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Theoretical Investigation of Magnetic Properties of MnBi By DFT+U Method Using elk Software

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Abstract. A half metallic -ferromagnet MnBi exhibits metallic behavior in one spin direction while the other spin direction shows semiconducting behavior. This unique property makes MnBi a promising material for spintronic devices. Besides this absence of rare-earth elements in compositions, the large magneto crystalline anisotropy, high-temperature reasonable magnetization, the positive temperature coefficient of coercivity and the moderate Curie temperature make MnBi magnets very potential for high-temperature magnet application. In addition, it has good magneto-optical properties with potential applications in erasable magneto-optical memory devices. In this work we investigated magnetic properties of MnBi by DFT+U method using elk software. We have got magnetic moment 6.54μ_B-at 315 K which is high enough from experimental value 3.60μ_B.

1 Introduction

Motors of electric vehicles are operated at elevated temperatures which require the maximum energy product of permanent magnet[1]. Nd-Fe-B, a rare earth magnet has the highest (BH)max of 59 Mega Gauss Oersted (MGOe) at room temperature [2], where as the most widely used low energy ferrite magnets has low energy below 6 MGOe. However due to thermal instability i.e. a large negative temperature coefficient of H_{ci}, a low Curie temperature (T_c) of 523K[3] and also the scarcity of rare earth elements, Nd-Fe-B is not desirable for such high energy motors. In this context, low temperature phase(LTP)-MnBi, a rare earth free permanent magnet can be usable at the operating temperature of the motors of electric vehicles. Besides this presently miniaturization in modern and advance technology need permanent magnets which are capable of achieving performance as like as rare earth permanent magnets and cost-effective. LTP- MnBi has attracted remarkable attention due to its high magnetic moment and cost-effectiveness [4]. It is an interesting ferromagnetic material in terms of both structurally and magnetically. Due to their approximately half-filled 3d bands, manganese alloys often exhibit antiferromagnetic order; nonetheless, MnBi is one of the few ferromagnetic manganese compounds that can be utilized as a permanent magnet

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[5]. Ferromagnet MnBi with half metals exhibits metallic behavior in one spin channel while the other spin channel has a gap at the Fermi level. As a result, the aforementioned state may exhibit over 100% spin polarization, making it suitable for use as spin injectors in spin-dependent devices such as magnetic random-access memory [6]. The other magnetic properties of MnBi are a large Kerr rotation [7], with a high Curie temperature of 630K and a high coercivity which increases with temperature [8]. At 630K, LTP-MnBi experiences a first-order phase shift from the ferromagnetic (FM) state to the paramagnetic (PM) state as the temperature rises from room temperature (RT). This shift is accompanied by a structural change from the NiAs-type to a distorted Ni_2In-type hexagonal structure (high-temperature phase: HTP) [9].

In 1904 Heusler was first reported the ferromagnetic nature of MnBi [10]. In 1943 Guillaud were conducted the most thorough research on MnBi in his PhD thesis. He was the first to create the hexagonal MnBi compound and investigate its many magnetic properties [11]. Spin reorientation and a corresponding increase of magnetic anisotropy with temperature was also first observed by him. Neutron diffraction [8, 12] and nuclear magnetic resonance (NMR) [13] studies on LTP-MnBi also revealed this spin reorientation. Nevertheless, a detailed explanation of the relationship between the structural and magnetic properties is still lacking [11–14]. A number of theoretical investigations have been conducted to comprehend the magnetic characteristics of MnBi [15–19]. In this work we systematically studied the electronic structure and magnetic properties of MnBi through detailed investigations of density of states and band structure by DFT+U method using elk code [20].

2 Crystal Structure

Figures and The LTP phase of MnBi is ferromagnetic and has a hexagonal NiAs-[21] structure (P63/mmc symmetry, group number 194) with six and three-fold symmetry, is primitive with two mirror and one glide planes [22]. The unit cell consists of two Mn atoms at the Wyckoff 2a sites (0,0,0) and (0,0,1 /2) and two Bi atoms at the Wyckoff 2c sites (1 /3, 2/ 3, 1/ 4) and (2 /3, 1/ 3, 3/ 4) [23]. There is a first order phase transition from ferromagnetic to a paramagnetic [24] state above 630K (HTP). The MnBi compounds in the LTP phase have the Bi has $6s^2 6p^3$ as its valence electron configuration, and Mn has a configuration of $[Ar]3d^5 4s^2$. Figure 1 shows the unit cell and molecular compound for MnBi. The atomistic modelling is carried out using VESTA software [25].

