

**STUDY OF DOPING AND DISORDER ON HALF METALLICITY OF
TRANSITION METAL BASED HEUSLER ALLOYS**

**FINAL REPORT
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1. Overview of the problem

The magnetic memory based devices serve as the basis for information processing and storage in today's world. V. Poulsen was the first person who demonstrated the magnetic recording in 1898. His magnetic recording device was consisting of a wire wrapped around a drum. In 1928, the first magnetic tape recorder was developed by F. Pfleumer. Early magnetic storage devices were designed to record analog audio signals. In fact, magnetism in metals has been the backbone of information storage from many years. In the past three decades, however, tape recording has been gradually replaced by digital recording. The discovery of the giant magnetoresistance (GMR) 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 showing a wide variety of functionality. The efficient spin-polarized carrier injection and transport is a major hindrance for the practical implementation of the spintronic devices. The 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. Such types of novel materials are known as half-metallic ferromagnets (HMFs) and can be considered as hybrid between metals and semiconductors. Therefore, the HMFs exhibit 100% spin polarization at the E_F which is supposed to maximize the efficiency of magneto-electronic devices. Till date, various materials have been proposed for achieving half-metallic (HM) ferromagnetism. Amongst them, Heusler alloys are most prominent for applications in spintronics. The Heusler alloys are named after a German mining engineer Friedrich Heusler, who studied these alloys in 1903. These alloys are illustrious right from the time of their discovery due to the tendency of exhibiting a number of miscellaneous magnetic phenomena like antiferromagnetism, heavy fermionic behavior or Pauli paramagnetism, itinerant and localized magnetism and helimagnetism.

The research in transition metal based Heusler alloys is one of the most fascinating topics in current scenario due to a wide variety of interesting phenomena. In addition to the observed HM ferromagnetism in some of these alloys, there exist several reasons to pick out these alloys. The first one is the variety of properties of transition metals (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 high Curie temperatures and coherent growth on top of conventional semiconductors because their lattices, in certain cases, match closely to the semiconductors.

The semi-Heusler alloys XYZ are ternary intermetallics involving generally two different transition metals (X and Y), and a sp -element (Z). They crystallize in the cubic MgAgAs-type or $C1_b$ -type structure. This structure consists of three filled and one vacant interpenetrating fcc sublattices [1]. In principle, the semi-Heusler alloys form a ternary stuffed variant of classical electron closed-shell semiconductors which crystallize in a zincblende (ZnS-type) lattice, such as GaAs. The eight valence electrons are distributed among three atoms instead of two. The third atom occupies the octahedral vacancies in the ZnS-type lattice. This fact automatically leads to a formation of a rocksalt-like sublattice characterized by ionic bonding interaction [2]. The HMFs, like NiMnSb semi-Heusler alloys have interesting physical properties and are attractive for research community due to their potential for technological applications particularly in the field of spintronics i.e. tunnel junctions, spin valves etc. [3]. NiMnSb has relatively high Curie temperature ($T_C = 730$ K), well above the room temperature, HM character and structural similarity with common semiconductors. The HM ferromagnetism observed in NiMnSb has boosted the research activities in semi Heusler alloys from both theoretical and experimental front. The semi-Heusler alloys NiMnZ ($Z = \text{Si, P, Ge and As}$) were predicted as HMFs with high T_C (715–1050 K) by Dinh *et al.* [4] using Monte-Carlo simulation technique. Galanakis *et al.* [5] studied NiCrSi and NiMnSi with the full-potential non-orthogonal local orbital minimum-basis band structure scheme (FPLO) and the full-potential screened Korringa-Kohn-Rostoker (FSKKR) method within the local spin density approximation (LSDA). They found that both the FPLO and FSKKR methods yielded nearly the same DOS and minority-spin gap. Zhang *et al.* [6] predicted NiCrM ($M = \text{P, As, Sb, S, Se and Te}$) as HMFs by FPLAPW method within LSDA formalism. Luo *et al.* [7] predicted that NiCrAl,

NiCrGa and NiCrIn are possible half-metals with an energy gap in the minority spin channel and 100% spin polarization at the Fermi level (E_F).

