CHAPTER 5

Effect of Magnetic Field on the Ground State

Magnetic Properties of Ca$_3$Co$_{2-x}$Fe$_x$O$_6$

5.1 Introduction

In the zero field neutron diffraction study of the compounds Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ ($x = 0, 0.2$ and $0.4$), described in Chapter 4, it is observed that these compounds ordered magnetically in an incommensurate spin density wave (SDW) structure, having a modulation and an alignment of the spins along the crystallographic $c$ axis, below their respective Néel temperatures ($T_N = 25, 20$ and $17$ K, for $x = 0, 0.2,$ and $0.4$ compounds, respectively). Further, a coexistence of the magnetic long-range and short-range ordering has been observed down to $1.5$ K (below $T_N$).

In the present chapter, the effect of an external magnetic field on the nature of magnetic ordering in the compounds Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ ($x = 0, 0.1, 0.2,$ and $0.4$) is described. First (in Sec. 5.3.1), the author discusses the results of the dc magnetization study, where, an indication of the presence of a field-induced transition from a ferri-to-ferromagnetic state is observed. Field induced transitions generally arise from a competition between Zeeman energy and exchange energy or crystal-field anisotropy. The microscopic understanding of the field induced transitions in these geometrically frustrated compounds with a triangular lattice arrangement of spin chain is of fundamental interest because an interplay between geometrical frustration and high magnetic field results in many novel magnetic states.

In order to achieve a microscopic understanding of the effect of an external magnetic field on the magnetic correlations at microscopic length scale in these quasi-1D
spin-chain compounds, the author has carried out a detailed neutron powder diffraction study down to 1.5 K and up to a field of 4 T for the compound Ca$_3$Co$_{1.8}$Fe$_{0.2}$O$_6$. A field-induced phase transitions from the zero field incommensurate spin density wave (SDW) structure ($T_N \sim 20$ K) to a commensurate amplitude modulated (AM) structure, and then to a ferrimagnetic structure have been observed. Besides, the effect of an applied field on the observed short-range spin-spin correlation has been brought out. The results of the neutron diffraction study are described in Sec. 5.3.2. The results have been published [77] in international scientific journals.

Here it may be noted that in the present chapter, the effect of an external magnetic field on the magnetic properties of these compounds has been investigated using the powder samples. In powder sample, the direction of the field relative to the easy axis changes due to the powder averaging. The analysis of the $M(H)$ curves is difficult because of the presence of a strong magnetic anisotropy, which can spoil many interesting features. However, in the neutron powder diffraction study, by analyzing the field and temperature dependence of the integrated intensities of the antiferromagnetic reflections, one can get a useful qualitative information regarding the field-induced magnetic phase transitions. The measurements on twin-free single crystals of these compounds will be of great help to provide further insight on the microscopic nature of the magnetic ordering in these compounds. Moreover, in single crystals, one can apply a magnetic field transverse to the Ising axis ($c$ axis for the studied compounds in the present thesis) and obtain an experimental transverse field magnetic phase diagram, which can be compared with the theoretical results of the transverse field Ising model.

5.2 Experimental Details

Polycrystalline samples of the compounds Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ ($x = 0, 0.1, 0.2,$ and 0.4) were prepared by the conventional solid-state reaction method as described in
Chapter 2.

The dc magnetization measurements were carried out on all the samples using a commercial (Oxford Instruments) vibrating sample magnetometer. For the zero-field-cooled (ZFC) magnetization measurements, the samples were first cooled from room temperature down to 2 K in zero field. After applying the magnetic field of 1 kOe at 2 K, the magnetization was measured in the warming cycle with the field on. Whereas, for the field-cooled (FC) magnetization measurements, the samples were cooled down to 2 K in the same field (1 kOe) and the FC magnetization was measured in the warming cycle under the same field. The hysteresis curves were recorded at 1.5 K over +110 to -110 kOe applied field.

The neutron diffraction experiments on the compound Ca$_3$Co$_{1.8}$Fe$_{0.2}$O$_6$ were performed by using the cold neutron powder diffractometer DMC at the Paul Scherrer Institute (PSI), Switzerland (λ = 2.46 Å). In zero magnetic field, diffraction patterns were recorded in the temperature range of 1.5 - 100 K. The diffraction patterns by applying an external magnetic field up to 4 T were recorded over the temperature range of 4.2 - 50 K using the pressed-powder pellets. The diffraction data were analyzed by the Rietveld method using the FULLPROF program [40] The representation theory analysis was performed using the SARAH software [41].