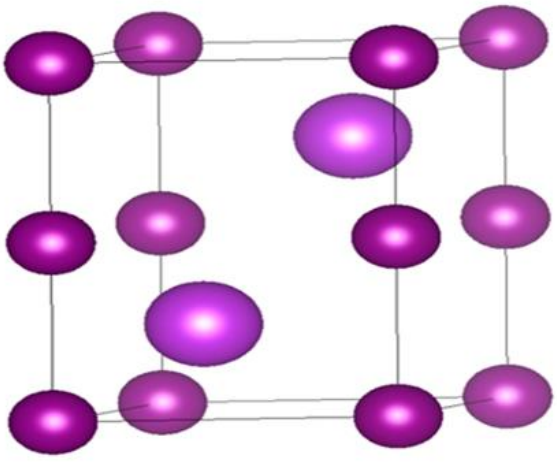

Fig. 1: Unit cell of MnBi crystal structure.

3 Method of calculation

The In this investigation, we applied the DFT+U calculation method based on the density functional theory (DFT) using elk code to study structural and magnetic properties of MnBi. Elk is an all- electron linearised augmented plane-wave (FP-LAPW) code for determining the properties of crystalline solids [26]. The process of solving of many-electron systems is time-consuming and complex. While precise solutions for the electronic structure of solids are frequently outside the scope of current theory, many practical approaches have been found to be effective. Of these, density functional theory (DFT) has proven to be one of the most effective and can predict a wide range of physical and chemical processes seen in condensed matter. In DFT, energy, E, is treated as a functional of electron density, ρ, denoted E[ρ], where ρ depends on the set of electronic wavefunctions. While early formulations of DFT, treating electrons as a purely non-interacting gas, were largely inaccurate, DFT has since evolved as a powerful method for computing the electronic properties of a system. The general energy expression in DFT is then, [27]

$$E[\rho] = E_K[\rho]+V_{ne}[\rho]+V_{ee}[\rho]+E_{xc}[\rho] \qquad (1)$$

with $E_K[\rho]$ as the kinetic energy, $V_{ne}[\rho]$ as the Coulombic potential between electrons and nuclei, and $V_{ee}[\rho]$ is the Coulombic repulsion between electrons and includes a correlation part. $E_{xc}[\rho]$ is the exchange-correlation energy which corrects for the treatment of electrons as non-interacting in the Kohn-Sham equation. The development of DFT has yielded many different approximations of the exchange-correlation energy, and a variety of implementations have since arisen. Each approach has its own advantages and disadvantages.

One of the biggest challenges in completing accurate DFT calculations is deciding which electronic properties should be taken into account first. For example, many otherwise accurate exchange-correlation energy approximations are strictly spin unpolarized, which means they can't account for the spin-orbit coupling that has a significant impact on some materials. This case is examined here. Spin-orbit coupling (SOC) is caused by interactions between the magnetic dipoles of the electrons' intrinsic and orbital angular momentum. Strong evidence suggests that SOC significantly lowers the band-gap energy in all-inorganic perovskites [24,28]. Unfortunately, some exchange-correlation energy approximations may ignore spin polarization, obscuring the appearance of such effects in DFT computations; therefore, the choice of exchange-correlation energy approximation should be based on the DFT calculation's goal. The full-potential linearized augmented plane-wave (FP-LAPW) method is readily applicable to the periodic system of a crystal. The LAPW method allows the accurate and efficient solution of a solid's band structure, particularly in transition metals [29]. The DFT+U approach enhances the description of materials containing localized electrons, especially transition metal oxides with d or f orbitals, by adding an on-site Coulomb correction (the "U" term) to the standard Density Functional Theory (DFT). By introducing a Hubbard-like model that encourages electrons to localize on specific atomic orbitals, it corrects for the self-interaction error inherent in DFT, which understates electron-electron repulsion. This results in more accurate predictions of structural, magnetic, and electronic properties and its main advantage is it is within the realm of DFT.

Elk performs a variety of DFT calculations in a two-variational step process. In the first variational step, the electron density was used to solve the scalar potential and E-field, where $\hat{H}$ is the Hamiltonian,

$$\hat{H} = T + V + E\cdot\mathbf{r} + V_{xc} \qquad (2)$$

Where $\hat{H}$ is the Hamiltonian, T is the kinetic energy, V_{xc} is the external and exchange correlation energy potential, and $E \cdot \mathbf{r}$ is the energy vector field. In Elk, core states are treated truly relativistically by treating them with the Dirac equation, while valence states are treated

with the relativistic Schrödinger equation. All remaining states were treated with the Kohn-Sham equation. These were all solved within the FP-LAPW method as described in Density Functional Theory. Elk code version 9.6.8 was used to calculate the electronic and magnetic properties of MnBi.

