measurement, temperature, etc. Additionally, for polycrystalline materials, hardness is a function of grain size. In case of thin films and coatings, their hardness depends on the nature of the substrate [32,44,45].

#### 4. Conclusions

First principles total-energy plane-wave pseudo-potential calculations were used to calculate lattice parameters, cohesive energy, formation enthalpy and bond length of FeB,  $Fe_2B$  and  $Fe_3B$ . The *ab-initio* calculations confirm clearly that the occurrence of magnetism in a solid not only increases its lattice constant and reduces its bulk modulus (i.e., makes the solid softer), but also affects its structural stability. The calculated results in two cases, FM and NM, with PBE exchange-correlation functional using ultra-soft pseudo-potential are credible when we use spin-polarized method to obtain the correct ground state properties of  $Fe_xB$ , but also crucial to achieve accurate cell constants because some values are in good agreement with experimental data.

The charge calculations, average bond length and average overlap population indicate that the bonding in the two compounds FeB and  $Fe_2B$  show covalent B–B bond, combined ionic-covalent Fe–B bond character and metallic Fe–Fe bond. Mulliken population analysis further support the conclusion that the charge transfer occurs from metal to boron. The stronger covalent interactions of B–B and Fe–B produce higher cohesive energy for  $Fe_xB$  in FM case than for  $Fe_xB$  in NM case.

The calculated hardness  $H$  from Fe–B and B–B bonds of FeB,  $Fe_2B$  and  $Fe_3B$  are predicted from Mulliken populations using GGA-PBE (USP) method. The calculated values of 26.25, 18.34 and 17.34 GPa for  $Fe_xB$  in FM and 29.30, 19.76 and 19.44 GPa for  $Fe_xB$  in NM agree well with the previous study and experimental Vickers hardness. It also implies that it can be an effective tool in predicting the hardness of metal-borides. It is evident that the hardness of B–B bond is significantly larger than Fe–B bond in FeB and  $Fe_2B$

compounds because of the large bond overlap population in two cases, FM and NM. In the case of  $Fe_3B$ , the Fe–B bond is harder than B–B bond because B–B bond has large bond length in this compound.

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