5.3 Results and Discussion

5.3.1 Dc-magnetization Study

5.3.1.1 ZFC and FC Magnetization vs Temperature

The temperature dependence of the ZFC and FC dc magnetization for all samples under $H = 1$ kOe is shown in Fig 5.1. Inverse magnetic susceptibility vs temperature has been plotted in the inset of Fig 5.1. It is clear from Fig. 5.1 that the high tem-
Chapter 5. Effect of Magnetic Field on the Ground State Magnetic Properties of \( \text{Ca}_3\text{Co}_{2-x}\text{Fe}_x\text{O}_6 \) (\( x = 0, 0.1, 0.2, \) and 0.4). The open circles and the solid line correspond to ZFC and FC modes, respectively. Insets show inverse dc susceptibility vs temperature curves fitted with the Curie-Weiss law.

The temperature magnetic susceptibility obeys the Curie-Weiss law \( \chi_{\text{mol}} = C_{\text{mol}}/(T - \theta_p) \), here \( C_{\text{mol}} \) is molar Curie constant and \( \theta_p \) is the paramagnetic Curie temperature. The value of \( \theta_p \) decreases as the concentration of iron increases; reaching 17.6 and 7.5 K for \( x = 0.1 \) and 0.2, respectively against \( \theta_p = 27.9 \) K for \( x = 0 \) and it becomes
negative (-1.6 K) for \( x = 0.4 \) sample, which indicates that at this higher concentration of iron, antiferromagnetic (AFM) interaction dominates over ferromagnetic (FM) interaction. The effective paramagnetic moment \( \mu_{\text{eff}} = (3C_{\text{mol}}k_B/N_A\mu_B^2)^{1/2} \approx (8C_{\text{mol}})^{1/2} \), where \( k_B \) stands for Boltzmann constant and \( N_A \) stands for Avogadro number], obtained from the slope of \( \chi^{-1} \) vs \( T \) curves, are depicted in Fig. 5.2. Theoretically expected (spin-only) values of the \( \mu_{\text{eff}} \) using the expression

\[
\mu_{\text{eff}} = \sqrt{(1-x)g^2S_{\text{Co}}^2(S_{\text{Co}}^2 + 1) + xg^2S_{\text{Fe}}^2(S_{\text{Fe}}^2 + 1)} \mu_B
\]

with \( g = 2 \) are also shown in Fig. 5.2. Here \( \mu_{\text{eff}} \) has been calculated (assuming spin only contribution) by considering \( \text{Co}^{3+} \) at octahedra (OCT) site in the low spin (LS) state \( (S = 0) \), \( \text{Co}^{3+} \) at trigonal prisms (TP) site in the high spin (HS) state \( (S = 2) \), and \( \text{Fe}^{3+} \) at TP site in the HS state \( (S = 5/2) \) [50]. For the parent compound \( \text{Ca}_3\text{Co}_2\text{O}_6 \), experimental value (4.8 \( \mu_B \) per formula unit) matches with the theoretical value (4.89 \( \mu_B \) per formula unit) and for iron substituted samples, experimental \( \mu_{\text{eff}} \) values are higher than the theoretically expected values. If we assume that the orbital moment of \( \text{Co}^{3+} \) is not quenched in the TP site (orbital moment of \( \text{Fe}^{3+} \) is
zero since it has half filled 3d shell), the calculated values of $\mu_{\text{eff}}$ are higher than the observed values (Fig. 5.2). If we consider that orbital momentum is partially quenched, theoretical values of the $\mu_{\text{eff}}$ (considering different values of $L$) do not match with the experiment values. Another possibility of observing higher experimental values of effective paramagnetic moment as compared to the theoretically expected spin only values for Fe substituted compounds may be LS to HS transition of octahedral Co$^{3+}$ ions that are located near Fe$^{3+}$ ions [91], which could also be responsible for the slight increase of cell constants for the present Fe substituted compounds. An increase of cell parameters by such a spin transition has been reported in literature [91]. Such a transition is possible [91] because covalency of the Fe-O bond is higher than the covalency of Co-O bond (i.e. electronegativity of Fe$^{3+}$ is higher than that of Co$^{3+}$; 1.9 and 1.8 respectively [92]). Under the framework of spin transition for Co$^{3+}$ at the octahedral site, the $\mu_{\text{eff}}$ can be calculated using the expression

$$\mu_{\text{eff}} = \sqrt{(1-x)g^2S_{\text{Co}}^{\text{TP}}(S_{\text{Co}}^{\text{TP}}+1) + x g^2S_{\text{Fe}}^{\text{TP}}(S_{\text{Fe}}^{\text{TP}}+1) + x f g^2S_{\text{Co}}^{\text{OCT}}(S_{\text{Co}}^{\text{OCT}}+1)} \mu_B$$