The applications of Heusler alloys in advanced spin based devices are only due to their exotic property i.e. half-metallicity. Many unusual features arise from the HM nature of these alloys. The half metallicity is a very delicate property and is strongly influenced by the structural disorders and distortion in the particular systems. Further, it is very important to check whether this property is of robust nature in a specific 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 project work, the electronic and magnetic properties of transition metal based Heusler alloys have been studied with an effort to understand the effect of doping, distortion and disorder on the magnetism and half metallicity of these alloys. To achieve this goal, full potential calculations of the ground state properties of some selected Heusler alloys have been performed.

2. Theoretical Approach

The most popular and successful approach for performing first-principles electronic structure and total energy calculations for a wide range of materials and biomolecules is density-functional theory (DFT). The DFT is related to correlated many-body systems and is an extremely successful approach for the description of ground state properties of metals, semiconductors and insulators. This has become the primary tool for the calculations of electronic structures of materials and to predict their ground state properties accurately.

The first principles solid-state calculations of the electronic structures of some Heusler alloys were performed using the relativistic all electron full potential linearized augmented plane wave (FPLAPW) method as implemented in the WIEN2k code [8]. The calculations are based on the DFT [9]. The generalized gradient approximation (GGA) within Perdew-Burke-Ernzerhof parameterization [10] was used to construct exchange and correlation (XC) potentials in the calculations. The k-space integration was performed by the modified tetrahedron method [11]. For these calculations, the radii of the muffin-tin spheres representing all the atoms were chosen so as to obtain nearby touching sphere. The maximum value for the orbital quantum number (l_{\max}) for the waves inside the atomic spheres was 10. The wave function in the interstitial region

was expanded by plane waves with a cut-off decided by $R_{\text{MT}}k_{\text{max}} = 7$, while the charge density was expanded using Fourier expansion up to $G_{\text{max}} = 12 \text{ a.u.}^{-1}$. The convergence of the calculated eigen values was checked with respect to the number of augmented plane waves and also with respect to the number of k-points used. The energy convergence criterion was set to 10^{-4} Ry/cell and the charge convergence was also monitored along with it.

3. Major Problems and Outcomes

(I) $\text{Cr}_{2-x}\text{Fe}_x\text{CoZ}$ ($Z = \text{Al, Si}$) inverse Heusler alloys

After reviewing the literature, we observed that there are plenty of studies for effect of doping of half-metallicity and magnetism in $L2_1$ -type Heusler alloys but there are only few studies concerning the effect of doping in inverse Heusler alloys, which are rather more important than their full-Heusler counterparts. We have been motivated by this point and demonstrated in this work that how position of E_F can be pinned in middle of $E_{g\downarrow}$ via doping of Fe for Cr in Cr_2CoZ ($Z = \text{Al, Si}$) inverse Heusler alloys to get the maximum degree of spin polarization. Thus, this work is concerned with the effect of doping of transition metal atom on electronic and magnetic properties of ternary inverse Heusler alloys. The tuning of E_F has been demonstrated via doping of Fe for Cr in $\text{Cr}_{2-x}\text{Fe}_x\text{CoZ}$ ($Z = \text{Al, Si}$) ($x = 0, 0.25, 0.50, 0.75$ and 1) Heusler alloy to get the maximum degree of spin polarization. The parent compounds, Cr_2CoZ ($Z = \text{Al}$ and Si), are not the half-metallic ferromagnets but the substitution of Fe for Cr shifts the E_F towards the middle of minority-spin gap which make them true HMF.