4. Results and discussions

We started our calculation with density of states (DOS) and electronic band structure of LTP-MnBi from ground states energies. Density of states depends only on the angular momentum quantum number, l. In LTP-MnBi has been observed that the major contribution to the DOS is mainly from the Mn 3d-orbitals. In MnBi, each Mn atom has the electron configuration [Ar] $3d^5 4s^2$, the PDOS shows the 3d and 4s states. A sharp and high peak has been observed in fig.2 for 3d-orbital near the Fermi level (very close to 0 eV) in the PDOS of Mn. This corresponds to the high density of states which implies 3d state is strongly localized and it is the property of transition material. High DOS near the Fermi level which also indicates Mn provides many available states for electrons to move. It enhances electrical conductivity and magnetic interaction. Fig.3 shows the PDOS of bismuth in MnBi where a high peak is observed in 6s orbital. Since the s orbital is far from Fermi level this band is fully occupied. There is a significant density of states near 0 eV. Fig.3 also shows that p and d states are hybridized in conduction band. This hybridization plays major role in electronic transport behavior, magnetic properties etc. The spin up and spin down peaks of the Bi states have the same energy levels. The spin up and spin down electrons cancel each other out when symmetry exists below the Fermi level. As a result, the substance is anti-ferromagnetic. Strong Mn-Bi hybridization enhances magnetic stability and also it influences magneto crystalline anisotropy.

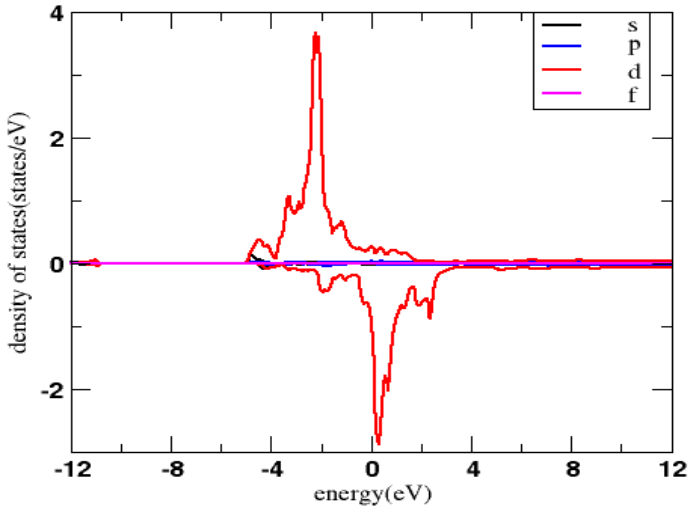

Fig. 2. PDOS of Mn (Graph plotted using GRACE software) [30].

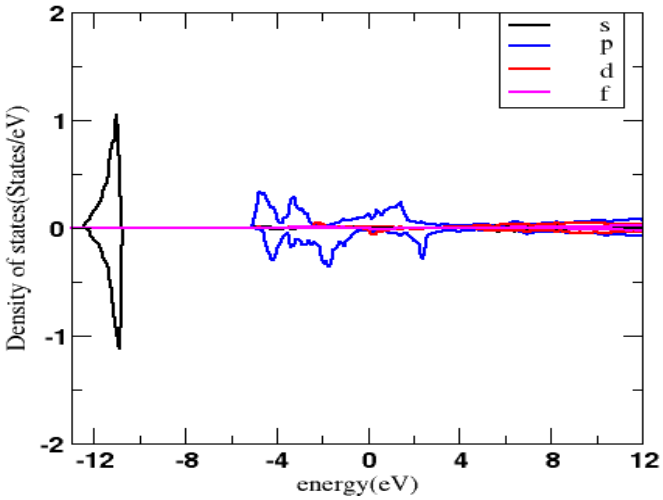

Fig. 3. PDOS of Bi (Graph plotted using GRACE software)

Mn 3d-orbitals, as shown in Fig.4, contribute mostly to the total DOS in MnBi, this causes the majority of spin states to be occupied in the alloy because Mn has a half-filled 3d orbital, its DOS contribution divides almost evenly between both occupied and unoccupied states. LTP-MnBi's Fermi level (E_F) is slightly above the majority-spin state and slightly below the minority-spin state. The DOS surrounding the E_F is degenerate. The concentration of states near 0 eV suggests Mn contributes significantly to the conduction properties of MnBi.