with $g = 2$ (Fig. 5.2). Here $f$ is the fraction of Co$^{3+}$ ions (at the octahedral site) that undergo LS to HS transition for each Fe$^{3+}$ substituted ion. The experimental and the theoretical values match for $x = 0.1$ and 0.2 by taking $f = 0.75$ (Fig. 5.2). For $x = 0.4$, the experimental and the theoretical values match by taking $f = 0.34$. The observed lower value of $f$ for the $x = 0.4$ sample can be explained by the fact that for a higher concentration of iron, there could be pairs/sequence of Fe$^{3+}$ ions along the chain, so the effective number of Co$^{3+}$ ions (with Fe$^{3+}$ ions as nearest neighbors) showing transition from LS to HS is small. For the parent compound Ca$_3$Co$_2$O$_6$, there is a sudden increase in the magnetization at around
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$\text{Ca}_3\text{Co}_{2-x}\text{Fe}_x\text{O}_6$

Figure 5.3: Unit cell of $\text{Ca}_3\text{Co}_{2-x}\text{Fe}_x\text{O}_6$ ($x = 0, 0.1, 0.2,$ and 0.4), showing selected (Co1-O-Co2 and Co2-O-Co2) bond angles. Paths of interchain and intrachain exchange interactions are also shown as $J'$ and $J$, respectively. Only selected atoms are shown for clarity.

25 K and also there exists a peak in the magnetization at around 10 K. These observations are consistent with the reported results for this compound [42, 53]. In literature, two kinds of magnetic exchange interactions have been considered for this spin-chain compound [59]. The exchange interaction $J$ between the magnetic Co2 ions located at TP site along the chain axis ($c$ axis) is FM and the superexchange interaction $J'$ between the magnetic Co2 ions (via oxygen ions) is AFM (Fig. 5.3). Sudden increase in the magnetization at around 25 K has been ascribed in literature [42, 46, 52–61, 93–97] as due to the combined effect of FM ordering along the chain and AFM ordering between chains. This argument is supported by the simultaneous
appearance of AFM and FM Bragg peaks in the neutron diffraction pattern at $T \sim 25$ K [62, 63] and sharp peak in the specific heat (under zero fields) [54] at the same temperature. This type of spin configuration has been described as the onset of the partially disordered antiferromagnetic (PDA) state and it is supported by the muon spin relaxation study [78]. While peak in the magnetization curve at around 10 K is considered as an indicative of magnetic transition to the ferrimagnetic (FIM) state [68].

From the temperature dependence of FC and ZFC dc-magnetization (shown in the Fig. 5.1) it is evident that for all the samples, a bifurcation between FC and ZFC magnetization is found at lower temperatures. This bifurcation in FC and ZFC magnetization may be taken as the signature of geometrical frustration due to triangular lattice of Ising Co moments in the $ab$ plane. Results of the reported low temperature Mössbauer study [64] show that Fe$^{3+}$ remains in the paramagnetic state in the FM ordered chains below 25 K. Figure 5.1 also indicates that as the concentration of iron increases, magnetization decreases. This decrease in the magnetization and $\theta_p$ (negative for $x = 0.4$) indicates that as the concentration of iron increases the long range FM ordering along the chain is reduced (due to reduced correlation length between Co moments along the chain) and AFM interchain interaction dominates over the FM intrachain interaction. This has been ascribed to a different magnetic character of Co host (Ising) and Fe impurity (Heisenberg) spins [50].

Figure 5.4 depicts the temperature dependence of molar susceptibility, where $\chi T$ vs $T$ is plotted. It reveals four main features (i) in the high temperature range (150 - 300 K), $\chi T$ approaches its paramagnetic limit, (ii) as temperature is decreased below 150 K, $\chi T$ starts increasing giving the signature of a short-range ordering along the chains, (iii) with further decreasing the temperature, a dip in $\chi T$ vs $T$
Figure 5.4: Plots of $\chi T$ vs $T$ for Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ ($x = 0, 0.1, 0.2, 0.4$) derived from FC magnetization curves. Solid lines represent the fitted curve using Eq. (5.3). For $x = 0.1$ and 0.2, $\chi T$ values are shifted down by 5 and 10 emu K mol$^{-1}$ Oe$^{-1}$, respectively for clarity.
plot is found, and (iv) a sharp increase in the $\chi T$ below the dip temperature and then again a decrease of $\chi T$ at lower temperatures down to 2 K. The temperature corresponding to the dip varies with $x$ (24.83 K for $x = 0$ and 3.59 K for $x = 0.4$). The dip in the $\chi T$ vs $T$ plot may be ascribed to a FIM ordering at low temperatures [98]. The decrease in the $\chi T$ at low temperature ($T < 7$ K) has been assigned to a spin frozen state in literature [99] for the parent compound Ca$_3$Co$_2$O$_6$.

