Effect of Mn content in $\text{Fe}_{(1-x)}\text{Mn}_x\text{B}$ ($x = 0, 0.25, 0.5, 0.75$ and 1) on physical properties - ab initio calculations

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Structural, electronic, intrinsic magnetic, anisotropic elastic properties, sound velocities and Debye temperature of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ ($x = 0, 0.25, 0.5, 0.75, 1$) transition metal monoborides have been studied by first-principles calculations within the method of virtual crystal approximation (VCA) based on density-functional theory (DFT) through generalized gradient approximation (GGA). The average magnetic moment per cell increased with increasing of Mn content, which could be associated with the relationship between the composition and magnetic properties. The observed magnetic behavior of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ compounds can be explained by Stoner model. Lattice parameters and Debye temperature agree well with the experimental values. Furthermore, we have plotted three-dimensional (3D) surfaces and planar contours of the directional dependent Young and bulk moduli of the compounds on several crystallographic planes, to reveal their elastic anisotropy versus Mn content (x) in $\text{Fe}_{(1-x)}\text{Mn}_x\text{B}$.

Keywords: monoborides; DFT; virtual crystal approximation (VCA); magnetic moment; anisotropic elastic properties

1. Introduction

The properties of transition metal alloys and transition metal borides have been under intense study for decades [1, 2]. One of these properties is magnetization. It has been given special attention because of its applications in the electronics industry. Previous studies provided us with the insight on the role of d-orbital electrons in iron borides, indicating that the electrons are hybridized in a subtle way [3]. Moreover, magnetic properties have been shown to be correlated with the electronic structure [4] as well as the long-range spin interactions [5]. Various transition metal alloys and transition metal boride materials have been studied, in both experimental analysis and theoretical calculations, for example, MnB [6, 7], $\text{Fe}_{(1-x)}\text{B}_x$ [8, 9], $\text{Fe}_x\text{Mn}_{(1-x)}$ [10], Fe_xB [11, 12], $\text{Fe}_{80-x}\text{Mn}_x\text{B}_{20}$ [13] and $\text{Fe}_{(1-x)}\text{Mn}_x\text{B}_{78/22}$ [14]. However, there has been done relatively little research on transition metal alloy borides $\text{Fe}_{1-x}\text{Mn}_x\text{B}$. Both FeB and MnB have the same

orthorhombic (Pnma) structure [15, 16], and it is interesting to investigate the profile of change in magnetic properties of the material if some of Mn atoms are replaced by Fe in MnB.

In this paper, we investigate the effect of Mn content on physical properties (structural, electronic, intrinsic magnetic, anisotropic elastic properties, sound velocities and Debye temperature) of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ ($x = 0, 0.25, 0.5, 0.75$ and 1) alloys at 0 GPa by first-principles calculations within the virtual crystal approximation (VCA) framework [17]. The VCA approach ignores any possible short range order and assumes that on each potentially disordered site there is a virtual atom averaging the behaviors of the actual components.

This approach neglects the alloying effects such as local distortions around atoms and it cannot be expected to reproduce the finer details of the disordered structures very accurately. Despite this limitation, it often produces acceptable and useful results. The VCA allows calculations on disordered systems to be carried out at the same cost as calculations for ordered structures. For example, in case of $\text{Fe}_{0.5}\text{Mn}_{0.5}\text{B}$ alloys, the virtual transition

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metal atom will have atomic number 25.5. However, there are no data available in the literature about theoretical C_{ij} on these solid solution alloys and they are given only for single-crystals (FeB and MnB). So far, these values are not directly comparable to elastic moduli deduced from experiments made on polycrystalline films and bulk materials. The lattice parameters, total density of states (TDOS), intrinsic magnetic and elastic constants of a single-crystal are determined and discussed. Furthermore, anisotropic elastic constants and moduli at a polycrystalline scale in three dimensional (3D) surfaces and planar contours of Young and bulk moduli of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ compounds on several crystallographic planes, ((1 0 0), (0 1 0) and (0 0 1)) have been computed and plotted to reveal their elastic anisotropy. The sound velocities and Debye temperature have also been predicted from elastic constants.

