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Research Article

Effect of Mn Doping on the Electronic and Magnetic Properties of Full Heusler Alloy Co_2FeSi

[1]Pramila Kumari Pokhrel, [1]Gopi Chandra Kaphle*

[1]*Central Department of Physics, Tribhuwan University*, Kathmandu, Nepal

**Corresponding author email:* gopi.kaphle@cdp.tu.edu.np

ABSTRACT

Heusler compounds are one of the largest families of ternary intermetallics with broad range of applications. In this work, we inspected the electronic and magnetic properties of full Heusler alloy Co_2FeSi and the effect induced by doping Mn atom on those properties. We employed plane wave pseudo-potential method based on DFT framework implemented in Quantum ESPRESSO code using PBE type of functional for exchange correlation energy. The calculation demonstrates that Co_2FeSi exhibits metallic nature in the majority spin state and semi-conducting nature in minority spin state with indirect energy gap of ≈ 0.132 eV and shows chances of weakened half-metallicity as indicated by the presence of band gap below fermi level. The calculated total magnetic moment is 5.44 μ_B/cell which is found to be deviated from Slater-Pauling rule $M = N_V - 24$ for full Heusler compounds. The site selectionfor doping was based on the empirical rule for atomic occupation established for Heusler alloys and the calculation of formation energy. The calculation of formation energy at B and D site showed B site as more favorable for doping for both 25% and 50% concentration. At 25% Mn concentration, calculation shows Co_2FeSi has typical metallic behavior for spin-up electrons, but semi-conducting behavior with decreased gap below fermi level for spin-down electrons showing no half-metallicity whereas for 50% Mn concentration the gap gets broadened by 0.089645 eV. The calculated magnetic moment for 25% and 50% Mn doping is 21.93 μ_B/cell and 21.69 μ_B/cell respectively. Our calculation depicts that the chances of half-metallicity decreases for 25% concentration of Mn atom and increases for 50% Mn concentration.

Keywords: Heusler compounds, intermetallics, half-metallicity

I. INTRODUCTION

Increased interest in the field of spintronic has enlarged the search of new materials exhibiting half-metallic ferromagnetic property at room temperature [1]. The half metallic ferromagnets are characterized by the existence of metallic behaviour in the majority spin channel and semi-conducting behaviour in the minority spin channel around the Fermi level. Half metallic property is assumed to play a germane role for spintronics applications. Half metallic ferromagnetism was observed in NiMnSb by de Groot et al. which is a semi-Heusler alloy [2]. Since then a series of other full and semi heusler alloys have been studied continuously. Amongst Heusler compounds as well as half-metallic ferromagnets, Co_2FeSi has been found to have highest Curie temperature of 1100K and magnetic moment of 6 μ_B/cell[3].

Heusler alloys are generally represented by generic formula X_2YZ, where X and Y denote transition metal whereas Z is III-V group element. Heusler alloys that crystallizes in $L2_1$ structure with space group $Fm\bar{3}m$ (225) [prototype structure is Cu_2MnAl] are called full-Heusler compounds. For these compounds sequence of atoms is X-Y-X-Z. Co_2FeSi is a full Heusler alloy that crystallizes in $L2_1$ structure [4]. This structure consists of a fcc lattice with 4 atoms as basis: X at (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4), Y at (1/2, 1/2, 1/2) and Z at (0, 0, 0) in Wyckoff position.

According to Kandapal et. al for a compound to show half-metallic character, the magnetic moment has to be an integer[5]. For integer value of magnetic moment, a real gap arises in the minority density of states at the Fermi level which is the character of half metallic ferromagnet. The total magnetic moment of the compoundobeys the Slater-Pauling rule i.e $M_T = Z_T - 24$ as studied by Wurmehl et al. [3]. In accordance to this theory, the compound has magnetic moment of 6μ_B/cell where M_T is the magnetic moment of the compoundand Z_T is the number of valence electron in the given compound. Co_2FeSi has 30 valence electrons.

Doping is the phenomena of introducing impurities intentionally in the material for the purpose of modulating its electrical, optical and structural properties. In order to inspect the changes in the electronic and magnetics properties of pristine Co_2FeSi, Mn was doped in B site i.e. Fe site as supported by literature [6] and the calculation of formation energy. The calculation of formation energy revealed B site as the favorable site for doping Mn atom for both 25% and 50% concentration.

II. METHODS

The computational work has been carried out using Quantum Espresso (QE) [7] codes based on density functional [8, 9]. PBE functional for exchange and correlation energy developed by Perdew, Burke and Ernzerhof was utilized [10]. The total energy convergence threshold and force convergence threshold was set to 10^{-5} Ry and 10^{-3} Ry/Bohrs respectively. For self-consistent total energy calculations, the Brillouin zone was sampled in k-space using the Monkhorst-Pack scheme with appropriate number of mesh of k-points determined from the convergence tests. For the

geometrically optimised structure, we conducted relax calculation under Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme until the energy difference between two consecutive scf calculations was less than 10^{-6} Ry.