5.3.1.2 Intrachain and Interchain Exchange Interactions

The intrachain exchange constant can be determined by fitting the experimental $\chi T$ vs $T$ curves [99, 100]. Theoretical studies show that the parallel [99] and the perpendicular [101] susceptibilities for, $S = 2$, 1D Ising spin chain are given by

$$\chi_\parallel T = \frac{3}{4} g^2 \exp(8J/k_B T) \quad (5.1)$$

and

$$\chi_\perp T = \frac{3}{4} g^2 . \quad (5.2)$$

Here $g$ is the Lande factor, $k_B$ stands for the Boltzmann constant, and $J$ is the intrachain exchange constant. For polycrystalline (powder) sample, susceptibility can, therefore, be written as

$$\chi_p T = 1/3 \chi_\parallel T + 2/3 \chi_\perp T . \quad (5.3)$$

Equation (5.3) is strictly valid for the $S = 2$, Ising spin-chain. But our system (except Ca$_3$Co$_2$O$_6$) is not $S = 2$, 1D Ising spin-chain system (for Fe$^{3+}$ ions, value of $S$ is 5/2). In literature, no theoretical expression is available for $S = 2$ and $S = 5/2$ mixed spin system. We have, therefore, used Eq. (5.3) to estimate the approximate
value of the exchange constant $J$. This type of approximate method has already been used in literature [97] for $\text{Ca}_3\text{Co}_{2-x}\text{Cr}_x\text{O}_6$, where Co$^{3+}$ ions are in the HS and the LS states at the TP and OCT sites, respectively, and Cr$^{3+}$ ions at the OCT site are in the HS ($S = 3/2$) state. By fitting the high temperature part of the $\chi_P T$ vs $T$ curves using Eq. (5.3) (Fig. 5.4) as per the procedure followed in literature [97], we have estimated the value of intrachain exchange constant $J$ (shown in Table 5.1). It is found that as the concentration of iron increases, $J$ decreases. For instance as $x$ increases from 0 to 0.2, $J$ decreases from 8.1 to 4.3 K, and for $x = 0.4$ it becomes negative ($J = -0.7$ K). Positive value of $J$ refers that intrachain interaction is FM while negative value of $J$ indicates that interaction is AFM. The derived negative value of $J$ for the $x = 0.4$ sample is consistent with the negative value of $\theta_p$ for this sample. Here we give some physical argument to explain the negative value of $J$. For $\text{Ca}_3\text{Co}_{2-x}\text{Fe}_x\text{O}_6$, when concentration of Fe is low (small value of $x$), the probability of having Fe pairs or clusters in a Co chain is very small and Fe$^{3+}$ ions are mainly isolated. For small value of $x$, iron limits the correlation length by breaking FM ordering between Co$^{3+}$ ions along the $c$ axis and reduces the strength of intrachain exchange coupling constant $J$. When $x$ increases ($> 0.2$), the formation of pairs of Fe$^{3+}$ ions along the chain is probable. There may be AFM exchange interaction (via oxygen) between Fe$^{3+}$ ions along the chain (Fig. 5.3) which can give the negative value of $J$. This can lead to a FIM ordering (with negative $\theta_p$) at low temperatures. For the $x = 0.2$ and 0.4 compounds, a coexistence of magnetic short-range and long-range ordering, below $T_N$, has been confirmed from the zero field neutron diffraction study (Chapter 4). We have observed that the correlation lengths for both magnetic short-range ordering (SRO) and long-range ordering (LRO) do not differ very much for the $x = 0.2$ and 0.4 compounds, indicating that Fe ions in a chain are located preferentially very close to each other for higher concentration of iron ($x = 0.4$).
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This confirms that a higher concentration (for $x = 0.4$) of Fe hardly breaks the ferromagnetic bonds further as compared to that for the lower concentration of Fe (for $x = 0.2$).