2. Method of calculations

In order to calculate electronic structures, magnetic and mechanical properties of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$, we used the pseudo-potential plane wave (PPPW) method implemented by the CASTEP packages [18]. We focused on the non-empirical Perdew-Burke-Ernzerhof PBE [19] generalized gradient approximation GGA as functional form, which ensures the normalization condition on the exchange-correlation hole.

For the method of virtual crystal approximation, the electron number used to calculate the density of states (DOS) and magnetism is the mean electron number of the linear combination of TM1 and TM2. In this approximation, the nuclear and valence charges of the TM atom are continuously altered from Mn = 25 to Fe = 26 to represent different cases in $\text{Fe}_{1-x}\text{Mn}_x\text{B}$.

The crystal structures of FeB and MnB calculated here refer to P. Mohn *et al.* [1], with the space group Pnma and lattice parameters for FeB: $a = 5.317 \text{ \AA}$, $b = 2.95 \text{ \AA}$ and $c = 3.964 \text{ \AA}$; and for MnB $a = 5.493 \text{ \AA}$, $b = 2.992 \text{ \AA}$ and $c = 4.147 \text{ \AA}$.

The lattice constants of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ were determined by the structure relaxation. The kinetic

energy cut-off value was selected as 500 eV, which is sufficient to obtain the reliable results.

Total energies were evaluated in the first irreducible Brillouin zone with the following Monk-Horst-Pack grids [20]: $(8 \times 12 \times 10)$ for all compounds. The fraction x in the method of virtual crystal approximation plays the role of mean electron number. For the treatment of the disordered ternary alloy, we used the virtual crystal approximation VCA, in which the alloy pseudopotentials are constructed within the first-principles VCA scheme. Elemental ionic pseudopotentials of FeB and MnB are combined to construct the virtual pseudopotential of the $\text{Fe}_{1-x}\text{Mn}_x\text{B}$.

$$V_{VCA} = (1 - x)V_{FeB} + xV_{MnB} \quad (1)$$

The formation energy E_f of the $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ alloys is determined as follows:

$$E_f(x) = E_T(\text{Fe}_{1-x}\text{Mn}_x\text{B}) - (1 - x)E_T(\text{FeB}) - xE_T(\text{MnB}) \quad (2)$$

$\text{TM}_{1(1-x)}\text{TM}_2\text{B}$, $Z = Z_1(1 - x) + Z_2(x)$ is the average of electron number, where Z_1 and Z_2 represent the electron number of TM1 and TM2 (TM1 = Fe, TM2 = Mn) respectively.

2.1. Structural properties and stability

The ternary $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ ($x = 0, 0.25, 0.5, 0.75$ and 1) ferromagnetic alloys with space group Pnma (SG:62) have been studied in the orthorhombic phase. The optimized equilibrium lattice constant and theoretical and experimental values of cohesive and formation energies of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ are summarized in Table 1 and shown in Fig. 1. Also, the total magnetic moment and bulk modulus are shown in Fig. 1 and Fig. 2. It must be noted that the equilibrium lattice parameter has been computed from the structural optimization, using the Broyden-Fletcher-Goldfarb-Shanno minimization (BFGS) [21–24]. Our calculated equilibrium lattice parameters for $\text{Fe}_{1-x}\text{Mn}_x\text{B}$, are in reasonable agreement with the experimental data [15, 25, 26]. The computed lattice constant for $(\text{Fe}_{1-x}\text{Mn}_x)\text{B}$ is plotted against Mn fraction in Fig. 1. The deviation from linear dependence is distinct.

The calculated cohesive energies of $Fe_{1-x}Mn_xB$ ($x = 0, 0.25, 0.5, 0.75$ and 1) are also presented in Table 1. It has been shown that the mixing enthalpy of alloys can be represented as a sum of a negative contribution due to electron transitions during the alloy formation and positive contribution due to the difference between the widths of the d-bands of the pure components [27].

Fig. 1 shows the total magnetic moment of $Fe_{1-x}Mn_xB$ vs. fraction of Mn. The magnetic moments of FeB and MnB are about $1.12 \mu_B$ per atom and $1.83 \mu_B$ per atom, respectively, which agrees well with the previous studies [7, 28].

