SUMMARY

OVERVIEW OF THE PRESENT STUDY

The discovery of magnetoresistance (MR), where the resistance of a thin film (ferromagnetic-nonmagnetic layer sandwich) is strongly magnetic field dependent, introduces a new horizon to existing conventional charge based devices [1-2]. It is known for more than 150 years that a magnetic field can change electrical resistance in a material, ever since first documented observation of MR in 1855 by William Thomson [3]. He reported that the electric conductivity of iron wire is diminished by longitudinal magnetization. The discovery of the giant magnetoresistance (GMR) [4-5] effect may be considered as the key event which revolutionized the field of digital recording. This helped the scientific community to investigate the novel materials based devices which manipulate both the spin and the charge of the electron. These are so called “spintronic” devices and may lead to more exotic information devices, capable of a wide variety of functionality [6-9].

The efficient spin-polarized carrier injection and transport is a major hindrance for the practical implementation of the spintronic devices. Many conventional ferromagnetic metals can have a substantial degree of spin polarization but are often unsuited for the advanced spin based technology due to low spin polarization and lack of efficient spin injection into conventional semiconductors due to resistivity differences and the formation of Schottky barriers.

A new class of materials which shows conduction by charge carriers of one spin direction exclusively absorbed a lot of attention considering their possible applications in spintronics [10]. Such types of novel materials are known as half-metallic ferromagnets (HMFs) and can be considered as hybrids between metals and semiconductors. Therefore, the HMFs exhibits 100% spin polarization at the $E_F$ which is supposed to maximize the efficiency of spintronics devices [11-12]. Till date, various materials have been proposed to be HMFs [13-19]. Amongst them, Heusler alloys [20-21] are most prominent to be used in spintronics applications.
MOTIVATION

Heusler alloys have raised the curiosity amongst the scientific community due to their unusual behavior right from the discovery of the ferromagnetic nature of Cu$_2$MnAl (in spite of its non-magnetic constituents) by F. Heusler. The research in transition metal (TM) based Heusler alloys is one of the most fascinating topics presently due to wide variety of interesting phenomena [22-23]. The research in transition metal based Heusler alloys is one of the most fascinating topics presently due to wide variety of interesting phenomena. In addition to the observed half metallic (HM) ferromanetism in some these alloys, there exist several reasons to pick out these alloys. The first one is the variety of properties of TMs and their compounds due to partly filled $d$ subshells, which are not only much more complicated, but have some important peculiarities in comparison with simple metals. The second reason is that these alloys generally display a high Curie temperatures and a coherent growth on top of conventional semiconductors because their lattices, in certain cases, matches closely to the semiconductors.

The applications of Heusler alloys in advanced spin based devices are only due to their exotic property i.e. half-metallicity. It is a very delicate property and is strongly influenced by the structural disorders and distortion in the particular systems [24-25]. Further, it is very important to check whether this property is sole nature of a particular alloy or can be changed with some doping. Therefore, the sustainability of this property under various disorders and distortions, and enhancement of minority band gap via suitable doping is of central importance.

In this thesis, we have systematically investigated the electronic and magnetic properties of transition metal based Heusler alloys with an effort to understand the effect of doping, distortion and disorder on the half-metallicity and magnetism. This study is of upmost importance in order to utilize Heusler alloys in device applications.

OBJECTIVES

The specific objectives of the present study were as follows:

1. To study the electronic and magnetic properties of semi Heusler alloy, NiCrSi and alloys obtained by substituting Si with Ge and P (i.e. NiCrGe and NiCrP) in order
to search the new candidates showing HM ferromagnetism and to understand the basic of the unusual property i.e. half-metallicity in these systems.

2. To study the effect of Fe-doping on half-metallicity and magnetism in Cr$_{2-x}$Fe$_x$CoZ (Z = Al and Si) inverse Heusler alloys. This study is focused on the tuning the Fermi level in order to get the higher spin polarization.