Interactions between the chains in the $ab$ plane give deviation from the 1D spin system. The deviation from the ideal 1D character of Ising chain can be taken into account by introducing the mean field correction to the ideal 1D Ising spin model. Mean field correction to the $S = 1/2$, 1D Ising spin-chain is available in literature, and it has been used [101] to evaluate the interchain exchange constant. However, in literature no mean field expressions, either for $S = 2$ Ising spin-chain or for $S = 2$ and $S = 5/2$ mixed spin system, exist. It will be of great importance to evaluate the interchain interaction if the mean field corrections for such spin systems are available. An alternate option to calculate interchain interaction is by using ferri-to-ferromagnetic transition field ($H_{FIM-FM}$). A field induced FIM to FM-like transition is found in our $M$ vs. $H$ study (Fig. 5.5). In a model of Ising spin-chain [97], interchain interaction is related to $H_{FIM-FM}$ through the relation $J' = \frac{gB H_{FIM-FM}}{12S}$. For the present system of mixed spins ($S = 2$ and $S = 5/2$), assuming $S = 2$ and $g = 2$, we have derived the value of $J'$ as used for $S = 2$ and $S = 3/2$ mixed spin-chain system in literature [97]. The value of $J'$ varies from -0.20 K for $x = 0$ to -0.32 K for $x = 0.4$. Therefore, as the concentration of iron increases from 0 to 0.4, interchain interaction increases. Since the distance between magnetic ions perpendicular to the chain axis, and the bond angle via oxygen do not change by iron substitution, the increase in the value of $J'$ can be understood by assuming that the strength of exchange coupling for Co2/Fe-O-Co2/Fe pathway is greater than that of the Co2-O-Co2. This is consistent with the fact that Fe is known to introduce negative exchange interactions. Fe$^{3+}$ has five electrons in the $d$ orbital, while Co$^{3+}$ has six, and also spin character of host (Co) is Ising while impurity (Fe)
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Figure 5.5: Hysteresis curves at 1.5 K for Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ ($x = 0, 0.1, 0.2$, and 0.4). Virgin magnetization curves (first leg) show a possible field induced FIM to FM transition (marked by arrows).
Table 5.1: Magnetic exchange constants for Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ samples.

| $x$ | $J$(K) | $J'$(K) | $|J'/J|$ |
|-----|--------|--------|--------|
| 0   | 8.13   | -0.20  | 0.025  |
| 0.1 | 6.13   | -0.27  | 0.044  |
| 0.2 | 4.39   | -0.30  | 0.068  |
| 0.4 | -0.71  | -0.32  | 0.451  |

is of Heisenberg nature. The ratio $|J'/J|$ characterizes the “one dimensionality” of the magnetic system. It varies from 0.025 for $x = 0$ to 0.451 for $x = 0.4$ as shown in the Table 5.1. In literature, Clardige et al. reported $J'/J \sim 0.33$ for Sr$_3$CuPtO$_6$ (Heisenberg chain compound) [102] and they concluded that it should not be considered as 1D magnetic system due to a higher value of $J'/J$. Since for the present $x = 0.4$ compound $|J'/J| \sim 0.451$, this compound should also not be considered as 1D magnetic system. The ratio is very small for Ca$_3$Co$_2$O$_6$ hence it has predominantly a one dimension character. We can, therefore, conclude that as the concentration of iron increases, the one dimensional character of Ising spin chains is reduced.

The previous report by Flahaut et al. [97] on substitution of Co$^{3+}$ by Cr$^{3+}$ in Ca$_3$Co$_2$O$_6$ shows that as the concentration of Cr increases from $x = 0$ to $x = 0.1$ in Ca$_3$Co$_{2-x}$Cr$_x$O$_6$, both $J$ and $J'$ decrease. Here we would like to point out that effects of substitution of Cr are much different from the present study where Fe is substituted. The Cr$^{3+}$ substitutes the LS Co$^{3+}$ at octahedral site and it is in the HS state ($S = 3/2$). In Ca$_3$Co$_{2-x}$Cr$_x$O$_6$, solubility range of Cr$^{3+}$ is limited to about 10 at. % occupation of octahedral site. In the Cr substitution case, cell constants $a$ and $c$ change by $\sim 0.14$ % and 0.08 %, respectively, for the change in $x$ from 0
to 0.15, whereas in the present case, the cell constant $a$ changes only by 0.01 % for the change in $x$ from 0 to 0.4.

### 5.3.1.3 Field Dependent Magnetization

Figure 5.5 depicts hysteresis loops (field up to 110 kOe) at 1.5 K for all the samples. It is evident from Fig. 5.5 that virgin magnetization ($M$) varies linearly with field in a small field region. It is also found that a large hysteresis exists in $M$ versus $H$ curves of all samples but as the concentration of iron increases, these curves become less hysteric. The magnetization saturates for $x = 0$ but for $x = 0.1$, 0.2, and 0.4 samples the magnetization does not saturate even under the highest applied field. Experimentally observed values of the remanent magnetization and the coercive fields are shown in Fig. 5.6. It is clear that as the concentration of iron increases both remanent magnetization and coercive field decrease. It is, therefore, evident that the magnetic hardness decreases with Fe substitution. This is consistent with the observed fact that with increasing Fe concentration, the 1D character of Ising spin chains is reduced.