When the fraction of manganese x becomes larger, the magnetic moment gradually increases. As the fraction x increases from 0 to 1, the occupation of the minority states decreases (Fig. 3). Also, the bulk modulus B of $Fe_{1-x}Mn_xB$ calculated using the stress-strain method, and by applying the Voigt-Reuss-Hill approximation [29], is plotted against Mn fraction in Fig. 2.

2.2. Density of states

Usually, in order to induce some significant change in crystal structure, high pressures, substituting an atom by another etc., are needed. By increasing the pressure on FeB, the magnetic moment decreases as a linear regression and suddenly, at a critical pressure, an abrupt collapse of magnetic moment occurs [11], but with increasing Mn concentration (Mn substituting Fe) we can see that the density of spin-down reveals a strong peak of the minority band which gradually shifts above the Fermi level causing an increase in the magnetic moment.

Total densities of states, DOS, for $Fe_{1-x}Mn_xB$ compounds are shown in Fig. 3. The most obvious feature of $Fe_{1-x}Mn_xB$ compounds is the metallic character at the Fermi level.

It was interesting to study the profile of change in the magnetic properties of the material when some of the 3D atoms were replaced by neighboring 3D atoms in the compound. To gain some hints on the magnetic ground state of the compounds, Stoner model was used

with the condition of existence of magnetism $N(E_F)I > 1$, where $N(E_F)$ is the non-spin polarized partial density of states of transition metal atom at Fermi energy and I is the exchange-correlation integral calculated by Janak [30]. Table 2 shows the stability of the TM-B monoborides according to Stoner model. The magnetic properties of $Fe_{1-x}Co_xB$ and $Mn_{1-x}Fe_xB$ were reported in the literature [31, 32] and we found somewhat the same results as were obtained by the KKR and VCA methods.

Also, it is seen that the total densities of spin down and spin up are shifted a little bit from $x = 0.0$ (FeB) to $x = 1.0$ (MnB) from the right to the left (Fig. 3). It is important to conclude that the changes in the total DOS at the Fermi level with x , determine low-temperature properties of the Fermi liquid [33, 34], such as specific heat coefficient, spin susceptibility etc.

2.3. Elastic properties

The elastic constants of orthorhombic crystalline $Fe_{1-x}Mn_xB$ compounds are presented in Table 3 and shown in Fig. 4 as a function of x content. Generally, the elastic constants C_{11} , C_{22} and C_{33} are very high, which indicates the high resistance to the axial compression in these directions. Moreover, it is shown in Table 3 that the elastic constants C_{11} , C_{22} and C_{33} are larger than C_{44} , C_{55} and C_{66} , indicating that $Fe_{1-x}Mn_xB$ are mechanically anisotropic and the shear deformation is easier to take place than other deformation forms. It is well known that the elastic constant C_{44} is one of the most important parameter indirectly governing the indentation hardness of a solid [35]. A large C_{44} implies a strong resistance to monoclinic shear in the (1 0 0) plane. The higher C_{44} at 0 GPa for FeB ($x = 0$) than those for the other compounds means that its ability to resist shear distortion in the (1 0 0) plane is the strongest.

The results in Table 3 indicate that $Fe_{1-x}Mn_xB$ have relatively strong anisotropic elastic constants resulting in the directional dependence of the moduli. Notably, the values of $C_{11}(C_{66})$ are relatively smaller than those of $C_{33}(C_{44})$ at 0 GPa, implying

Table 1. The calculated ground state properties of Fe_{1-x}Mn_xB (experimental values are listed in brackets). Total cell energy E_{total} [eV/f.u.], cell parameters [a, b, c in Å] volume V [Å³], Bulk modulus [GPa], total magnetic moment TMM [μB] and cohesive energy E_{coh} [eV/f.u.].

