3.1 Introduction

The research on HM Heusler alloys is intense and several such alloys have been studied [1-14] so far. An interesting case can also be the HM ferrimagnets (HMFi) or HM antiferromagnets [15-16]. In such type of compounds, the different TM atoms in the unit cell have antiparallel magnetic spin moments. These materials are much more desirable than their ferromagnetic counterparts in magneto-electronic applications. This is mostly due to the fact that the small value of the total magnetic moment in these systems provides additional advantages [21]. For example, they do not give rise to strong stray fields in devices and are less affected by external magnetic fields. Some perfect Heusler alloys like FeMnSb and Mn$_2$VAl are predicted to show half-metallicity in conjunction with ferrimagnetism [22-23]. These alloys possess small magnetic moment and high $T_C$ [17] due to strong direct exchange interaction between like atoms. Various theoretical and experimental studies have been devoted to these systems [17-20]. The notion of HM ferrimagnetism evolved with the excellent article of Leuken et al. [15] in which they proposed, by first-principles calculations, the possibility of realizing HM antiferromagnets, i.e., systems with 100% spin polarization of the conduction electrons without showing a net magnetization. Liu et al. [8] studied the electronic structures and magnetic properties of Mn$_2$CoZ ($Z$ = Al, Ga, In, Si, Ge, Sn and Sb) alloys with Hg$_2$CuTi-type or X-type structure and found that the alloys with $Z$ = Al, Si, Ge, Sn, and Sb are HMFi. They also successfully synthesized the Mn$_2$CoZ ($Z$ = Al, Ga, In, Ge, Sn, Sb) and confirmed the X-structure instead of the conventional $L2_1$-type structure using the x-ray diffraction method and Rietveld refinement. Meinert et al. [20] successfully prepared epitaxial thin films of the HM Mn$_2$CoGa alloy by dc magnetron co-sputtering and revealed the antiparallel alignment of the two inequivalent Mn moments which established the ferrimagnetism of this alloy. Galanakis et al. [18] in 2007 introduced the concept of fully compensated ferrimagnets (FCF) with Cr$_2$MnZ ($Z$ = P, As, Sb and Bi) alloys which have exactly 24 valence electrons per unit cell and almost vanishing magnetic moment according to Slater-Pauling rule. Meinert et al. [17], using ab initio band structure calculations, showed that the Mn$_2$CoZ ($Z$ = Al, Ga, In, Si, Ge, Sn and Sb) alloys crystallize in X-type structure. The indirect, long-
ranged interactions are exponentially damped and the intra-sublattice interactions are mostly antiferromagnetic. The values of $T_C$ calculated within the mean field approximation are in reasonable agreement with experimental data for Mn$_2$CoSn and Mn$_2$CoSb. Recently, Galanakis *et al.* [24] presented the wide first-principles calculations on the inverse Heusler alloys having the chemical formula X$_2$YZ, where X = Sc, Ti, V, Cr, or Mn; Z = Al, Si, or As; and the Y ranges from Ti to Zn. Out of these studied alloys, many have been identified as HMFi. All the studied alloys showed half-metallicity and their calculated magnetic moment were found to be in accordance with the Slater-Pauling rule. The authors proposed three different variants of this rule for the inverse Heusler alloys depending on the chemical type of the constituent transition-metal atoms: (1) When X = Sc or Ti, Slater-Pauling rule become $m = n_v - 18$, where $n_v$ is the total number of valence electrons in the unit cell. (2) When X = Cr or Mn, the magnetic moment followed by $m = n_v - 24$, and (3) when X is Cr or Mn and Y is Cu or Zn, the HM alloys follow an $m = n_v - 28$ rule due to the fully occupied Cu (Zn) d states.

Besides the inherent presence of HM ferrimagnetism in ordered alloys, this feature can also be created in ferromagnetic Heusler alloys via proper doping. Luo *et al.* [25] demonstrated this by doping Co$_2$CrAl full-Heusler alloy (which is ferromagnet having a spin magnetic moment of 3 $\mu_B$) with Cr. Their study clearly indicates that the magnetic moment can be adjusted from 3 $\mu_B$ to zero without destroying the half-metallicity. This is quite significant for practical applications because with this knowledge, one can easily prepare materials for spintronics devices with strong-ferromagnetic, weak-ferromagnetic or non-magnetic properties and high spin polarization by adjusting the Cr composition. Galanakis *et al.* [26] presented an alternative way to design FCF for realistic spintronic applications by simply doping of Co atoms in the Mn$_2$VAl and Mn$_2$VSi. Özdoğan *et al.* [27] demonstrated the induction of HM ferrimagnetism in Co$_2$MnZ Heusler alloys, where Z stands for Al, Ga, Si, Ge or Sn, by creating Mn antisites at the Co sites, these impurity Mn atoms couple antiferromagnetically with the Co and Mn atoms at the perfect sites while keeping the HM character of the parent alloys.