The spatial dimensionality ($d$) of arrangement of magnetic ions in the present system can be deduced from the approach of the magnetization to its saturation value ($M_S$) in the high field region [103, 104]. This dependency is given by

\[
\frac{M_s - M}{M_s} \propto (H)^{(d-4)/2}
\]  

(5.4)

Here, the proportionality constant is given by $\delta = (C/M_s)^{(4-d)/2}$ with $C$ as magnetocrystalline anisotropy constant. According to Eq. (5.4), approach of magnetization to its saturation value $\Delta M/M_s$ (here $\Delta M = M_S - M$) obeys $H^{-3/2}$ and $H^{-1/2}$ dependence for the 1D and three-dimensional (3D) interaction of magnetic ions, respectively. Figure 5.7 depicts the variation of $\Delta M/M_s$ with $H^{-3/2}$ and
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Figure 5.6: Variation of remanent magnetization and coercive fields with composition. Solid lines are guide to the eye.

$H^{-1/2}$ for all the samples at 1.5 K. Inset of Fig. 5.7 depicts variation of anisotropy constant ($C$) with composition, derived from the slope $[= (C/M_s)^{3/2}]$ of $\Delta M/M_S$ vs $H^{-3/2}$ curves. The results show that for $x = 0$, 0.1, and 0.2 samples, $\Delta M/M_S$ is proportional to $H^{-3/2}$ and hence imply the 1D character of the spatial arrangement of magnetic ions in these samples. For $x = 0.4$ sample, $\Delta M/M_S$ deviates from $H^{-3/2}$ dependence, which can be ascribed as deviation from ideal 1D character of this sample (consistent with highest derived value of $|J'/J|$). The decrease of anisotropy constant ($C$) with the increase of iron concentration (inset of Fig. 5.7) is also consistent with the aforesaid argument.

5.3.2 Neutron Diffraction Study of Field-induced Magnetic Phase Transitions in Ca$_3$Co$_{1.8}$Fe$_{0.2}$O$_6$

Figure 5.8 (a) depicts the Rietveld refined neutron diffraction pattern for the compound Ca$_3$Co$_{1.8}$Fe$_{0.2}$O$_6$ at 1.5 K (well below $T_N \sim 20$ K) in zero applied field. As shown in the inset of Fig. 5.8 (a), the antiferromagnetic reflections appearing in
Figure 5.7: Plots of $\Delta M/M_S$ vs $H^{-3/2}$ (open circles) and $\Delta M/M_S$ vs $H^{-1/2}$ (solid triangles) obtained from high field region of virgin magnetization curves. Straight lines represent linear fit of $\Delta M/M_S$ vs $H^{-3/2}$. Inset shows variation of anisotropy constant with composition.
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Figure 5.8: The Rietveld refined neutron diffraction patterns of Ca$_3$Co$_{1.8}$Fe$_{0.2}$O$_6$ at (a) 1.5 K under zero applied field, (b) 4.2 K under an applied field of 2 T: experimental data (open circle), calculated curve (solid line), and difference (solid line at bottom). The upper vertical marks are the nuclear Bragg reflections, lower vertical marks are the magnetic reflections. The $(hkl)$ values for the satellite peaks which appear below $T_N$ are also listed. The insets in (a) and (b) show the Rietveld refined patterns for two different values of the propagation vector.

The neutron diffraction pattern can be indexed with the incommensurate propagation vector $k = \{0, 0, 1.0182 (9)\}$, and the magnetic structure corresponds to the SDW structure [105]. Moreover, in zero applied field, a magnetic short-range ordering (SRO) coexists with the long-range ordering (LRO) at all temperatures below $T_N$, as described in Chapter 4. Figure 5.8(b) depicts the Rietveld refined neutron diffraction pattern at 4.2 K under an applied field of 2 T. As shown in the inset
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Figure 5.9: Schematic diagram of (a) AM state and (b) ferrimagnetic state, projected on the \( ab \) plane. In Figs. (a) and (b), the circles represent the Ising spin chain, and the plus (+) and minus (-) signs correspond to the direction (along the positive \( c \) axis and negative \( c \) axis, respectively) of representative moments in the spin chains. The values of the moments within the three nearest spin chains are marked.

of Fig. 5.8(b), the observed antiferromagnetic reflections can be indexed with the commensurate propagation vector \( \mathbf{k} = \{0, 0, 1\} \) and the magnetic structure corresponds to the AM structure, in which moments lie along the crystallographic \( c \) axis. The amplitude of the moments in the unit cell is given by \( M_{L,j(j=6a,6b)} = M_j \cos(2\pi \mathbf{k} \cdot \mathbf{R}_L) \). Here \( M_j \) is the maximum moment and \( \mathbf{R}_L \) is the translation vector with respect to the zeroth-cell. The amplitudes of the site moments in the unit cell, labelled by the centring translation, \( \mathbf{R}_L = (2/3, 1/3, 1/3) \) and \( (1/3, 2/3, 2/3) \), are modulated by \(-0.5\). The observed amplitude modulated (commensurate) magnetic structure is very much different from the zero field spin-density wave (SDW) magnetic structure, having incommensurate propagation vector \( \mathbf{k} = \{0, 0, 1.0182(9)\} \).