Parameters	X = 0	X = 0.25	X = 0.5	X = 0.75	X = 1
E _{total}	-3773.90	-3511.63	-3305.60	-3093.16	-2927.61
a	5.317 (5.495) ^{exp1}	5.510 (5.521) ^{exp2}	5.483 (5.532) ^{exp2}	5.517 (5.553) ^{exp2}	5.493 (5.56) ^{exp3}
b	2.950 (2.946) ^{exp1}	2.986 (2.951) ^{exp2}	2.982 (2.961) ^{exp2}	2.989 (2.968) ^{exp2}	2.992 (2.977) ^{exp3}
c	3.964 (4.053) ^{exp1}	4.052 (4.043) ^{exp2}	4.077 (4.104) ^{exp2}	4.122 (4.125) ^{exp2}	4.147 (4.145) ^{exp3}
V	62.176	66.66	66.68	67.97	68.153
B	261.90 259.1 ^a	206.43	205.60	233.83	305.6 286.6 ^b
T _{MM}	4.49	5.93	6.61	7.43	7.73
E _{coh}	-13.153	-1.44	-3.79	-4.54	-17.01

exp1 [25], exp2 [26] and exp3 [15], ^a[40], ^b[41]

Fig. 1. The calculated lattice parameters and experimental values (left panel), cohesive and formation energies as a function of Mn content (x) (right panel).

that the intra-layer chemical bonds are weaker than those between the layers.

The mechanical stability criteria at 0 GPa can be represented in a uniform manner for an orthorhombic structure as:

$$\begin{aligned}
 C_{ii} &> 0 (i = 1; 2; 3; 4; 5; 6), \\
 C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) &> 0, \\
 (C_{11} + C_{22} - 2C_{12}) &> 0; (C_{11} + C_{33} - 2C_{13}) > 0, \\
 (C_{22} + C_{33} - 2C_{23}) &> 0
 \end{aligned} \quad (3)$$

It is clear from Table 3 that all elastic constants are consistent with the restrictions of orthorhombic crystal, which reveals that all these Fe_{1-x}Mn_xB compounds are mechanically stable.

The elastic constants C_{11} , C_{22} and C_{33} characterize the x, y and z directions resistance to linear compression, while C_{44} , C_{55} and C_{66} characterize the shear deformation.

It is obvious that the calculated elastic constants C_{33} for Fe_{1-x}Mn_xB compounds are larger than C_{22} and C_{11} for Mn percentage ranging from 0.25, 0.5,

Fig. 2. The calculated total magnetic moment and bulk modulus as a function of Mn content x .

Table 2. The stability of the $Fe_{1-x}Mn_xB$ monoborides according to Stoner model.

	$N_{TM}[E_F]$	I_{TM}	$N_{TM}[E_F] \cdot I_{TM}$
$X = 0$	8.02	0.46	3.69
$X = 0.25$	6.2	0.45	2.79
$X = 0.5$	5.1	0.44	3
$X = 0.75$	5.81	0.42	2.46
$X = 1$	6	0.41	2.46

0.75 to 1, which indicates that these compounds are more incompressible along the z axis (c direction) than along the x and y axes (a and b directions) ($C_{33} > C_{22} > C_{11}$). Though MnB ($x = 1$) is more resistant to the compression in b direction.

The elastic anisotropic nature can be explained using the ratios of C_{11}/C_{22} and C_{11}/C_{33} .

The C_{11}/C_{22} and C_{11}/C_{33} ratio = 1.0 means the same resistance to linear compression along the x , y and z axes. If C_{11}/C_{22} and C_{11}/C_{33} are larger than 1.0 for a crystal, the y and z axes are more compressible than the x axis; while the x axis is more compressible than the y and z axes with C_{11}/C_{22} and C_{11}/C_{33} smaller than 1.0. A large deviation of C_{11}/C_{22} and C_{11}/C_{33} ratio from 1.0 means a larger difference in linear compression along the x , y and z axes. Moreover, the C_{44}/C_{11} , C_{55}/C_{22} and

C_{66}/C_{22} ratios for all x concentrations are less than 1.0 which shows a weaker resistance to shear deformation compared with the resistance to the uni-directional compression.

The arithmetic average of the Voigt and Reuss bounds is known as the Voigt-Reuss-Hill (VRH) average, which is regarded as the best estimation of the theoretical value for the polycrystalline elastic modulus equation:

$$G_H = (G_R + G_V)/2, B_H = (B_R B_V)/2 \quad (4)$$

The Young modulus and Poisson ratio can be computed using relations:

$$E = 9BG/(3B + G), \nu = (3B - 2G)/(6B + 2G) \quad (5)$$

The calculated polycrystalline bulk modulus B , shear modulus G , according Voigt-Reuss-Hill approach, Young modulus E and Poisson's ratio ν are presented in Table 4 and Table 5.