A reduction in the total number of valence electrons, which ultimately reduce the total spin magnetic moment, by suitable doping, is found to be an effective way to achieve a virtual shift of $E_F$ within the minority-spin gap [28-31]. For instance, the experimentally
observed high tunneling magnetoresistance (TMR) effect of 175% at room temperature in the magnetic tunneling junction (MTJ) using a ferromagnetic electrode of equiatomic Co$_2$FeAl$_{0.5}$Si$_{0.5}$ [32] is related to the central position of the E$_F$ within the band gap. Similarly, the initial increase in the spin polarization with x in the Co$_2$Fe$_{1-x}$Cr$_x$Si series is attributed to the same effect [31].

The effect of doping on the HM and magnetic properties of conventional Heusler alloys has been thoroughly studied [33-37]. It has been found that the half-metallicity can be retained with proper substitution. It has been shown that the substitution of Fe for Cr and Mn for Ti in Co$_2$CrGa and Co$_2$TiGa, respectively, helps to stabilize the L2$_1$-type structure and the HM properties [36, 38]. So, doping in Heusler alloys can offer an excellent possibility to discover new materials with half-metallicity [25]. The shifting of E$_F$ in the center of a large minority-spin gap (E$_g$$^\downarrow$) by doping with another suitable element can lead to several new materials with desirable properties. Several off-stoichiometric Heusler alloys, such as (XX')$_2$YZ, X$_2$(YY')Z, and X2Y(ZZ'), were studied in the last decade [6, 34, 39] for HM ferromagnetism. Kallmayer et al. [40] studied the effect of substituting Fe for Mn in Co$_2$MnSi films and showed that the experimental extracted magnetic spin moments are compatible with the half-metallicity for small degrees of doping.

It is established that Fermi level tuning would be one of the essential techniques to achieve the materials with higher spin polarization [11, 41]. Tezuka et al. [42] demonstrated this by obtaining a larger value of effective spin polarization in Co$_2$FeAl$_{0.5}$Si$_{0.5}$ as compared to the stoichiometric composition i.e. Co$_2$FeSi or Co$_2$MnAl. Inomata et al. [43] demonstrated large TMR, 16% at room temperature and 26.5% at 5 K, in Fe doped Co$_2$Cr$_{0.6}$Fe$_{0.4}$Al Heusler alloy film. The enhancement of spin polarization was also confirmed using Fe doping in Co$_2$MnSn and measured by Andreev Reflection technique [44].

After reviewing the literature, we observed that there are plenty of studies for effect of doping on 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 as discussed above. We have been motivated by this point and demonstrated in this chapter that how position of E$_F$ can be pinned in
middle of $E_{\text{g}}$ via doping of Fe for Cr in $\text{Cr}_2\text{CoZ}$ ($Z = \text{Al, Si}$) inverse Heusler alloys to get the maximum degree of spin polarization.

This chapter 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, $\text{Cr}_2\text{CoZ}$ ($Z = \text{Al and Si}$), are not the HMFs but the substitution of Fe for Cr shifts the $E_F$ towards the middle of minority-spin gap which make them true HMF.

### 3.2 Details of the calculations

The electronic structure calculations of stoichiometric and off-stoichiometric $\text{Cr}_2-x\text{Fe}_x\text{CoZ}$ ($Z = \text{Al and Si}$) Heusler alloys where $x = 0.0, 0.25, 0.50, 0.75$ and $1.0$, were carried out using the density functional theory (DFT) [45] based full potential linearized augmented plane wave (FPLAPW) method as implemented in WIEN2k code [46]. The exchange and correlation (XC) potentials were constructed using generalized gradient approximation (GGA) within the parameterization of Perdew–Burke–Ernzerhof [47]. In FPLAPW calculations, the core states were treated fully relativistically, whereas for the valence states, a scalar relativistic approximation was used. Additionally, the valence wave function inside the muffin-tin (MT) sphere was expanded up to $l_{\text{max}} = 10$. The Radii of MT sphere ($R_{\text{MT}}$) for various atoms were taken in the present calculations such as to ensure the nearly touching spheres. The plane wave cut-off parameters were decided by $R_{\text{MT}}k_{\text{max}} = 7$ (where $k_{\text{max}}$ is the largest wave vector of the basis set such that $k_{\text{max}}$ controls the accuracy of the calculation) and $G_{\text{max}} = 12$ a.u.$^{-1}$ for Fourier expansion of potential in the interstitial region. A conventional $1\times1\times1$ cell of 16 atoms was generated to simulate the various doping concentrations. The k-space integration was carried out using the modified tetrahedron method [48] in which $17 \times 17 \times 17$ k-point mesh was used as base for the integration resulting in 455 k-points for stoichiometric composition and 63 k-points for doped alloys in the irreducible Brillouin zone. The energy convergence criterion was set to $10^{-4}$ Ry/cell and the charge convergence was also monitored along with it. Further, full relaxations of the internal atomic coordinates had also been carried out prior to studying the electronic and magnetic properties of the present systems.
The conventional ternary Heusler alloys with stoichiometric composition, \(X_2YZ\) and \(XYZ\), exist in \(L2_1\)- and \(C1_b\)-type crystal structures, respectively, with \(X\) and \(Y\) as the two transition metal (TM) atoms and \(Z\) as a main group element.