III. Results and Discussion

The band structure of the primitive Co_2FeSi was calculated taking optimized value of energy cut-off 140Ry and lattice parameter 5.63Å. The band structure for spin-up channel exhibited metallic nature at fermi level, thus implying the strong metallic character of spin-up electrons which is depicted in figure 1. On contrary to this, the band structure for spin-down channel exhibited an indirect band gap at about 1 eV below the E_f . Further, the plot for the minority band shows that the band gap is of indirect type since Conduction Band Minimum(CBM) lies at point X and Valence Band Maximum(VBM) lies at symmetric point Γ below the fermi level as shown in figure 2. We measured the band gap to be 0.132 eV. This indicated that we may not have 100% spin polarization at fermi level, as required for half-metal [3]. Hence, the compound Co_2FeSi cannot exhibit perfect half- metallic properties.

Calculated magnetic moment of Co_2FeSi is 5.44 μ_B/cell. It is found that magnetic moment of constituent atom has site dependency i.e magnetic behavior of atom depended on neighboring atoms. The compound doesn't show half-metallic character, since the value of magnetic moment is not an integer. The experimental magnetic moment calculated by Wurmhel et al is $(5.97\pm0.05)\mu_B$/cell[3]. Galankis calculated the magnetic moment and found it to be $5.9\mu_B$/cell[11]. The discrepancy between experimental and calculated value of magnetic moment is caused due to complete absence of on-site electron-electron correlation in the approximation that is utilized for calculation [12].

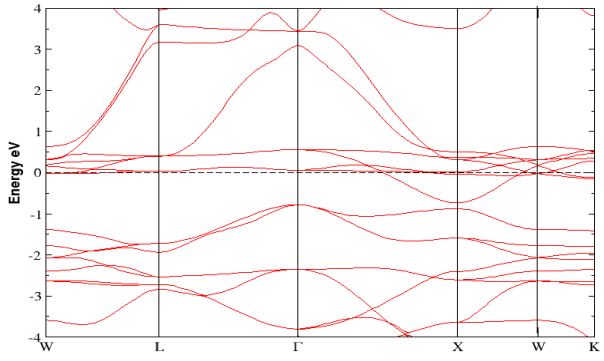

Fig. 5. Band structure for Majority spin

Further, Density of States (DOS) of primitive Co_2FeSi was calculated to check the nature of spin up and spin down electrons. It showed the similar nature as showed by the bands. Spin up states showed metallic nature in the spin up channel, while a gap near the Fermi level was found in the minority state as displayed by the Figure 3.

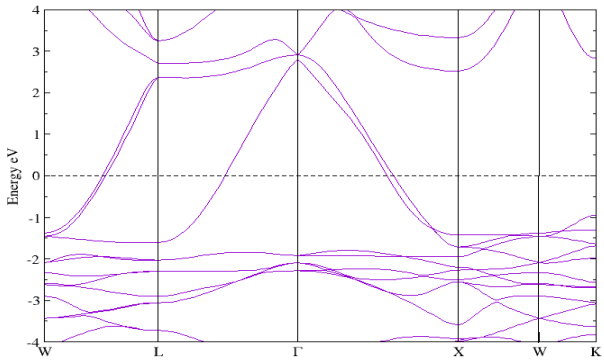

Fig. 6. Band Structure for minority spin

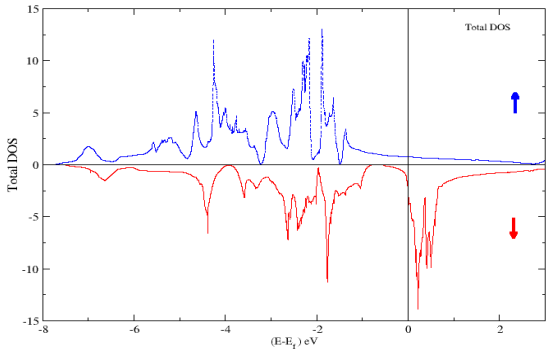

Fig. 7. DOS of Pristine Co_2FeSi

In order to check the condition of half-metallicity, the primitive Co_2FeSi was doped by Mn to 25%. After replacing 1 atom of Fe by Mn, the DOS calculations were performed. Figure 4 for DOS revealed the metallic nature in the spin up channel, while a gap near the fermi level was found in the minority state as similar to pristine Co_2FeSi. Here, the gap which was there in the pristine Co_2FeSi in the minority band near the fermi level was found to be reduced because of the presence of density of states. The band gap was reduced down by ≈ 0.018944 eV. Since no clear band gap was evident at fermi energy, 100% spin polarization is not possible. Doping Mn at 25% concentration, the fermi level was found to be switched slightly into valence band of spin down channel, thus the chances of half metallicity has reduced significantly.