A conventional $1 \times 1 \times 1$ cell of base compound Cr_2CoZ ($Z = \text{Al/Si}$) with 16 atoms was used to simulate the various doping concentrations. The Cr_2CoZ ($Z = \text{Al}$ and Si) inverse Heusler alloys crystallize in X -type 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. This is clearly shown in Fig. 1 along the diagonal of the primitive cell of Cr_2CoSi inverse Heusler alloy. In our nomenclature, they are represented by Cr^{I} and Cr^{II} . Beside this, Co and Z atoms reside at 4b and 4d sites, respectively. The parent Cr_2CoZ ($Z = \text{Al}$ and Si) inverse Heusler alloys were proposed by Skaftouros *et al.* [12].

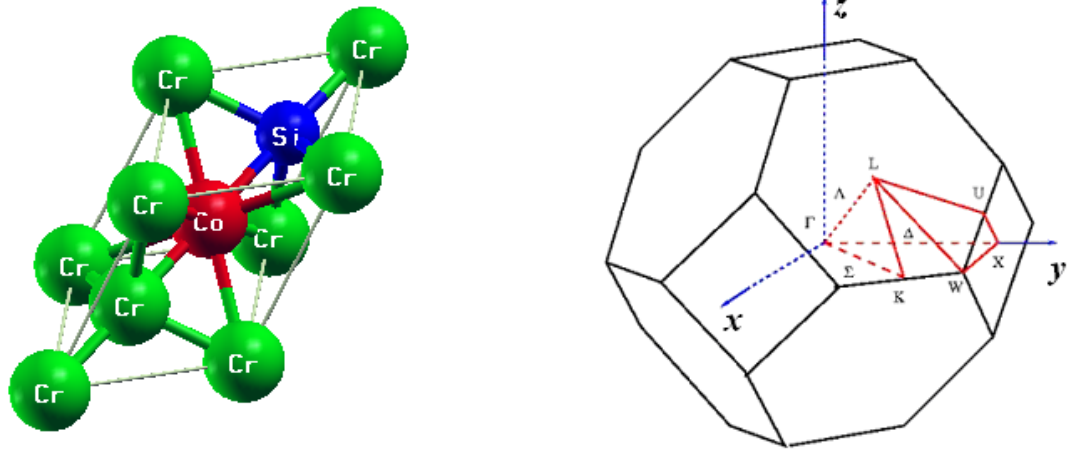


Fig. 1 The primitive cell of Hg₂CuTi-type Cr₂CoSi inverse Heusler alloy (left) and corresponding Brillouin Zone (BZ) and its IBZ (in red color) on right.

Outcomes

- Both parent (undoped) alloys, Cr₂CoAl and Cr₂CoSi, are not found to be true half-metallic ferromagnets. However, the calculated spin polarization, 68 % for Cr₂CoAl and 94 % for Cr₂CoSi, is quite appreciable.
- The half-metallicity starts to appear in Cr_{2-x}Fe_xCoAl for $x = 0.50$ and for $x = 0.25$ in Cr_{2-x}Fe_xCoSi Heusler alloys.
- For $x = 1.0$, the resultant alloys emerge out to be stable in Y-type structure. These end compounds so obtained, CoFeCrAl and CoFeCrSi, are true half-metallic ferromagnets with integer magnetic moment of 1.00 μ_B and 3.00 μ_B per formula unit, respectively, which is in accordance with the Slater-Pauling rule for a half-metal.
- The calculated formation energies for both end alloys advocate the structure stability for these alloys and these trends are in the agreement with the previously calculated values of formation energies.
- The calculated values of minority-spin gap and half-metallic gap are found maximum for end alloys in both cases.
- The spin polarization increases with increase in doping concentration of Fe. The electron dopant behaviour of Fe for this substitution may be the possible reason for enhancement of spin polarization.

- The Fermi level tuning in $\text{Cr}_{2-x}\text{Fe}_x\text{CoZ}$ ($Z = \text{Al}, \text{Si}$) alloys can be an essential technique to achieve higher spin polarization and the proposed systems may be used as the ideal candidate for spin valves and magnetic tunnel junction applications.