The unit cell of \(L2_1\)-type structure, adopted by the full-Heusler alloy like \(\text{Co}_2\text{MnSi}\), consists of four interpenetrating fcc lattices as basis as shown in Fig 3.1.

![Fig. 3.1](image.png)

**Fig. 3.1** A diagrammatic representation of crystal structure of the Heusler alloy. The unit cell consists of four sites as basis: \(A\) \((0,0,0)\), \(B\) \((\frac{1}{4},\frac{1}{4},\frac{1}{4})\), \(C\) \((\frac{1}{2},\frac{1}{2},\frac{1}{2})\) and \(D\) \((\frac{3}{4},\frac{3}{4},\frac{3}{4})\) in Wyckoff coordinates [49].

Generally, the site preference of different 3\(d\) elements in Heusler alloys is determined by the number of their valence electrons [50]. The elements with more valence electrons tend to enter the \((A, C)\) sites and form a \(\text{Cu}_2\text{MnAl}\) type \(L2_1\)-type structure, whilst the elements with less valence electrons prefer the \(B\) sites and form a \(\text{Hg}_2\text{CuTi}\)-type or \(X\)-type structure; the \(D\) sites generally occupied by main group elements. In case of \(\text{Co}_2\text{MnSi}\) full Heusler alloy, the 3\(d\) elements Mn with fewer \(d\) electrons than Co tend to occupy the \(B\) sites whereas elements with more electrons prefer the \((A, C)\) sites and Si occupies the \(D\) site [51]. This is also the case in most of the predicted HM Heusler alloys. But, in case of \(\text{Cr}_2\text{CoSi}\) the fewer \(d\) electrons elements Cr choose the \((A, C)\) sites whereas, Co enter the \(B\)
site and Si occupies D site. This type of occupation is exactly opposite to what is in the case of \(L2_1\)-type structure and suggests a new way for discovering candidates for HM materials.

### 3.3 Results and discussion

The results for various Fe-doping in \(\text{Cr}_2\text{CoZ} (Z = \text{Al and Si})\) inverse Heusler alloys with the stoichiometric counterpart (presented for comparison) have been discussed as under:

#### 3.3.1 Structural properties

The \(\text{Cr}_2\text{CoZ} (Z = \text{Al and Si})\) inverse Heusler alloys crystallizes in \(X\)-type structure and the Wyckoff positions for this structure are 4a (0,0,0), 4b (½, ½, ½ ), 4c (¼, ¼, ¼ ) and 4d (¾, ¾, ¾ ), where Cr occupies the two inequivalent 4a and 4c sites as nearest neighbors. This is clearly shown in Fig. 3.2 along the diagonal of the primitive cell of \(\text{Cr}_2\text{CoSi}\) inverse Heusler alloy. In our nomenclature, they are represented by \(\text{Cr}^I\) and \(\text{Cr}^{II}\) and we use this terminology throughout the text. Beside this, Co and Z atoms reside at 4b and 4d, respectively.

![Fig. 3.2](image)

The primitive cell of \(\text{Hg}_2\text{CuTi}\)-type \(\text{Cr}_2\text{CoSi}\) inverse Heusler alloy (left) along with corresponding Brillouin Zone (BZ) and its IBZ (in red color) on right.

The parent \(\text{Cr}_2\text{CoZ} (Z = \text{Al and Si})\) inverse Heusler alloys are recently proposed by Skaftouros \textit{et al.} [24]. Both alloys energetically favor \(X\)-type structure which has been
confirmed in this work using Murnaghan equation of state [52]. Fig. 3.3 shows the optimization plots for Cr$_2$CoSi in $L2_1$- and $X$-type structure as a representative. The unit cells of undoped and doped Cr$_{2-x}$Fe$_x$CoSi ($x = 0.25$) are shown in Fig. 3.4 (a) and Fig. 3.4 (b), respectively.

