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SPIN-RESOLVED DFT STUDIES OF A NOVEL ZrFeBi HALF-HEUSLER ALLOY

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ABSTRACT

First principles calculation have been used to investigate the structural, magnetic, electronic and magnetic properties of a novel ZrFeBi half Heusler alloy in five different phases. A spin resolved DFT calculation was also used to study the electronic band structures and their corresponding partial density of states of the five phases. The different phases are represented as types, 1,2,3,4 and 5. It was observed that that all the phases are ferromagnetic and types 2 and 4 possess a magnetic moment of 1μ_B. Types 1, 3 and 5 are found to be metallic in both majority and minority spin channels where as types 2 and 4 show half metallic character. Types 2 and 4 are found to be mechanically stable and are also found to be ductile in nature.

1. Introduction

The discovery of half Heusler HH alloys by Friedrich Huesler in 1903 [1] has gained the interest of experimentalist and theorist in recent times because of the vast areas in which they can find application. The main reason why they are very useful in the industry is because of the various range of multifunctional properties they exhibit. Such properties make it possible for the HH alloys to be used as thermoelectric materials[2], topological insulator[3], superconductors[4], piezoelectric materials[5,6], spin torque devices[7], magneto-electronic devices[8] and spintronics devices[3]. The concept of spintronics is that spins are the carrier of information unlike the conventional devices where electric charges are the carrier of information. Half metals are examples of compounds that exhibit this concept of spin transport. The half-metallic property is a phenomenon possessed by compounds which gives them the ability to behave as a metal in one spin orientation and as a semiconductor in another spin orientation. This phenomenon was first proposed by De Groot and his colleagues in 1983 [9]. Ever since then the search for half-metals among HH alloys have been on the increase [10]. Although several compounds such as perovskite alloys [11], s-p binary compounds [12], full Heusler alloys[13] and ferromagnetic oxides [14], have been found to possess half-metallic character, the Heusler family which include half Heusler, full Heusler and quarternary Heusler

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alloys have been the most studied compounds in this field. This is due to the fact that there are several interesting properties that can be predicted by just knowing the number of valence electrons of these alloys [7]. Several possible Heusler alloys with huge potentials are yet to be explored. Interestingly, half Heusler alloys that are half-metal obey the Slater-Pauling rule. The Slater-Pauling rule helps to predict the total magnetic moment of half Heusler alloys. Once the total magnetic moment is an integer, then the alloys could posses the half-metallic property. Half Heusler alloys are cubic in nature and have a general formula XYZ. The search for more HH with the half-metallic property is still ongoing because of the possibilities of generating several HH alloys from a combination of three different elements. Over the years, the HH alloys have been studied in different phases in order to determine which phase is the most stable and to understand the reasons while some of the phases show half-metallic character [15,16]. Also very few haIf-metals with low magnetic moment are available. This low magnetic moment possessed by half-metals makes them useful as spin torque devices. With the challenges mentioned above, the search for half-metals with low magnetic moment was carried out on ZrFeBi HH alloy in five different phases. The remaining part of this work is organized as follows. Section 2 presents the computational details, Section 3 presents the discussion of the structural, magnetic, electronic and mechanical properties of ZrFeBi. Finally, Section 4 ends with conclusion.

2. Computational details

First principles calculation based on the density functional theory (DFT) has been used to compute the structural, electronic, magnetic and mechanical properties of ZrFeBi half Heusler alloy in different phases. The different phases are represented as types 1, 2, 3, 4 and 5. A generalized gradient approximation (GGA) type of exchange correlation functional was used. The projected augmented wave type of pseudopotential as implemented in QUANTUM ESPRESSO[17] was used. Since the HH alloy is novel, variable cell relaxation was carried out to determine the lattice constant which was used to optimized the kinetic energy cut-off and k-point as well as the optimized lattice constant. Spin polarization calculation was used to compute the half-metallic properties of the HH alloys. A value of 70Ry was used as the kinetic energy cut-off for types 1,2,3 and 5 while 75Ry was used for type 4. Also 9X9X9 was used as the k-point for types 2, 3 and 4 wile 10X10X10 was used for types 1 and 5. Mechanical properties was done using the thermo_pw code[18].