$Fe_{1-x}Mn_xB$ at a concentration ($x = 0$) is ductile since $B/G > 1.75$ and $\nu > 0.26$, while $Fe_{1-x}Mn_xB$ is brittle ($B/G < 1.75$ and $\nu < 0.26$) at 0 GPa for the 0.25, 0.5, 0.75 and 1 concentrations.

2.4. Elastic anisotropy

Three-dimensional surface representations showing the variation of the Young and bulk moduli have been plotted in Fig. 5 and Fig. 6.

Fig. 3. Calculated total and partial DOS of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$. Dashed line represents the Fermi level.

The plane projections ((1 0 0), (0 1 0) and (0 0 1) plane) of the directional dependencies of the Young and bulk moduli are given in Fig. 5 for comparison.

The calculated values of anisotropic factors for monoborides $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ are shown in Table 4. For an isotropic crystal, all the three factors must be one, while any value smaller or greater than one is

Table 3. The calculated full set of elastic constants for $Fe_{1-x}Mn_xB$ along with other available values.

Species	Elastic constants								
	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}
MnB	392.05	510.74	497.17	181.33	154.92	148.62	12.11	167.69	211.28
$Fe_{0.25}Mn_{0.75}B$	414.4 ^a	527.7 ^a	504.8 ^a	171.1 ^a	147.5 ^a	127.7 ^a	215.8 ^a	218.4 ^a	175.8 ^a
$Fe_{0.5}Mn_{0.5}B$	359.25	462.46	478.41	159.16	126.96	121	205.63	157.76	201.06
$Fe_{0.75}Mn_{0.25}B$	352	420	464.22	149.08	100	94.72	202.37	151.26	210.67
FeB	347	377.4	474.7	139.5	92.6	111	203	155	179
	389.82	438.36	557.07	286.85	183.12	239.72	18.8	132.25	212.01
	373.7 ^b	434.1 ^b	503.4 ^b	246 ^b	184.4 ^b	209.1 ^b	207.4 ^b	117.7 ^b	193.7 ^b

^a[40], ^b[41].Table 4. Polycrystalline elastic properties and anisotropic factors of $Fe_{1-x}Mn_xB$ compounds.

Species	B_V	B_R	G_V	G_R	A_1	A_2	A_3	A_u	A_G	A_B
MnB	263.3 ^a	260.5 ^a	179.2 ^a	172.5 ^a	1.46 ^a	0.94 ^a	1.57 ^a	0.21 ^a	1.93 ^a	0.53 ^a
$Fe_{0.25}Mn_{0.75}B$	207.3	205.6	163.2	155.6	1.41	0.90	1.60	0.25	2.38	0.40
$Fe_{0.5}Mn_{0.5}B$	205.9	205.2	169.1	160.3	1.31	0.87	1.78	0.28	2.67	0.19
$Fe_{0.75}Mn_{0.25}B$	235.1	232.5	172.8	165.8	1.28	0.98	1.61	0.22	2.05	0.56
FeB	308.4 ^a	302.8 ^a	155.7 ^a	125.5 ^a	1.57 ^a	1.04 ^a	3.38 ^a	1.22 ^a	10.74 ^a	0.91 ^a
	287.8 ^b	284.6 ^b	148.5 ^b	130.9 ^b	1.63 ^b	0.91 ^b	2.45 ^b	0.68 ^b	5.85 ^b	0.62 ^b

^a[42], ^b[41]. Fig. 4. Elastic constant as a function of Mn content in $Fe_{1-x}Mn_xB$ compounds.

a measure of degree of elastic anisotropy possessed by the crystal.

The shear anisotropic factor for an orthorhombic crystal can be measured in three ways (Zener ratios)

1. The anisotropic factor for the $\{1\ 0\ 0\}$ shear planes between $[0\ 1\ 1]$ and $[0\ 1\ 0]$ directions is defined as:

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad (6)$$

2. The anisotropic factor for the $\{0\ 1\ 0\}$ shear planes between $[1\ 0\ 1]$ and $[0\ 0\ 1]$ directions is:

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \quad (7)$$

3. The anisotropic factor for the $\{0\ 0\ 1\}$ shear planes between $[1\ 1\ 0]$ and $[0\ 1\ 0]$ directions is:

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}} \quad (8)$$

Here, we plotted the Young modulus E , and bulk modulus B in different directions using spherical coordinates for $Fe_{1-x}Mn_xB$ compounds. For orthorhombic crystal class, the directional dependence of Young modulus E and bulk modulus B can be written as:

Table 5. The calculated bulk B, Young E and shear modulus G of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ [GPa], Poisson ratio ν and B:G ratio along with other available values.