In the SDW magnetic structure, the values of the moments in the lattice varies between \(+M_j\) and \(-M_j\), however, in the amplitude modulated structure (Fig. 5.9(a)), the values of the moments within the three nearest spin-chains with the \((x, y)\) coordinate as \((0, 0)\), \((2/3, 1/3)\), and \((1/3, 2/3)\) are \(+M_j\), \(-M_j/2\), \(-M_j/2\), respectively.
The observed crossover from incommensurate to commensurate magnetic ordering indicates a reduction of the spin frustration on the triangular lattice.

To describe further the effect of the magnetic field on the magnetic structure of the compound $\text{Ca}_3\text{Co}_{1.8}\text{Fe}_{0.2}\text{O}_6$, the observed magnetic Bragg peaks have been considered in two groups; (i) the first group corresponds to the satellite peaks, such as (100), (200), and (210) reflections which appear below $T_N$, and (ii) the second group corresponds to the peaks such as (110), (220), and (012) whose intensities appear on the top of the nuclear (fundamental) Bragg peaks. The temperature dependences of the integrated intensities of these Bragg peaks play a crucial role in determining the nature of the magnetic ordering of the compound in an applied magnetic field. A simple calculation using the Fullprof program [40] shows that the magnetic contribution in the intensity of fundamental (110) Bragg peak is zero in the case of the SDW/AM structure (Fig. 5.9 (a)), while the contribution is finite in the case of a ferromagnetic/ferrimagnetic (Fig. 5.9 (b)) structure [in each case, the moment was considered along the crystallographic $c$ axis]. In Fig. 5.10, we show the temperature dependence of the integrated intensities of the fundamental peaks (110) and (220) under magnetic fields of 0, 2, and 4 T. In magnetic fields of 0 and 2 T, the intensities of the two peaks show no enhancement below 20 K (Figs. 5.10 (a) and (b)). Under an applied field of 2 T, no enhancement in the intensity of these two peaks, confirms an AM-type magnetic structure. Whereas, in the absence of an external magnetic field, no enhancement in the intensities of these two peaks, corresponds to the SDW structure, as mentioned in Chapter 4 [73]. In the magnetic field of 4 T, below $\sim 20$ K, the intensity of (110) peak increases gradually with decreasing the temperature (Fig. 5.10 (c)), indicating that the magnetic structure is ferrimagnetic/ferromagnetic at a field of 4 T. We indeed find that magnetic structure at $H = 4$ T is ferrimagnetic, as evident from the following discussion. Figure 5.11
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Figure 5.10: Temperature dependence of the integrated intensity of the Bragg peaks (110) (solid circle) and (220) (open circle) in an applied magnetic field of (a) 0 T, (b) 2 T, and (c) 4 T. The solid lines are guides to the eye.
Figure 5.11: Temperature dependence of the integrated intensity of the Bragg peaks (100) (open triangle) and (200) (solid circle) in an applied magnetic field of (a) 0 T, (b) 2 T, and (c) 4 T. (d) Temperature dependence of the integrated intensity of the Bragg peak (210) in an applied magnetic field of 0 T (open circle), 2T (open triangle), and 4 T (hollow square). The solid lines are guides to the eye.
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depicts the temperature dependences of the integrated intensities of the satellite
Bragg peaks (100), (200), and (210) in applied magnetic fields. It is important to
mention here that the application of magnetic field does not change the number
of the additional magnetic Bragg reflections, it only affects their intensities and
positions. In an applied field of 4 T, the observed non zero intensities of the peaks
(100), (200), (210) [Figs. 5.11(c) and (d)] and an increase in the intensity of the
fundamental Bragg peak (110) [Fig. 5.10 (c)], below $T_N$, suggest that magnetic
structure is ferrimagnetic as shown in Fig. 5.9 (b). However, the intensity of the
satellite peaks (100), (200), and (210) in the ferrimagnetic phase is small compared
to the AM structure [Fig. 5.11]. This suggests that the AFM correlations between
spin chains are weakened or broken when field is increased to 4 T. When the field is
increased further (> 5 T), the spin system with the “broken spin chains” approaches
to its fully field induced ferromagnetic state as found in our earlier dc magnetization
study [77]. A similar field induced ferrimagnetic structure and/or ferromagnetic
structure has been reported in literature for the most intensely studied compounds
Ca$_3$Co$_2$O$_6$ and Ca$_3$CoRhO$_6$ of the $A_3MXO_6$ family [62, 66]. In the zero applied
magnetic field [Figs. 5.11(a) and (d))], the intensities of the peaks (100), (200), and
(210) increase gradually with decreasing temperature, corresponding to the SDW
structure, as reported earlier [73]. In magnetic fields of 2 and 4 T (Figs. 5.11(b),
(c), and (d)), a pronounced drop in the intensities of the peaks (100), (200), and
(210) has been observed at lower temperatures (below $\sim$ 12 K). The origin of the
observed reduction in the intensities of these peaks will be discussed later.