3. To search new quaternary Heusler alloy having the robust half-metallicity and which endures the practical limit of uniform and tetragonal distortion.

4. To study the effect of various anti-site disorders on half-metallicity and magnetism of Mn$_2$CoSi inverse Heusler alloy.

5. To study the effect of Mn-disorders on half-metallicity and magnetism of NiCoMnGa quaternary Heusler alloy.

In order to meet the above objectives, the entire work carried out for the present study has been divided into six chapters as per details given below:

Chapter 1: Basic Introduction

In this chapter, we have given a short introduction of overview of the research problem, spintronics, HM ferromagnetism and Slater-Pauling rule. The theory of Heusler alloys, classification and importance of Heusler alloys for spintronic devices are also discussed in details. An outline of density functional theory (DFT) and a description of XC potentials, Local Density Approximation (LDA), Local Spin Density Approximation (LSDA) and Generalized Gradient Approximation (GGA) are described. The introduction of Full Potential Linearized Augmented Plane Wave (FPLAPW) method, the one used for calculations comprising the thesis, has also been discussed in details.

Chapter 2: Ordered Heusler alloys

In this chapter, we have discussed the electronic properties of some pristine or ordered semi-Heusler alloys. The investigation of the electronic and magnetic properties of semi Heusler alloy, NiCrSi and alloys obtained by substituting Si with Ge and P (i.e.
NiCrGe and NiCrP) has been presented. The present work has focused on to search the new candidates showing HM ferromagnetism and to understand the basic of the unusual property i.e. half-metallicity in these systems, using FPLAPW method within GGA formalism for XC effects.

**Chapter 3: Cr$_{2-x}$Fe$_x$CoZ (Z = Al and Si) inverse Heusler alloys: Doping effect**

It is established that $E_F$ tuning would be one of the essential techniques to achieve the materials with higher spin polarization. Therefore, in this chapter, we have studied the effect of TM doping on the half-metallicity and magnetism of Cr$_2$CoZ (Z = Al and Si) inverse Heusler alloys to shift the Fermi level in middle of the minority-spin gap in order to have high spin polarized materials. The electronic and magnetic properties of Cr$_{2-x}$Fe$_x$CoZ (Z = Al and Si) for doping concentrations, $x = 0.25, 0.50, 0.75$ and $1.0$ have been investigated within GGA as XC functional.

**Chapter 4: FeCrMnSb Heusler alloys: Distortion effect**

In this chapter, we have discussed the electronic and magnetic properties of a newly predicted quaternary Heusler alloy, FeCrMnSb. This alloy is a true half-metallic ferromagnet and half-metallicity and magnetism has been analyzed within ±15% of uniform and tetragonal distortions.

**Chapter 5: Mn$_2$CoSi and NiCoMnGa Heusler alloys: Disorder effect**

The half-metallicity is a very fragile property which normally attributed to the ordering of a half-metallic material. But, as the real materials always contains a few degrees of anti-site disorders, it is necessary to take into account the effect of various disorders while studying the electronic and magnetic properties of Heusler alloys. Heusler alloys based thin-films often exhibit a degree of atomic disorder which leads to the lowering of spin polarization in spintronics devices. Therefore, we present in this chapter the study of atomic anti-site disorders effects on the half-metallicity of Heusler alloy. The work in the first part of this chapter solely concerns with electronic structure and magnetic properties of pristine Mn$_2$CoSi inverse Heusler alloy and its disordered
phases. Second part of this chapter is devoted to effect of Mn-disorder on half-metallicity and magnetism of NiCoMnGa quaternary Heusler alloy.