Species	B	E	G	ν	B:G
MnB	261.90	431.04	175.84	0.23	1.49
	259.1 ^a	450.2 ^a	186 ^a	0.21 ^a	1.49 ^a
$\text{Fe}_{0.25}\text{Mn}_{0.75}\text{B}$	206.43	380.29	159.39	0.19	1.30
$\text{Fe}_{0.5}\text{Mn}_{0.5}\text{B}$	205.60	389.95	164.69	0.18	1.25
$\text{Fe}_{0.75}\text{Mn}_{0.25}\text{B}$	233.83	409.14	169.30	0.21	1.38
FeB	305.6	365.7	140.6	0.30	2.17
	286.6 ^b	360.5 ^b	139.7 ^b	0.29 ^b	2.05 ^b

^a[40], ^b[41]

Fig. 5. Directional dependent Young moduli (in GPa) for $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ compounds.

For an orthorhombic system [36]:

$$\frac{1}{E} = (S_{11} + S_{22} + S_{33})l_1^4 + (2S_{12} + S_{66})l_1^2l_2^2 + (2S_{23} + S_{44})l_2^2l_3^2 + (2S_{13} + S_{55})l_1^2l_3^2 \quad (9)$$

$$\frac{1}{B} = (S_{11} + S_{12} + S_{13})l_1^2 + (S_{12} + S_{22} + S_{23})l_2^2 + (S_{13} + S_{23} + S_{33})l_3^2 \quad (10)$$

For an isotropic system, 3D directional dependence would give rise to a spherical shape, while the deviation degree of spherical shape reflects the degree of anisotropy. The surface constructions of Young and bulk moduli of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ compounds are shown in Fig. 7 and Fig. 8. The surface constructions of Young modulus and bulk modulus are similar to each other. The projections of the mechanical moduli are plotted in Fig. 7 and Fig. 8. It

Fig. 6. Directional dependent bulk moduli (in GPa) for $Fe_{1-x}Mn_xB$ compounds.

can be clearly seen that $Fe_{1-x}Mn_xB$ exhibits a pronounced deviation with respect to the spherical nature. Thus, the calculated values of anisotropic factors (A_u , A_G and A_B) for monoborides $Fe_{1-x}Mn_xB$ shown in Table 4, are all different than zero. The variation of Young modulus in all planes and directions shows that our compounds possess a minimum of Young modulus E , in $[1\ 0\ 0]$ direction, and a maximum of E $[0\ 0\ 1]$ direction. Therefore, the ordering of Young modulus as a function of the principal crystal tensile stress $[u\ v\ w]$ for $Fe_{1-x}Mn_xB$ are: $E_{[100]} < E_{[010]} < E_{[001]}$.

2.5. Acoustic sound velocities and Debye temperature

The acoustic velocities for $Fe_{1-x}Mn_xB$ compounds in the principal directions can be expressed by the following equations [37]:

$$[100]v_l = \sqrt{\frac{C_{11}}{\rho}}; \quad [010]v_{t1} = \sqrt{\frac{C_{66}}{\rho}};$$

$$\begin{aligned} [001]v_{t2} &= \sqrt{\frac{C_{55}}{\rho}}; \quad [010]v_l = \sqrt{\frac{C_{22}}{\rho}}; \\ [100]v_{t1} &= \sqrt{\frac{C_{66}}{\rho}}, \quad [001]v_{t2} = \sqrt{\frac{C_{44}}{\rho}} \\ [001]v_l &= \sqrt{\frac{C_{33}}{\rho}}; \quad [100]v_{t1} = \sqrt{\frac{C_{55}}{\rho}}, \\ [010]v_{t2} &= \sqrt{\frac{C_{44}}{\rho}} \end{aligned} \quad (11)$$

where ρ is the density of $Fe_{1-x}Mn_xB$ compound, v_l is the longitudinal sound velocity, v_{t1} and v_{t2} refer to the first transverse mode and the second transverse mode, respectively. The calculated densities, sound velocities and Debye temperatures for $Fe_{1-x}Mn_xB$ compounds are shown in Table 6. It is obvious that MnB compound has large sound velocities, for two reasons. First, its density is less than that of the other structures and second, is the highest magnetic moment. The anisotropic

Fig. 7. Projections of Young moduli for different crystal planes of $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ compounds.