**Fig. 3.3** The energy versus lattice parameter of (a) Cr$_2$CoAl and (b) Cr$_2$CoSi inverse Heusler alloys.

**Fig. 3.4** The unit cell of (a) undoped Cr$_2$CoSi inverse Heusler alloy and doped Cr$_{1.75}$Fe$_{0.25}$CoSi Heusler alloy.
Table 3.1: The calculated lattice parameters, total and atom-resolved spin magnetic moment (in $\mu_B$) along with spin polarization (P) of Cr$_{2-x}$Fe$_x$CoZ ($Z = \text{Al, Si}; x = 0.0, 0.25, 0.5, 0.75$ and $1.0$) Heusler alloys.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>$m_{\text{tot}}$</th>
<th>$m_{\text{Fe}}$</th>
<th>$m_{\text{Cr}}^{\text{I}}$</th>
<th>$m_{\text{Cr}}^{\text{II}}$</th>
<th>$m_{\text{Co}}$</th>
<th>$m_{\text{Z}}$</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_2$CoAl</td>
<td>5.77</td>
<td>0.00</td>
<td>-</td>
<td>-1.45</td>
<td>1.25</td>
<td>0.27</td>
<td>-0.02</td>
<td>0.68</td>
</tr>
<tr>
<td>Others [24]</td>
<td>5.80</td>
<td>0.01</td>
<td>-</td>
<td>-2.10</td>
<td>1.87</td>
<td>0.30</td>
<td>-0.05</td>
<td>-</td>
</tr>
<tr>
<td>Cr$<em>{1.75}$Fe$</em>{0.25}$CoAl</td>
<td>5.75</td>
<td>0.37</td>
<td>0.49</td>
<td>-1.48</td>
<td>1.28</td>
<td>0.39</td>
<td>-0.04</td>
<td>0.97</td>
</tr>
<tr>
<td>Others</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr$<em>{1.50}$Fe$</em>{0.50}$CoAl</td>
<td>5.72</td>
<td>0.80</td>
<td>0.25</td>
<td>-1.53</td>
<td>1.30</td>
<td>0.46</td>
<td>-0.05</td>
<td>0.99</td>
</tr>
<tr>
<td>Others</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr$<em>{1.25}$Fe$</em>{0.75}$CoAl</td>
<td>5.71</td>
<td>1.04</td>
<td>0.23</td>
<td>-1.61</td>
<td>1.35</td>
<td>0.71</td>
<td>-0.04</td>
<td>0.99</td>
</tr>
<tr>
<td>Others</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoFeCrAl</td>
<td>5.70</td>
<td>2.00</td>
<td>0.60</td>
<td>-</td>
<td>1.60</td>
<td>1.03</td>
<td>-0.04</td>
<td>1.00</td>
</tr>
<tr>
<td>Others [53]</td>
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<td>2.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Others [54]</td>
<td>5.73</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Cr$_2$CoSi</td>
<td>5.67</td>
<td>1.00</td>
<td>-</td>
<td>-0.76</td>
<td>1.15</td>
<td>0.69</td>
<td>-0.03</td>
<td>0.94</td>
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<td>Others [24]</td>
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<td>1.06</td>
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<td>0.54</td>
<td>-0.04</td>
<td>-</td>
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<tr>
<td>Cr$<em>{1.75}$Fe$</em>{0.25}$CoSi</td>
<td>5.65</td>
<td>2.22</td>
<td>0.43</td>
<td>-0.94</td>
<td>1.43</td>
<td>0.72</td>
<td>-0.03</td>
<td>0.99</td>
</tr>
<tr>
<td>Other</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr$<em>{1.50}$Fe$</em>{0.50}$CoSi</td>
<td>5.64</td>
<td>2.63</td>
<td>0.45</td>
<td>-0.97</td>
<td>1.45</td>
<td>0.86</td>
<td>-0.03</td>
<td>0.99</td>
</tr>
<tr>
<td>Others</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr$<em>{1.25}$Fe$</em>{0.75}$CoSi</td>
<td>5.62</td>
<td>2.80</td>
<td>0.45</td>
<td>-0.99</td>
<td>1.50</td>
<td>1.00</td>
<td>-0.04</td>
<td>1.00</td>
</tr>
<tr>
<td>Other</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoFeCrSi</td>
<td>5.61</td>
<td>3.00</td>
<td>0.32</td>
<td>-</td>
<td>1.64</td>
<td>1.06</td>
<td>-0.04</td>
<td>1.00</td>
</tr>
<tr>
<td>Others [53]</td>
<td>5.63</td>
<td>3.00</td>
<td>-</td>
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</tr>
</tbody>
</table>
As discussed in introduction, the position of $E_F$ in the $E_{\uparrow\downarrow}$ determines the quality of the half-metallicity. To have the large HM gap or spin-flip gap, $E_{sf}$, (energy for transition from half-metal to traditional ferromagnet/ferrimagnet), which would be the most desirable in half-metals for spintronics utility, the $E_F$ must lie almost in the middle of the $E_{\uparrow\downarrow}$. The modification of electronic structure and physical properties of $\text{Cr}_2\text{CoZ}$ ($Z = \text{Al, Si}$) Heusler alloys were carried out by doping with a fourth TM i.e. Fe which can provide a class of materials with tailored characteristics.