MAJOR OUTCOMES

The outcomes of the present study have been described in terms of the following important conclusions:

1. The NiCrZ Heusler alloys crystallize in $C1b$-structure such that the unit cell contains three atoms as basis with Ni atom at 4a (0,0,0), Cr at 4c ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and Z at 4d ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$) and with a void at 4b ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) in Wyckoff coordinates. We predict that these alloys are true HMFs, showing an indirect band gap in minority density of states (DOS). This gap is largest in case of NiCrSi (0.91 eV). This value of minority band gap reduces on substitution of $sp$-element in NiCrSi i.e. 0.75 eV for NiCrGe and 0.80 eV for NiCrP. This reduction is explained on the basis of hybridization between the TM atoms and $sp$-elements. The main contribution in total magnetic moment comes from Cr-$3d$ states. Moreover, it has an integer value in present alloys as expected by the Slater-Pauling rule for a half-metal.

2. The $\text{Cr}_2\text{CoZ}$ (Z = Al and Si) inverse Heusler alloys crystallize in $X$-structure and the Wyckoff positions for this structure are 4a (0,0,0), 4b ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$), 4c ($\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$) and 4d ($\frac{3}{4}$,$\frac{3}{4}$,$\frac{3}{4}$), where Cr occupies the two inequivalent 4a and 4c sites as nearest neighbors. Beside this, Co and Z atoms reside at 4b and 4d, respectively. Both parent alloys ($\text{Cr}_2\text{CoAl}$ and $\text{Cr}_2\text{CoSi}$) are not true half-metallic ferromagnets. However, the calculated spin polarization, 68 % for $\text{Cr}_2\text{CoAl}$ and 94 % for $\text{Cr}_2\text{CoSi}$, is quite appreciable. The gradual replacement of one Cr sublattice with Fe induces the half-metallicity in these systems. The half-metallicity starts to appear in $\text{Cr}_{2-x}\text{Fe}_x\text{CoAl}$ from $x = 0.50$ and from $x = 0.25$ in $\text{Cr}_{2-x}\text{Fe}_x\text{CoSi}$ Heusler alloys. For $x = 1.0$, the resultant alloys emerge out to be stable in $Y$-structure. The end alloys, CoFeCrAl and CoFeCrSi, are true HMFs with integer magnetic moment of 1.00 $\mu_B$ and 3.00 $\mu_B$ per formula unit, respectively, which are as desired by Slater-Pauling rule for a half-metal. The calculated formation energies for both end alloys advocate the structure stability for these alloys and agree with the previously calculated values of formation
energies. The maximum values of minority-spin gap and half-metallic gap or spin-flip gap are found to be 0.672 and 0.320 eV, respectively, for CoFeCrSi among all studied alloys. A very good agreement between the structural properties of CoFeCrAl with available experimental study is obtained which confirms the credibility of this work. The Fermi level tuning by Fe-doping makes these alloys highly spin polarized and thus these can be used as promising candidates for spin valves and magnetic tunneling junction applications.

3. The FeCrMnSb quaternary Heusler alloy is stable in $Y$-structure which is verified by performing energy minimization as a function of lattice constant with respect to the different possible site occupation, namely $Y_I$, $Y_{II}$ and $Y_{III}$. For $Y_I$ structure, the Wyckoff positions, 4a (0,0,0), 4b (½,½,½), 4c (¼,¼,¼), and 4d (¾,¾,¾) are occupied by Sb, Mn, Fe and Cr atom, respectively. Similarly $Y_{II}/Y_{III}$ structure is realized by placing Sb, Mn, Fe and Cr at (4a, 4d, 4b and 4c)/(4a, 4d, 4c and 4b), respectively. Further, this structure stability is also verified by various conditions governed by elastic constants $c_{ij}$. It is a true half-metallic ferromagnet with integer magnetic moment of 2.00 $\mu_B$ per formula unit which follows strictly the Slater-Pauling rule for half-metal. The maximum values of minority-spin gap and HM gap or spin-flip gap are to be 0.65 eV and 0.1 eV, respectively. The endurances of half-metallicity under uniform and tetragonal distortions is a prime necessity of a half-metallic material to be used in device applications. The half-metallic character of FeCrMnSb sustains within -6% to 9% of uniform distortion and -9% to 12% of tetragonal distortion. This make the FeCrMnSb quaternary Heusler alloy a potential candidate for applications of spin valves and magnetic tunnel junction applications technology.