Table 6. The density [g/cm^3], anisotropic sound velocities [m/s], average sound velocity [m/s] and Debye temperature [K] for the $\text{Fe}_{1-x}\text{Mn}_x\text{B}$ compounds.

Species	ρ	v_l	v_t	v_m	Θ_D
MnB	6.41	8799.67	5237.57	5798.51	671 356 ^{exp}
$\text{Fe}_{0.25}\text{Mn}_{0.75}\text{B}$	6.45	8059.37	4971.08	5483.87	635.14 645 ^{exp}
$\text{Fe}_{0.5}\text{Mn}_{0.5}\text{B}$	6.6	8026.35	4995.30	5505.34	641.76 602 ^{exp}
$\text{Fe}_{0.75}\text{Mn}_{0.25}\text{B}$	6.62	8331.89	5057.08	5587.98	651.43 562 ^{exp}
FeB	7.085	8342.24 7509 ^a	4454.74 4489 ^a	4976.19 4968 ^a	592.78 740 ^a 403 ^{exp}

^{exp}[26], ^a[41]

properties of sound velocities indicate the elastic anisotropy in these crystals. For example, the C_{11} , C_{22} , C_{33} determine the longitudinal sound velocities along $[1\ 0\ 0]$, $[0\ 1\ 0]$ and $[0\ 0\ 1]$ directions, respectively, the C_{44} , C_{55} and C_{66} correspond to the transverse modes [38].

As a fundamental parameter for the material thermodynamic properties, Debye temperature Θ_D is related to specific heat, thermal expansion and elastic constants. The Debye temperature can be estimated from the average sound velocity by the

following equation based on elastic constant evaluation [39]:

$$\Theta_D = \frac{h}{k} \left(\frac{3nN_A}{4\pi M} \right)^{\frac{1}{3}}$$

$$v_m = \left[\frac{1}{3} \left(\frac{1}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-\frac{1}{3}}$$

$$v_t = \sqrt{\frac{G}{\rho}}, \quad v_l = \sqrt{\frac{(B + \frac{4G}{3})}{\rho}} \quad (12)$$

Fig. 8. Projections of bulk moduli for different crystal planes of $Fe_{1-x}Mn_xB$ compounds.

The elastic wave velocities of these compounds are relatively large, because our compounds have large mechanical moduli and large densities. For Debye temperatures, the largest Θ_D is 671 K for MnB ($x = 1$), while the lowest one is 592.78 K for FeB ($x = 0$). It is well known that the Θ_D can be used to characterize the strength of covalent bonds in the solids. From Table 6, we conclude that the covalent bonds in MnB are stronger than in the other borides. In case of FeB, the smallest Θ_D implies strong metallic bonds between Fe atoms.

3. Conclusions

Structure, magnetic moment, elastic moduli, elastic anisotropy properties, and Debye temperatures of the $Fe_{1-x}Mn_xB$ ($x = 0, 0.25, 0.5, 0.75$ and 1) compounds have been examined and discussed from the first-principles calculations. The equilibrium structure and formation energy show that $Fe_{1-x}Mn_xB$, when $x = 1$ and $x = 0$ are energetically more stable than for other concentrations. The calculated ground-state parameters

are in good agreement with the other available theoretical data and experimental values. The values of B/G of these compounds indicate that the phases are brittle, except the case of FeB, which is ductile. The $Fe_{1-x}Mn_xB$ compounds show a certain degree of mechanical anisotropy.

The calculated sound velocities along $[1\ 0\ 0]$, $[0\ 1\ 0]$ and $[0\ 0\ 1]$ directions for $Fe_{1-x}Mn_xB$ imply that they are anisotropic.

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