(II). FeCrMnSb quaternary Heusler alloy

Apart from the conventional Heusler alloys i.e. X_2YZ ($L2_1$ -type structure) and XYZ (CI_b -type structure), where X and Y are the two TMs atoms and Z as a main group element, quaternary Heusler alloys ($\text{XX}'\text{YZ}$) are new structural variant of Heusler alloys family which have come to the center of attraction of materials scientists in the last decade only. The primitive cell of $L2_1$ -type structure contains four atoms that form the base of fcc primitive cell. The result is a lattice with $Fm\bar{3}m$ (space group no. 225) symmetry where the Wyckoff positions, 4a (0,0,0), 4b ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), and 8c ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) are occupied by Z, Y and X atoms, respectively, as depicted in Fig. 2(a).

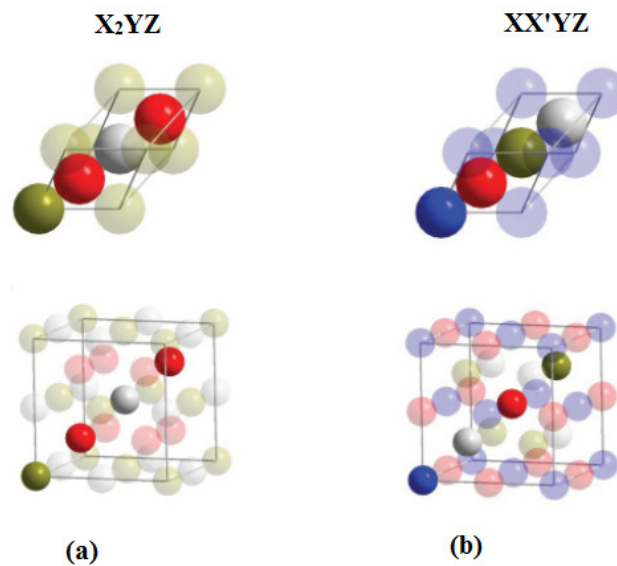


Fig. 2 Crystal structure of (a) full-Heusler alloy or $L2_1$ -type structure and (b) quaternary Heusler alloy or Y-type structure [13]. The highlighted spheres represent the position of atoms on principal diagonal.

The simple-cubic sublattice is lost if one of the X atoms is replaced by a third type of transition metal X' [13]. In this way, a new alloy can be obtained which crystallizes in Y-type structure (Prototype LiMgPdSn) with no inversion symmetry

(space group 216- $F\bar{4}3m$). The Wyckoff positions 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 ($\frac{3}{4},\frac{3}{4},\frac{3}{4}$) are occupied by Z, Y, X and X', respectively, as shown in Fig. 2(b).

A large number of possible atomic combinations in this type of alloy guides a way to design a wide range of new materials. The tuneability of electronic and magnetic properties of these systems with different combinations of atoms can be used to engineer the novel materials to meet the demand of spintronics. The recent studies [14-16] on quaternary Heusler alloys demonstrated their potential in the field of spintronics. In continuation to the wide spectrum of Heusler alloys, in this work, we propose a new quaternary Heusler alloy (FeCrMnSb) which can be proved as an ideal candidate for spintronic applications. Further, as the lattice mismatches with adjacent layers in a material can be possible due to induced strains when it is incorporated in to a device [17], therefore, it is necessary to analyze the effect of distortions on HM property of this alloy. Hence for device utility of FeCrMnSb, we also studied it under the effect of uniform and tetragonal strains.

As mentioned above, the quaternary Heusler alloys crystallize in Y-structure and based on the relative positions of three TMs (Fe, Cr and Mn), in present case, three structures Y_I , Y_{II} and Y_{III} may be possible. For Y_I structure, the Wyckoff positions, 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 ($\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$) were occupied by Sb, Mn, Fe and Cr atom, respectively. Similarly Y_{II}/Y_{III} structure was realized by placing Sb, Mn, Fe and Cr at (4a, 4d, 4b and 4c)/(4a, 4d, 4c and 4b), respectively.