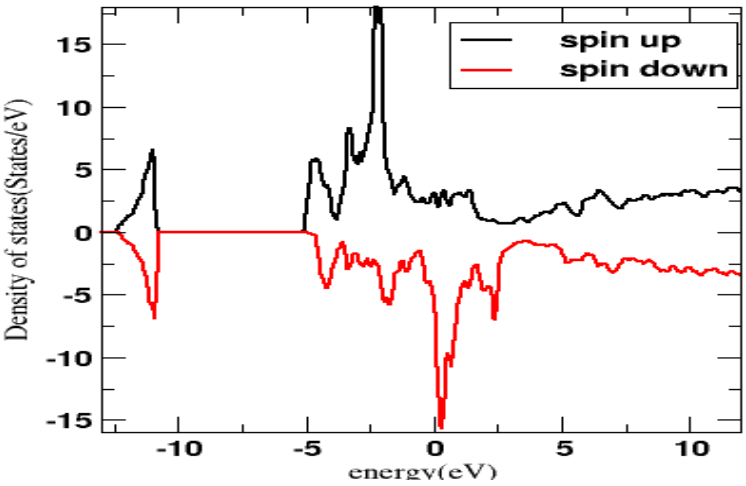

Fig. 4. TDOS of MnBi (Graph plotted using GRACE software)

From fig.5 we can see the dashed red line at E=0 eV conventionally signifies the Fermi level which indicates the highest occupied energy level at T=0K. The spin polarized band structure of NiAs-type hexagonal MnBi shows majority (spin-up) bands in the upper panel and minority (spin down) bands in the lower panel. In both spin channels have the bands those cross the Fermi level, which indicates that MnBi is a metallic compound. In particular, there

is no bandgap at the Fermi level for either spin. This is consistent with first-principles reports that hexagonal MnBi is a ferromagnetic metal [31]. In this particular temperature (315K) MnBi is metallic not a half metallic because both spin-up and spin down bands cross the Fermi level. Everywhere in k-space, bands in one spin channel do not coincide in energy with the other. Spin-up and spin-down band energies differ at all high-symmetry points, reflecting exchange splitting. The exchange splitting of Mn 3d states is large enough which is responsible for high magnetic moment of MnBi. Spin splitting occurs due to large Mn moment and strong Bi spin-orbit coupling.

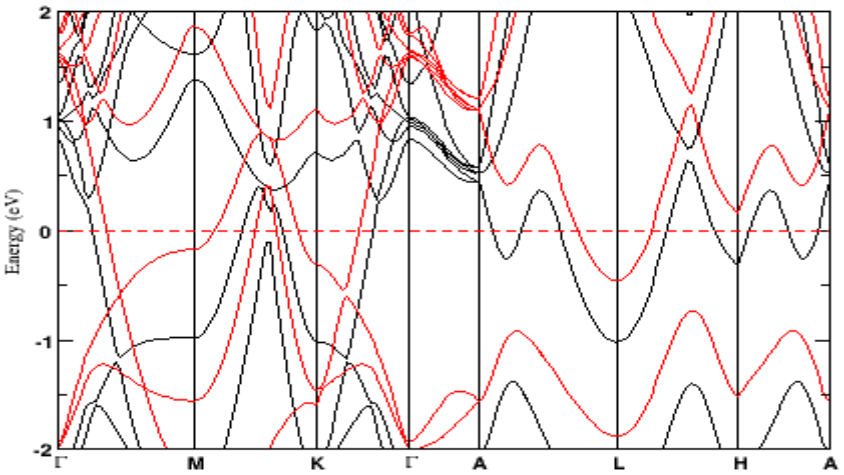

Fig. 5. Band structure plot of MnBi.

The FERMIDOS.OUT and GAP.OUT files of MnBi also indicates that pure MnBi is a good conductor. The LATTICE.OUT file provides unit cell volume. Volume of MnBi unit cell is 101.071Å^3. The MOMENT.OUT file also generates during the self-consistent field calculation. This output file gives the magnetic moment of MnBi is 3.27μB/f.u.

5 Conclusion And Future Prospective

From our DFT+U calculation we have got magnetic moment of MnBi is 3.27μ_B/f.u. which is close to experimental value. The core and valence states were treated relativistically in Elk. Since Elk allows an arbitrary number of core states, increasing the number of core states treated by the Dirac equation might provide a more accurate potential with which the code would calculate the conduction band states and calculations more accurately. Our theoretical studies reveal that MnBi is a spin-polarized ferromagnetic transition metal.

In near future we will do the substitutional doping in MnBi of different element and will study the band structure of doped MnBi. For detail study of structural properties of MnBi we will do the Phonon calculation by the method of DFT+U using elk code.

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