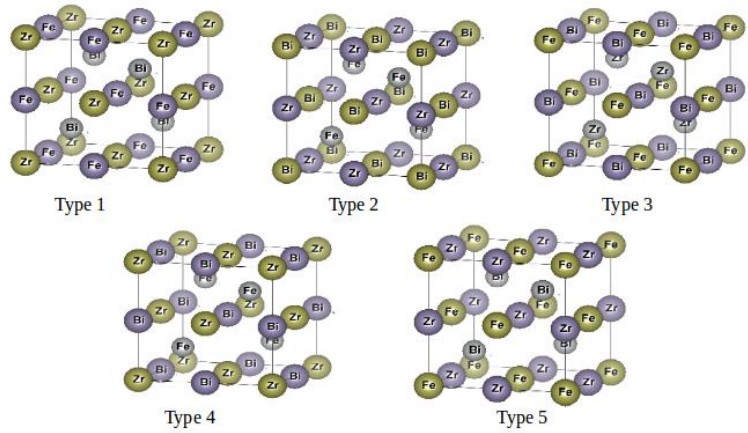

Fig 1: Crystal structure of ZrFeBi in five different phases

Table 1 The lattice constant a (Å), bulk modulus B (GPa), pressure derivative B' magnetic moment (μ_B), the magnetic state M_g, total ground state energy E_{tot} (Ry) and formation energy E_f (Ry) of ZrFeBi, ferromagnet FM.

Structure	M_g	**a**	**B**	B'	μ_{tot}	E_{tot}	E_f	Half-metal
Type I	FM	6.613	77.0	3.89	2.67	-1542.7609	−1.434	No
Type II	FM	6.326	101.9	5.98	1.02	-1542.89601	−3.269	Yes
Type III	FM	6.712	60.5	4.63	2.05	-1542.76358	−1.470	No
Type IV	FM	6.324	101.7	5.14	1.03	-1542.89521	−3.268	Yes
Type VI	FM	6.614	78.4	354	2.68	-1542.76093	−1.434	No

3. Results and discussions

3.1 Structural properties

The structural properties of ZrFeBi in the five different phases have been studied and parameters associated to structural properties are shown in Table 1. The half Heusler alloys are known to crystallize in the $C1_b$ crystal structure with space group F-43m (no. 216). The usual Wyckoff positions occupied by the XYZ atoms of the HH alloys are 4a (0,0,0), 4b(1/2,1/2,1/2), 4c(1/4,1/4,1/4) where the Y atom is usually any of the transition metals and the Z atom is taken from the group III, IV or V. The commonly used Wyckoff positions for HH alloys in five different phases are presented in Table 2 while the figures representing each phases are shown in Fig 1. The structural optimization of the five phases was carried out by fitting the total energy curve versus the lattice parameter to a Birch Murnaghan equation of state. The optimized lattice parameter, bulk modulus and the pressure derivative of the bulk modulus for the ferromagneticstates in the five phases were thereafter determined as shown in Table 1. Fig. 2 shows the graph of total energy versus lattice parameter for the five phases indicating the ZrFeBi is ferromagnetic in the five phases. Fig. 3 also show the graph of total energies versus lattice parameter in the ferromagnetic state for the five phases in order to ascertain the most stable phase. It is observed that types 2 and 4 are the most stable phases with type 2 slightly lower in energy than type 4. This shows why type 2 phase is the most commonly used configuration in literature[7]. Since the half Heusler alloy is a novel material, the formation energies in the three phases are computed using eq. (1).

$$E_f(ZrFeBi) = E_T(ZrFeBi) - (E_g(Zr)+E_g(Fe)+E_g(Bi)) \quad (1)$$

where $E_T(ZrFeBi)$ denotes the total energy of the HH alloy ZrFeBi, $E_g(Zr)$, $E_g(Fe)$, and $E_g(Bi)$ denote the total energies per atom for each elements. The negative formation energies of ZrFeBi in the three phases as shown in Table 1 indicating that the three phases can be synthesized experimentally.