![Graph showing lattice parameters vs. Fe concentration](image)

**Fig. 3.5** The variation of lattice parameters ($a$) with Fe-concentration ($x$) in $\text{Cr}_{2-x}\text{Fe}_x\text{CoZ}$ ($Z = \text{Al, Si}; x = 0.0, 0.25, 0.5, 0.75$ and $1.0$) Heusler alloys.

The variation of lattice parameters ($a$) of resultant alloys as a function of doping concentration $x$, is shown in Fig. 3.5. The lattice parameters of $\text{Cr}_{2-x}\text{Fe}_x\text{CoZ}$ ($Z = \text{Al and Si}$) decrease linearly with the increase in $x$. The optimized lattice parameters are summarized in Table 3.1. The unit cells of $\text{Cr}_{2-x}\text{Fe}_x\text{CoSi}$ for various doping concentration are shown in Fig. 3.6

### 3.3.2 Density of states

The generic total DOS (TDOS) of $\text{Cr}_2\text{CoZ}$ ($Z = \text{Al and Si}$) inverse Heusler alloys are almost similar. Fig. 3.7 (upper panel) shows the calculated DOS of both alloys. It clearly manifests the strong metallic character of the majority-spin channel (MAC).
Fig. 3.6 The unit cells of doped (a) $\text{Cr}_{1.75}\text{Fe}_{0.25}\text{CoSi}$, (b) $\text{Cr}_{1.50}\text{Fe}_{0.50}\text{CoSi}$, (c) $\text{Cr}_{1.25}\text{Fe}_{0.75}\text{CoSi}$ and (d) FeCrCoSi Heusler alloys.

The presence of finite DOS at $E_F$ in minority-spin channel (MIC) separates them from the HMF category. Although these alloys do not have a gap in MIC yet the calculated values of spin polarization, $P = \frac{n_{\uparrow}(E_F) - n_{\downarrow}(E_F)}{n_{\uparrow}(E_F) + n_{\downarrow}(E_F)}$ are still appreciable i.e. 68% and 94% for $\text{Cr}_2\text{CoAl}$ and $\text{Cr}_2\text{CoSi}$, respectively.

In order to have better insight of the electronic structure, we present the $d$-DOS of TM atoms of the stoichiometric alloys in lower panel of Fig. 3.7.

The features of TDOS for both compounds are quite similar except for some detailed difference. Therefore, we have taken $\text{Cr}_2\text{CoSi}$ as representative and explained the necessary ingredients of the TDOS. In MAC, a three peaks structure is identified. The two are in bonding region whose origin is $e_g - t_{2g}$ splitting of $d$-states of $\text{Cr}^{\text{I}}$ and Co atoms in the cubic crystal field [8]. The third one in antibonding region is mainly of $\text{Cr}^{\text{I}}$ nature. The $d$-states of $\text{Cr}^{\text{II}}$ atom present in a localized manner at $E_F$. 

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Fig. 3.7  Total DOS (upper panel) and partial DOS (lower panel) of stoichiometric \( \text{Cr}_2\text{CoZ} (Z = \text{Al, Si}) \) inverse Heusler alloys. \( E_F \) corresponds to Fermi level.