4. All three possible disorders namely $DO_3$-, $A2$- and $B2$-type are investigated in details. The mixing of the position of Mn atoms by Co atoms in Mn$_2$CoSi inverse Heusler alloy results in the $DO_3$-type disorder. The $B2$-type disorder was modeled by swapping the position of Si atoms by Co atoms, whereas the $A2$-type disorder was realized by the replacement of Mn atoms by Si atoms. These disorders were simulated using a Mn$_2$CoSi supercell composed of 16 atoms (eight Mn atoms, four Co atoms and four Si atoms). Therefore the smallest amounts of disorders that can be
introduced were 12.5% for A2 or DO$_3$-type and 25% for B2-type disorder in 1×1×1 cell of Mn$_2$CoSi inverse Heusler alloy. The B2-type disorder destroys the half-metallicity, whereas it sustained for DO$_3$- and A2-type disorders. Lower formation energy/atom for A2-type disorder than other two disorders in Mn$_2$CoSi advocates the stability of this disorder. The total magnetic moment shows a strong dependence on the disorder and the change in chemical composition. The 100% spin polarization even in the presence of few disorders explicitly supports that these disorders should not be a hindrance for Mn$_2$CoSi inverse Heusler alloy to be used in device applications. Second part of this chapter is concerned with Mn-disorder in (Ni,Co)MnGa quaternary Heusler alloy. The excess of Mn in Ni$_{1-x}$CoMn$_{1+x}$Ga is created by using the (1×1×1) supercell. The minimum disorder, therefore, that can be introduced is 25%. Along with the same calculation procedure adopted above, the full relaxations of internal atomic coordinates have also been carried out prior to study the electronic and magnetic properties of present systems. We observe that the increasing Mn concentration in Ni$_{1-x}$CoMn$_{1+x}$Ga (x = 0, 0.25, 0.50 and 0.75) lowers the ferromagnetic character of parent (Ni,Co)MnGa alloy. This change creates two inequivalent Mn sites aligning antiparallel to each other and generates the ferrimagnetic ordering in all resultant disordered alloys. Further this replacement onsets a structural change from Y- to X-structure. A suitable band gap in minority spin channel places these disordered alloys, Ni$_{1-x}$CoMn$_{1+x}$Ga (x = 0.50, 0.75) in the category of HM ferrimagnets. This gap actually depends on how Ga-p states interact with hybrids of TM-d states. Due to very high degree of spin polarization, these can also serve as the potential candidate for spintronic applications. The highest magnetic moment is found to be 4.95 $\mu_B$ for ordered (Ni,Co)MnGa alloy whereas it decreases with increase in Mn-concentration for disordered systems. The variation of half metallicity with increasing Mn concentration is analyzed. The stability of FM and FiM for present ordered and disordered alloys, respectively, is also examined.

FUTURE PERSPECTIVES

Some of the future projections of our study are:
Summary

1. Having understood the effect of doping, distortion and disorder in Heusler alloys, there is still a vast scope to understand the other factors such as the interface states and temperature driven excitations which can also destroy the most central properties of Heusler alloys i.e. half-metallicity. So one of our future perspectives will be to incorporate these factors in the ab initio calculations.

2. After the in-depth study of half-metallicity in ordered, doped, distorted and disordered Heusler alloys in bulk form, our next aim will be to study these effects in thin film structures because it suits the actual device fabrication.

3. The three-dimensional topological insulators (3DTIs) based on Heusler alloys are currently at the focused research. These alloys might play a vital role in realization of quantum spin hall effect and hence the in quantum computation. The semi-Heusler alloys can be made topological insulator via strain engineering. So, we will also investigate the new Heusler alloys with the signature of 3DTIs.

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