Table 2: The Wyckoff positions for the three atoms of the ZrFeBi HH alloys in five different phases

Phases	4a (0,0,0)	4b(1/2,1/2,1/2)	4c(1/4,1/4,1/4)
Type I	X	Y	Z
Type II	Z	X	Y

Type III	Y	Z	X
Type IV	X	Z	Y
Type VI	Z	Y	X

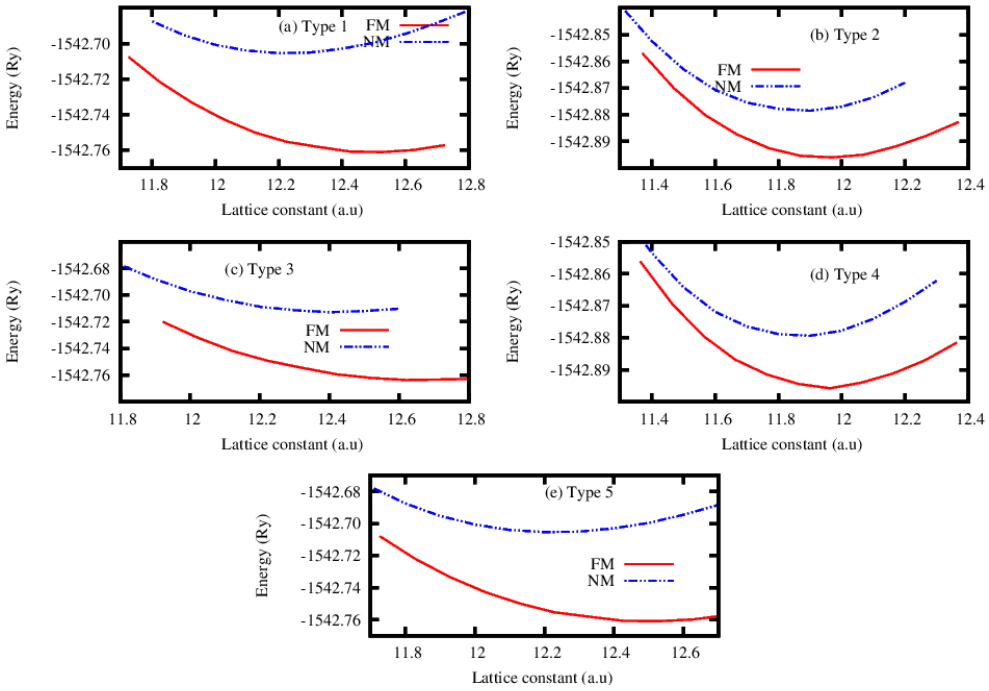

Fig 2 Total energy per unit cell as a function of lattice constant for (a) type 1, (b) type 2, (c) type 3, (d) type 4 and (e) type 5 in ferromagnetic state (FM) and non-magnetic state (NM) of ZrFeBi half Heusler alloys.

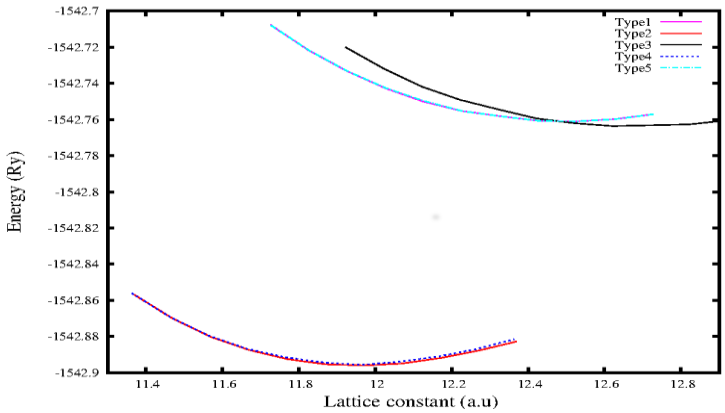

Fig 3 Total energy per unit cell as a function of lattice constant for type 1, type 2, type 3, type 4 and type 5 in ferromagnetic state (FM) of ZrFeBi half Heusler alloys.