In MIC, similar peaks exist in bonding region. The \( \text{Cr}^{\text{II}} \) states which are localized at \( E_F \) in MAC get blue shifted by ~ 1.0 eV relative to \( E_F \) due to large exchange splitting of Cr atoms. It is clear from the behaviour of DOS that the covalent hybridization between lower-energy Cr-\( d \) states and higher-energy Co-\( d \) states is responsible for the formation of bonding and antibonding states [6]. The p-states of Si-atoms lie deep from ~ -6.0 to -2.0 eV (not shown for brevity), do not take part in the formation of gap in MIC, nevertheless, they effectively determine the occupancy of \( p-d \) orbitals and decide the position of \( E_F \) by hybridization with TM-\( d \) states.
Fig. 3.8 shows the calculated total DOS of doped Cr$_{2-x}$Fe$_x$CoZ (Al and Si) Heusler alloys for $x = 0.0, 0.25, 0.50, 0.75$ and 1.0. As for the stoichiometric alloys, discussed above, the MAC holds the metallic character throughout for all doping concentrations here also. The DOS in MIC, on the other hand, changes its nature continuously with the Fe substitution. The gradual replacement of one of the Cr sublattices with Fe splits the DOS at $E_F$ in MIC. This splitting increase as we increase Fe-doping and complete replacement of one of the Cr sublattice with Fe creates new quaternary Heusler alloys, CoFeCrZ (Al and Si) which crystallize in Y-type structure. To confirm the site occupation, the formation energies for all possible Y-type structures i.e. $Y_I$, $Y_{II}$ and $Y_{III}$ were calculated as shown in Fig. 3.9.

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 Fe, Co, Cr and Z atom, respectively. Similarly, $Y_{II}$/$Y_{III}$-structure was realized by placing Z, Co, Cr and Fe at (4d, 4c, 4b and 4a)/(4d, 4c, 4a and 4b), respectively.
The formation energies for various site occupations were calculated by:

\[ E_{\text{form}} = E_{\text{tot}} - (E_{\text{Fe}} + E_{\text{Cr}} + E_{\text{Co}} + E_{\text{Z}}) \]

where \( E_{\text{tot}} \) represent the total energy of \( Y \)-type structure per formula unit, and \( E_{\text{Fe}}, E_{\text{Cr}}, E_{\text{Co}} \) and \( E_{\text{Z}} \). It is clear from the calculated formation energies: for CoFeCrAl (\( E_{\text{form}} = -0.99 \) eV) and for CoFeCrSi (\( E_{\text{form}} = -2.81 \) eV) that \( Y_I \)-type structure is energetically most stable for these quaternary Heusler alloys.

The calculated values of formation energies are in good agreement with the calculations of Gao et al. [53]. The calculated lattice constant (Table 3.1) and the site occupation of various atoms in CoFeCrAl quaternary Heusler alloy are in accordance with the recent experiment study by Nehra et al. [54] on this compound. This verifies the credibility of this work represent the total energies per atom for bulk Fe, Cr, Co and Z, respectively.

The variation of \( E_{g\downarrow} \) and \( E_{sf} \) with Fe concentration (\( x \)) is presented in Fig. 3.10. After the onset of half metallicity, for \( x = 0.50 \), there is linear increase in it both energy gaps, \( E_{g\downarrow} \) and \( E_{sf} \), with higher value of \( x \). The highest value of \( E_{g\downarrow} \) and \( E_{sf} \) are found to be
0.485/0.672 and 0.156/0.320 eV, respectively, for CoFeCrAl/CoFeCrSi quaternary Heusler alloys.

Fig. 3.10 Minority-spin gap ($E_{g\downarrow}$) and spin-flip gap ($E_{sf}$) as a function of Fe-concentration ($x$). The sphere with solid line/dotted line (olive color) represents $E_{g\downarrow}/E_{sf}$ for Cr$_{2-x}$Fe$_x$CoAl and the square with solid line/dotted line (blue color) represents $E_{g\downarrow}/E_{sf}$ for Cr$_{2-x}$Fe$_x$CoSi where $x = 0.0, 0.25, 0.5, 0.75$ and $1.0$.

Fig. 3.11 The variation of spin polarization ($P$) with Fe-concentration ($x$) in Cr$_{2-x}$Fe$_x$CoZ ($Z = $ Al, Si; $x = 0.0, 0.25, 0.5, 0.75$ and $1.0$) Heusler alloys.
The variation of spin polarization with doping concentration (x) is shown in Fig. 3.11 which manifests that almost 100% for Cr\(_{2-x}\)Fe\(_x\)CoAl/Cr\(_{2-x}\)Fe\(_x\)CoSi onsets with x = 0.50/0.25. The spin polarization remains almost saturated at 100% for higher value of x in both alloys. The increment in spin polarization with the Fe-doping in Cr\(_{2-x}\)Fe\(_x\)CoSi, for example, may be due to behaviour of Fe as electron dopant for this substitution. Thus, the numbers of extra electrons are to be adjusted only in the MAC if the alloys have to follow the Slater-Pauling rule [6, 44].

![Spin-resolved d-DOS of Cr\(_{2-x}\)Fe\(_x\)CoZ (Z = Al, Si; x = 0.0, 0.25, 0.5, 0.75 and 1.0) Heusler alloys.](image)

**Fig. 3.12** Spin-resolved d-DOS of Cr\(_{2-x}\)Fe\(_x\)CoZ (Z = Al, Si; x = 0.0, 0.25, 0.5, 0.75 and 1.0) Heusler alloys.