The FeCrMnSb quaternary Heusler alloy after optimization was found be most stable in Y_I -type 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 ($\frac{3}{4},\frac{3}{4},\frac{3}{4}$), respectively, occupied by Sb, Mn, Fe and Cr atoms. This site occupation is shown in Fig. 3.

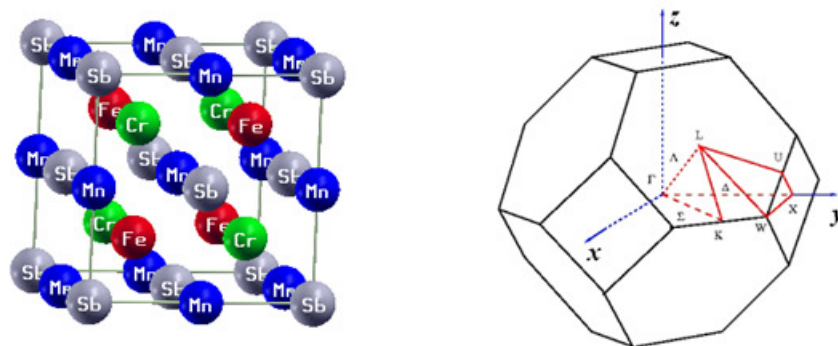


Fig. 3 Unit cell of FeCrMnSb quaternary Heusler alloy (left side) and the symmetry k -points in IBZ (right side).

Outcomes

- We have proposed a new quaternary Heusler alloy, FeCrMnSb as a HMF using first principles band structure calculations.
- The stability of the structure has been checked for different site occupations i.e. Y_I , Y_{II} and Y_{III} . The optimization of the cubic lattice parameters for all three possible configurations revealed the lowest energy for Y_I structure with a ferromagnetic ground state. The stability of Y_I structure is again confirmed using stability conditions governed by three independent elastic constants (c_{ij}).
- The HM gap appears in the minority spin channel. The alloy contains an indirect minority band gap along the Γ - X direction.
- The bonding states in the majority spin channel are mainly formed by Fe- d and Mn- d states, whereas Fe- d and Cr- d electrons are main building block of minority bonding states.
- The Sb- p states remain low ~ -4.0 eV, nevertheless, these states are effectively hybridized with d -states of TM atoms and determine the occupancy of p - d orbitals which further decides the position of E_F and hence energy gap MIC.
- The sensitivity of the half-metallicity of this alloy was analyzed under uniform strain and tetragonal distortion keeping the volume of unit cell constant and it is found that the half metallicity remains robust against the uniform strain from -6% to 9% and the tetragonal strain from -9% to 12%.
- The total spin magnetic moment of FeCrMnSb is found to be $2.0 \mu_B$ i.e. an integer value which is in accordance with the Slater-Pauling rule for a half-metal. The major part of total magnetic moment mainly comes from Mn site.
- The value of spin magnetic moment at Cr site is negative. This is due to the antiparallel alignment of Cr with rest of TM atoms which arises from the strong interatomic covalent interaction of the Cr- d , which leads to the antiferromagnetic alignment.

(III). Mn₂CoSi inverse Heusler alloy

While there is plethora of studies existing in the literature for the effect of disorders and defects on the physical properties of conventional Heusler alloys, we found a lack of such studies for inverse Heusler alloys and quaternary Heusler alloys. These alloys show a great potential in spintronic applications and deserve a thorough

study to understand the relation between spin polarization, magnetism and various possible disorders. So, we have highly motivated to study such alloys under the effects of various possible disorders. We have discussed the effect of various antisite disorders in inverse Heusler alloy, Mn_2CoSi , on half-metallicity and magnetism. We have selected Mn_2CoSi inverse ternary Heusler for this study due to its sustainable half-metallicity for wide range of lattice constant (5.4 \AA - 5.9 \AA) [18] and also because such type of alloys has already been synthesised [19].