3.2 Magnetic Properties

The magnetic properties of ZrFeBi HH alloy in the five phases have been examined. The total magnetic moment is determined from the contribution of individual local magnetic moments from atoms Zr, Fe and Bi.

The total magnetic moment for types 2 and 4 configuration is an integral value of $1\mu_B$. This value satisfy the Slater-Pauling rule which is determined by the expression $M=|V_N-18|$ where M is the magnetic moment and V_N is the number of valence electrons per formula unit. Whereas the magnetic moment for types 1, 3 and 5 are shown in Table 1 and they do not obey the Slater-Pauling rule. To understand how the magnetic moment of the HH alloy was formed, it is important to consider either type 2 or 4 since they obey the Slater-Pauling rule and because the Fe atom occupies the usual 4c(1/4,1/4,1/4) forming a tetrahedral positions with the Bi atom. During interaction, the d-orbital of the Fe atom undergoes a crystal field splitting which generate the triplet states (t_{2g}) and the doublet state (e_g). Because of the tetrahedral position formed, it makes the e_g (d_{z2} and d_{x2-y2}) states more stable with lower energy, hence the t_{2g} (d_{xy}, d_{xz} and d_{yz}) states interact to form a covalent bond with the sp^3 states of Bi forming $[FeBi]^{4-}$. The $[FeBi]^{4+}$ then hybridizes with the $[Zr]^{4-}$ ions. During this process, the Fe atom has gained one extra electron which is added to its previous 8 valence electrons making it 9 in total. It is these 9 electrons that are shared among the t_{2g} states and e_g states leaving one unpaired electron which constitute the magnetic moment of the HH alloy. The same principle is applicable to types 2 and 4.

3.3 Electronic properties

The electronic properties of ZrFeBi HH alloy in the five different phases have been computed using spin resolved density functional theory calculation, and it was observed however that only types 2 and 4 possessed the half-metallic nature as presented in Figs. 4 and 5. This is due to the fact that band gaps are seen around the the Fermi energies in the majority spin channels whereas the bands are seen crossing the Fermi energies in the minority spin channels of the band structures and partial density of states (PDOS). An indirect band gap is observed for both type 2 and 4 with a value of 1.182eV and 1.138eV respectively. Types 1,3 and 5 show metallic character in both majority and minority spins. In order to understand this phenomenon, it is important to use the same principle applied in explaining the magnetic moment in Section 3.2. During the hybridization of $[FeBi]^{4-}$ and $[Zr]^{4+}$ ions, the crystal field splitting of the Fe-5d orbital and Zr-5d orbitals interact to form the band gap near the Fermi energy. Bonding and anti-bonding are formed at valence and conduction band near the Fermi energy respectively. This bonding and anti-bonding can be seen in Figs 4 and 5. For the minority spin channels, the d-orbital is partially occupied near the Fermi energy while the d-orbital for the majority spin channels in the valence band is fully occupied. Type 2 and 4 are also found to posses 100% polarization around the Fermi energy making the ZrFeBi HH alloy a potential material in spintronics industry.

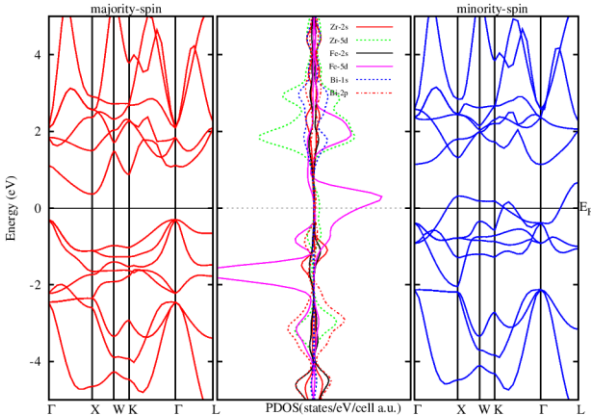

Fig 4 The electronic band structure and PDOS(at the middle) of ZrFeBi type 2 for both spin up and spin down channels.