This leads to the appearance of small DOS in MAC in the vicinity of E\(_F\). This is illustrated in Fig. 3.12 (left panel). For x = 1.0, Fe completely replaces one Cr sublattice and interaction between the TM atoms gets modified and E\(_F\) falls exactly in the middle of minority band gap. The strong hybridization between TM atoms and further with sp atoms might be the reason for the shifting of E\(_F\).

### 3.3.3 Magnetic properties

The Cr\(_2\)CoZ (Z = Al and Si) Heusler alloys are actually HM ferrimagnets [24] due to antiferromagnetic coupling between two inequivalent nearest neighbours Cr-atoms. Out
of two alloys, \( \text{Cr}_2\text{CoAl} \) is fully compensated ferrimagnet (FCF) \cite{16} with exactly 24 valence electrons. According to Slater-Pauling rule, \( m = n_v - 24 \), the total spin magnetic moment for FCF should be exactly zero. The calculated total and atom resolved spin magnetic moments are listed in Table 3.1. The calculated total spin magnetic moments are in accordance with Slater-Pauling rule for both \( \text{Cr}_2\text{CoZ} \) (\( Z = \text{Al} \) and \( \text{Si} \)). Co-atom carries local spin magnetic moment of 0.27 \( \mu_B \) for \( \text{Cr}_2\text{CoAl} \) and 0.69 \( \mu_B \) for \( \text{Cr}_2\text{CoSi} \). Z-atoms carry a negligibly small induced moment aligned antiparallel with Co. In both alloys, Cr-atoms carry magnetic moments with opposite polarity due to their mutual antiparallel alignment.

It can be explained in the following way: In Heusler alloys, there are primarily two magnetic processes, i.e. exchange splitting of \( d \)-states of magnetic atoms and the interatomic covalent interaction of \( d \)-states \cite{7}. The former equally favours both alignments i.e. ferromagnetic and antiferromagnetic, whilst only antiferromagnetic alignment dominates due to latter \cite{8}. More precisely, it is a competition between these two processes which decides the ferromagnetic or antiferromagnetic alignment of atomic magnetic moments in these alloys. The strong direct interaction between \( d \)-states of nearest neighboured inequivalent Cr-atoms makes them to align antiparallel with each other. Due to this, almost vanishing total spin magnetic moment appears in \( \text{Cr}_2\text{CoAl} \) FCF and a small value for \( \text{Cr}_2\text{CoSi} \) ferrimagnet.

When we move from \( x = 0.0 \) to \( x = 1.0 \) in \( \text{Cr}_{2-x}\text{Fe}_x\text{CoZ} \), the two extra electrons are added up and the number of valence electrons increases from 24 to 26 in \( \text{CoFeCrAl} \) and from 25 to 27 in \( \text{CoFeCrSi} \). This leads to the increase of total spin magnetic moments from 0.00 \( \mu_B \) to 2.00 \( \mu_B \) and 1.00 \( \mu_B \) to 3.00 \( \mu_B \) in \( \text{Cr}_{2-x}\text{Fe}_x\text{CoAl} \) and \( \text{Cr}_{2-x}\text{Fe}_x\text{CoSi} \) (for \( x = 1.0 \), respectively. As discussed for the stoichiometric composition, \( 3d \) states of TM atoms forms the common \( d \)-bands, hence localized partial magnetic moments composed of itinerant electrons are obtained \cite{7}. The \( d \)-DOS of \( \text{Cr}_{2-x}\text{Fe}_x\text{CoZ} \), Fig. 3.12, clearly indicate the localized behaviour of magnetic moment in this alloy.

The calculated total spin magnetic moments (Table 3.1) increase as \( x \) varies from 0.0 to 1.0. The \( \text{Cr}^{II} \) atom carries the major part of the total moment and this moment enhances with increasing Fe-doping. Further, the moment at Co site also shows a linear increase with incremental Fe substitution. Fe also carries a small moment for all concentrations in both systems and its ferromagnetic alignment with \( \text{Cr}^{II} \) atom possibly
leads to the enhancement of total spin magnetic moment of the resulting alloys. Z-atoms have a negligibly small magnetic moment, similar to the stoichiometric case, which aligns in antiparallel configuration. The magnetic properties of 3d-metals solely depend on the chemical environment surrounding them. As substitution of Cr with Fe changes the chemical environment and the reconstruction of the 3d bands takes place which leads to change in the magnetic moments.