The Mn_2CoSi inverse Heusler alloys crystallizes in X - type 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 ($\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$). Two inequivalent Mn atoms occupy the 4a and 4c sites as nearest neighbors as shown in Fig. 4. In our nomenclature, they are represented by Mn^I and Mn^{II} . Beside this, Co and Z atoms reside at 4b and 4d sites, respectively. All three possible disorders in Mn_2CoSi i.e. DO_{3-} , $A2$ - and $B2$ -type, have been investigated in detail. The supercell ($1 \times 1 \times 1$) has been used to introduce 12.5% DO_{3-} , $A2$ -type and 25% $B2$ -type disorders in the ordered Mn_2CoSi cell.

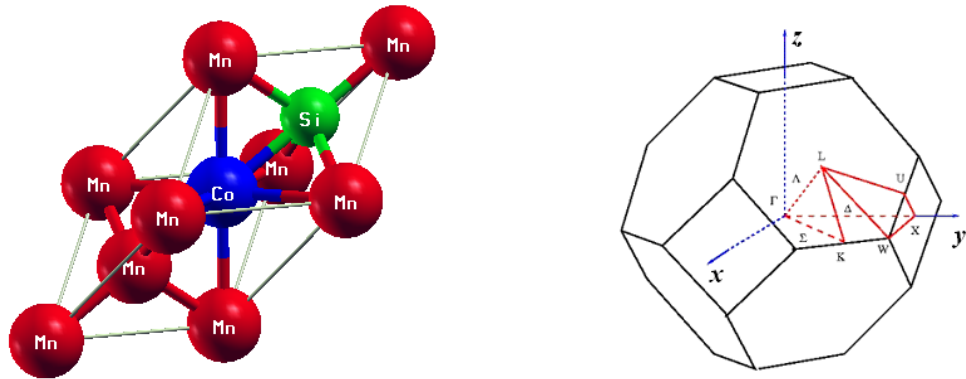


Fig.4 The primitive cell of Mn_2CoSi inverse Heusler alloy (Hg₂CuTi-type) and its corresponding Brillouin Zone (BZ) and irreducible BZ (IBZ) on right side (shown in red color).

Outcomes

- It is found that the $E_{g\downarrow}$ for DO_{3-} , $A2$ -type disorders keeps on increasing with the increase in amount of disorders and 100% spin polarization is maintained in both disorders for all concentrations.

- The inclusion of $B2$ -type disorder destroys the half-metallicity. Therefore, it should be avoided in the experimental fabrication of this alloy
- The calculated formation energy shows that the $A2$ -type disorder is most likely to occur. However, the 100% spin polarization for this assure that it may not hinder the use of Mn_2CoSi inverse Heusler alloy in spin based device application.
- We believe that the study of disorders in Mn_2CoSi Heusler alloy provides the authentic data for ground state properties which can be compared with the experiments in future.

(IV). Mn-disorder in NiCoMnGa quaternary Heusler alloy

The quaternary Heusler alloy, NiCoMnGa has been studied by incorporating anti-site disorder in order to check the robustness of half metallicity. This alloy is selected for this study because it has been predicted as HMF already and synthesized by Alijani *et al.* [20] with a high T_C (646 K), well above room temperature. We have discussed the effect of atomic Mn- disorder on the electronic and magnetic properties of ordered (Ni,Co)MnGa quaternary Heusler alloy. The important results of this study are presented for further experimental/theoretical investigations in future. The quaternary Heusler alloys can be distinguished from the conventional ternary $L2_1$ - and Cl_b -type Heusler alloys in terms of site occupancy of constituent atoms as shown in Table 1.