The magnetic moments of constituent atoms were also calculated. The calculation revealed that the ground state magnetic structure of Co_2FeSi consists of Si atom anti-ferromagnetically aligned with that of Co(A), Co(C), Fe and Mn. Thus, local ferromagnetic structure of Co(A)-Co(C)-Fe-Mn is formed. The total magnetic moment of Co_2FeSi is 21.93 μ_B/cell which is 0.08 μ_B/cell greater than that of conventional structure.

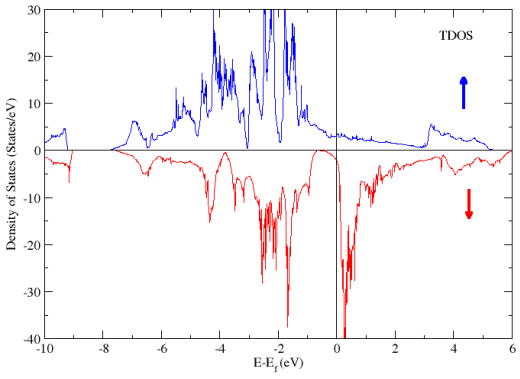

Fig. 8. DOS of 25% Mn doped Co2FeSi

DOS of spin up states for 2 Mn doped Co_2FeSi showed metallic nature similar to pristine band structure for majority state. Similarly, the gap was found to be widened which was found near the fermi level for minority spin state which is expressed by figure 5. Since no clear band gap is evident at fermi energy, 100% spin polarization is not possible. In comparison to the fermi energy of pristine Co_2FeSi, doping Mn at 50% concentration, Fermi gap has increased by ≈ 0.089645 eV. Since the width of band gap has increased and shifted near to the fermi level, the chances of half metallicity has risen in comparison to 25% Mn doping.

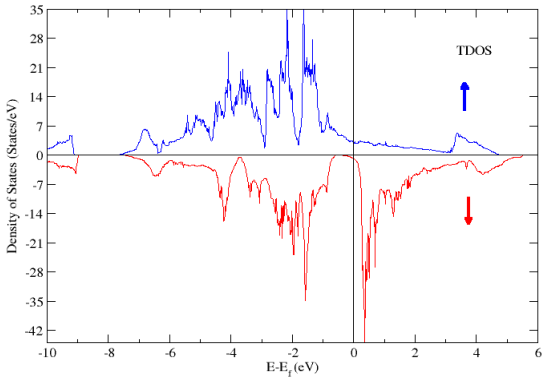

Fig. 9. DOS of 50% Mn doped Co2FeSi

The magnetic moment calculation revealed that the ground state magnetic structure of $Co_2Fe_{0.5}Mn_{0.5}Si$ contains Si atom anti-ferromagnetically aligned with that of Co(A), Co(C), Fe and Mn. Thus, local ferromagnetic structure of Co (A)-Co(C)-Fe-Mn is formed. The total magnetic moment of $Co_2Fe_{0.5}Mn_{0.5}Si$ is 21.69 μ_B/cell which is 0.14 μ_B/cell smaller than that of conventional structure.

IV. Conclusions

We have studied the band structure and DOS of Co_2FeSi and effects of doping Mn in the compound by first-principle calculation. The electronic structure calculations of pristine Co_2FeSi in the majority spin states show perfect metallic nature whereas for minority spin states an indirect energy gap near the Fermi level is observed to be 0.132 eV. Ground state magnetic structure of Co_2FeSi is found to be ferromagnetic with the magnetic moment of Si at D site aligned anti-ferromagnetically Co at A site, Co at C site and Fe at B site. The magnetic moment of Si was found to be very small in comparison to Co at A and C site and Fe atom at B site. Calculated magnetic moment of Co_2FeSi is 5.44 μ_B/cell. Doping of Mn was done according to the site preference rule and the results obtained from calculation of formation energy. Model of doped sample was created by substituting Fe atom at B site by Mn atom. Doping Mn at 25% concentration narrowed the band gap below the fermi level to some state extent. Thus, $Co_2Fe_{0.75}Mn_{0.25}Si$ is not found to be a perfect half-metal. Calculated total magnetic moment of $Co_2Fe_{0.75}Mn_{0.25}Si$ is 21.93 μ_B/cell which is not integer value. Integer value of magnetic moment signifies Half-metallicity. In case of 50% concentration of Mn atom, the fermi gap broadens in the minority spin channel than that of pristine Co_2FeSi. Thus, $Co_2Fe_{0.50}Mn_{0.50}Si$ likely holds more chances for half-metallicity. Calculated total magnetic moment of $Co_2Fe_{0.75}Mn_{0.25}Si$ is 21.69 μ_B/cell which is not integer value. The chances of half metallicity decreases in 25% Mn doped structure as the band gap gets narrowed. However, in the case of 50% Mn doped structure the band gap gets widened by 0.089645 eV indicating probably more chances for half-metallicity.

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