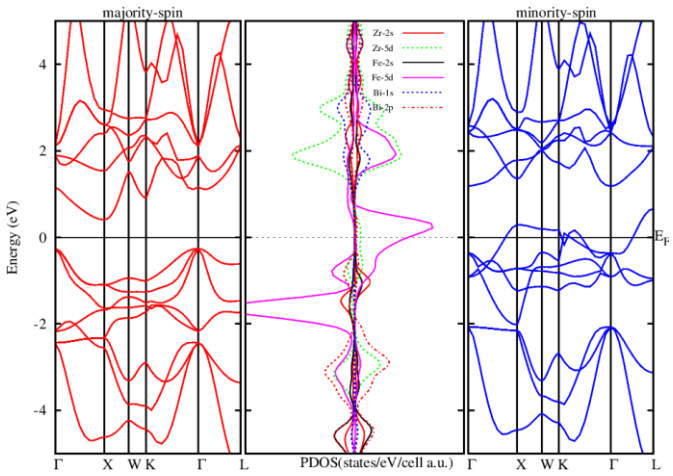

Fig 5 The electronic band structure and PDOS(at the middle) of ZrFeBi type 4 for both spin up and spin down channels.

3.4 Mechanical Properties

The mechanical properties of types 1 and 2 have been computed and the results are presented in Table 2. The elastic constant associated with cubic structures are C_{11}, C_{12} and C_{44} . The Born criteria for mechanical stability in cubic structures is given in eq. (2)[19].

$C_{11} > 0$, $C_{44} > 0$, $C_{11} > B > C_{12}$ and $C_{11}+2C_{12} > 0$, $C_{11}-C_{12} > 0$ (2)

From the results in Table 3 it is obvious that types 2 and 4 phases are mechanically stable. The mechanical properties have been carried out using the Voigt-Reuss-Hill approximation. It is observed that the mechanical properties of type 2 phase is slightly different from that of type 4 phase, this could be due to the difference in atomic configuration of the crystal structures. The B/G ratio for the two phases indicate that they are ductile in nature when compared to the critical ratio of 1.75 [20].The Poisson's ratio for both phases are slightly higher than the usual 0.25 mark representing ionic bonding. This indicates that the type of bonding within the atoms are ionic and metallic bonding [21] The mechanical properties of ZrFeBi are within acceptable range when compare to literature [10]

Table 3: The mechanical properties: the elastic constants C_{11}, C_{12} and C_{44} (GPa), shear modulus G (GPa), Young modulus E (GPa), Zener anisotropy A, Poisson's ratio υ and the B/G ratio of ZrFeBi in type 2 and type 4.

Compound	Type 2	Type 4
C_{11}	178.56	189.29
C_{12}	50.17	59.09
C_{44}	49.55	50.55
G	54.97	55.94
E	137.75	141.98
A	0.7719	0.7765
υ	0.2530	0.2691
B/G	1.854	1.818

4. Conclusion

We have investigated the structural, magnetic, electronic and mechanical properties of ZrFeBi in five different phases using first-principles approach. It is found that all five phases are ferromagnet but from their electronic properties, only types 2 and 4 phases are half-metallic in character. The magnetic moment of types 2 and 4 are found to be $1\mu_B$ satisfying the Slater-Pauling rule while types 1, 3 and 5 are $2\mu_B$ and above. Types 2 and 4 are found to be mechanically stable and are ductile whereas types 1,3 and 5 not mechanically stable. The high values of their shear and bulk modulus show that they have high resistance to shear and volume deformation respectively.

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