3.3.4 Bandstructures

Fig. 3.13 displays the band structures of Cr$_2$CoSi compounds with Hg$_2$TiCu-type structure for the spin-up (majority) and the spin-down (minority) electrons. In both spin channels of Cr$_2$CoSi, a low lying band, ranging from ~ -11.0 to ~ -9.5 eV, arises due to s electrons of $sp$-element (Si) which remains isolated from rest of the bands. These low lying valence bands are separated from the other valence bands by an energy gap of almost 2.0 eV, for both spin channels and thus remains unaffected by the Co-Cr or Cr-Cr exchange interaction. Therefore, the s electrons (of $sp$-element) have little influence on the magnetic moment and the formation of a band gap in minority spin channel.

![Spin-resolved bandstructure of Cr$_2$CoSi inverse Heusler alloy.](image)

Fig. 3.13   Spin-resolved bandstructure of Cr$_2$CoSi inverse Heusler alloy.
In both spin channels of Cr$_2$CoSi, a low lying band, ranging from \(-11.0\) to \(-9.5\) eV, arises due to $s$ electrons of $sp$-element (Si) which remains isolated from rest of the bands. These low lying valence bands are separated from the other valence bands by an energy gap of almost 2.0 eV, for both spin channels and thus remains unaffected by the Co-Cr or Cr-Cr exchange interaction. Therefore, the $s$ electrons (of $sp$-element) have little influence on the magnetic moment and the formation of a band gap in minority spin channel.

The energy region between \(-7.0\) eV and 0.0 eV consists mainly of the $d$ electrons of Cr and Co atoms. These dispersed bands are due to the strong hybridization of Cr-Cr and Cr-Co $d$ electrons, including a contribution from Si $p$ states in the occupied valence states. In MAC, these bands are completely overlapped in conduction band (CB) and valence band (VB) at $E_F$ resulting in a strong metallic character for this spin channel. However, for MIC the top of VB, at $I$-point, and bottom of CB, at X-point, touches each other which results in a small DOS at $E_F$. Hence an appreciable value (94%) of spin polarization at $E_F$ is obtained.

Fig. 3.14  Spin-resolved bandstructure of FeCrCoSi quaternary Heusler alloy.
The bandstructure of \( \text{Cr}_{2-x}\text{Fe}_x\text{CoSi} \) (\( x = 1 \)) Heusler alloy is shown in Fig. 3.14. For this value of \( x \), the alloy becomes the quaternary Heusler alloy \( \text{CoFeCrSi} \) which crystallizes in LiMgPdSn-type structure or \( Y \)-type structure. The band structure of this alloy is similar to \( \text{Cr}_2\text{CoSi} \) inverse Heusler alloy (as discussed above w.r.t. Fig. 3.13) except some detailed differences.

Unlike the case of \( \text{Cr}_2\text{CoSi} \), in the \( \text{CoFeCrSi} \) quaternary Heusler alloy has an indirect band gap at \( E_F \) along \( \Gamma - X \) direction in MIC which makes it a perfect HMF and an ideal choice for the future spin based devices. The detailed discussion on the bandstructure of quaternary Heusler alloys can be found in next chapter.

### 3.4 Conclusions

We presented the first principle calculations based of Fe-doping in \( \text{Cr}_2\text{CoZ} \) (\( Z = \text{Al, Si} \)) inverse Heusler alloys to investigate the half metallicity and magnetism in these alloys. Both parent (undoped) alloys, \( \text{Cr}_2\text{CoAl} \) and \( \text{Cr}_2\text{CoSi} \), are not found to be 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 half-metallicity starts to appear in \( \text{Cr}_{2-x}\text{Fe}_x\text{CoAl} \) for \( x = 0.50 \) and for \( x = 0.25 \) 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 \( Y \)-type structure. These end compounds, \( \text{CoFeCrAl} \) and \( \text{CoFeCrSi} \), are true half-metallic ferromagnets with integer magnetic moment of 1.00 \( \mu_B \) and 3.00 \( \mu_B \) 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 agree with the previously calculated values of formation energies. The calculated values of minority-spin gap and half-metallic gap are calculated and these are found maximum for end alloys for 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 \( \text{Cr}_{2-x}\text{Fe}_x\text{CoZ} \) (\( Z = \text{Al, Si} \)) these alloys can be proved as essential technique to achieve the materials with higher spin polarization and proposed systems may be used as the ideal candidate for spin valves and magnetic tunnel junctions.
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applications. We hope that the present work will encourage further experimental studies of half-metallic systems based on these Heusler alloys and promote more studies on the same.
$Cr_{2-x}Fe_xCoZ$ ($Z = Al$ and $Si$) Heusler alloys: Doping effect

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