Table 1: Possible structures of ternary and quaternary Heusler alloys

Formula	Prototype	Example	Occupancy sequence	Structure	Space group
$XX'YZ$	LiMgPdSn	NiCoMnGa	Ni-Co-Mn-Ga	Y	$F\bar{4}3m$
X_2YZ	Cu_2MnAl	Ni_2MnGa	Ni-Mn-Ni-Ga	$L2_1$	$Fm\bar{3}m$
X^*_2YZ	Hg_2CuTi	Mn_2NiGa	Mn-Mn-Ni-Ga	X	$F\bar{4}3m$
XYZ	$MgAgAs$	$NiMnGa$	Ni-Mn-(void)-Ga	Cl_b	$F\bar{4}3m$

The NiCoMnGa quaternary Heusler alloy crystallizes in Y -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

$(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$, respectively, occupied by Ga, Mn, Ni and Co atoms. This site occupation is shown in Fig. 5.

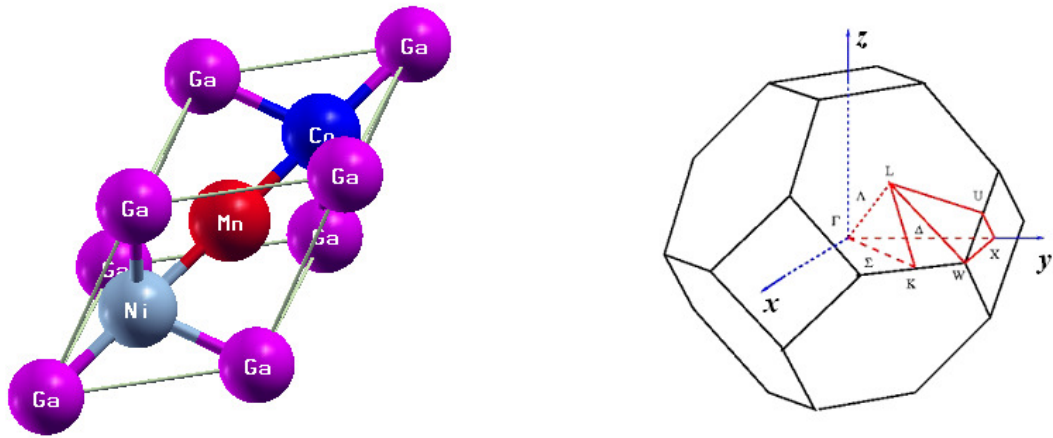


Fig. 5 The primitive cell of Y-type NiCoMnGa quaternary Heusler alloy (left) and its corresponding Brillouin Zone (BZ) and IBZ (in red color) on right.

In order to simulate the ground state properties of disordered $\text{Ni}_{1-x}\text{CoMn}_{1+x}\text{Ga}$ ($x = 0.25, 0.50, 0.75$) Heusler alloys from first-principles, the exact lattice constants for these in stable configuration should be found initially. As the present alloys are the intermediate ones between FM-(Ni,Co)MnGa ($x = 0$) and FiM- Mn_2CoGa ($x = 1$) HAs, therefore systematic structural optimization of these alloys have been performed in the neighbourhood of experimental lattice parameters of ordered (Ni,Co)MnGa HA in both, ferromagnetic (FM) and ferrimagnetic (FiM) configuration. The FiM configuration has been realized by flipping the spin of one of Mn-atoms whereas for FM configuration, the spins of both Mn-atoms have been kept same. Our calculations predict the stability of FiM ground state over the FM state for all the intermediate alloys.

Outcomes

- A systematic analysis of the transition from ferro- to ferri-magnetic ordering in stoichiometric (Ni,Co)MnGa quaternary Heusler alloy is presented by increasing Mn-disorder.

- The antiparallel alignment of magnetic moment of the extra Mn^{II} atom with respect to Mn^I atom initiates the FiM ordering in the studied disordered compounds.
- The total magnetic moment also decreases with increasing Mn-disorder.
- A suitable band gap in the minority spin channel places the 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 a very high degree of spin polarization, these can also serve as the potential candidate for spintronic applications.
- Our FPLAPW calculations present exhaustive data for a realistic comparison of electronic and magnetic properties of the studied disordered alloys with future experiments as the disorders cannot be ignored in experimental synthesis.

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List of Publication

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