Figure 5.12 describes the effect of magnetic field on the short-range magnetic
order. In zero applied field, the SRO is present at all temperatures below $T_N$ with
a constant volume ratio 13:7 of the magnetic Bragg intensities for the LRO and the
SRO, as mentioned in Chapter 4 [73]. Even under magnetic fields of 2 and 4 T,
Figure 5.12: The observed Bragg peak (100) (open circle) under an applied field of (a) 0 T, (b) 2 T, and (c) 4 T at 4.2 K; and (d) 0 T, (e) 2 T, and (f) 4 T at 16 K. In Figs. (a) - (d), the Bragg peak (100) is fitted (solid line) as a sum of two pseudo-Voigt peaks, where the width of the narrow peak (dotted line) is limited by the instrumental resolution function. In Figs. (e) and (f), the Bragg peak (100) is fitted with a single pseudo-Voigt profile having a width limited by the instrumental resolution function.

Figure 5.12: The observed Bragg peak (100) (open circle) under an applied field of (a) 0 T, (b) 2 T, and (c) 4 T at 4.2 K; and (d) 0 T, (e) 2 T, and (f) 4 T at 16 K. In Figs. (a) - (d), the Bragg peak (100) is fitted (solid line) as a sum of two pseudo-Voigt peaks, where the width of the narrow peak (dotted line) is limited by the instrumental resolution function. In Figs. (e) and (f), the Bragg peak (100) is fitted with a single pseudo-Voigt profile having a width limited by the instrumental resolution function.

a broadening (Bragg peak width larger than that expected from the instrumental resolution function) of the satellite Bragg peak (100) persists below $\sim 12$ K. However, the nature of the SRO (below 12 K) in applied magnetic field is different from that in zero applied field (discussed later). The profiles of the observed satellite Bragg peak (100) at all temperatures below $T_N$ ($\sim 20$ K) under zero applied field, and below $\sim 12$ K under applied fields, have been fitted using a combination of two pseudo-Voigt
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Figure 5.13: Temperature variation of the FWHM of the Bragg peak (100) in an applied field of (a) 0 T (b) 2 T and (c) 4 T. The FWHM expected from the instrumental resolution function is shown as solid horizontal line.

peaks, where the width of only one peak is limited by the instrumental resolution function. The derived temperature variation of the full width at half maximum (FWHM, convoluted peak width by considering both narrow and broad peaks), is plotted in Figs. 5.13 (a), (b), and (c). In zero applied field, the nature of the SRO is same as mentioned in Chapter 4 [73]. Figures 5.12 (a), (b), and (c) depict the fitted profiles at 4.2 K in the magnetic fields of 0, 2, and 4T, respectively. Above 12 K, under fields of 2 and 4 T, the width is limited by the instrumental
resolution indicating that the short-range magnetic order is converted into the long-range magnetic order. The profile of the Bragg peak corresponding to this long-range ordering [Figs. 5.12 (e) and (f)] has been fitted well using a single pseudo-Voigt function. In zero applied field, the SRO correlation length is $\sim 54$ Å at 4.2 K and it gets affected by the magnetic field. The SRO correlation lengths are $\sim 149$ and 110 Å at 4.2 K, and 86 and 62 Å at 7 K in an applied field of 2 and 4 T, respectively. Besides, the application of magnetic field affects the volume ratio of the LRO and SRO contributions (13:7 and 3:2 at 7 and 4.2 K, respectively, under applied field of 4 T). We also note that similar behaviour has been observed for the other peaks (200) and (210). Under an applied fields of 2 and 4 T, the enhancement of the SRO volume fraction with lowering of temperature could be responsible for the observed reduction in the intensity of the satellite Bragg peaks (100), (200), and (210) below $\sim 12$ K, shown in Fig. 5.11. Here it may be noted that in Chapter 4 [73], the presence of the SRO at all temperatures (below $T_N$), in zero applied field, was attributed to the different spin character of the Co$^{3+}$ (Ising) and Fe$^{3+}$ (Heisenberg) spins, due to which the Fe$^{3+}$ ions remains in the paramagnetic phase or freeze randomly at low temperatures. In the present study, we have observed that in magnetic fields of 2 and 4 T, the SRO is present only at low temperatures ($< 12$ K). This suggests that in applied fields, in a spin-chain, the Fe$^{3+}$ spins are aligned parallel to the Co$^{3+}$ spins for $12 < T < 20$ K. However, at low temperatures (below $\sim 12$ K), both Co$^{3+}$ and Fe$^{3+}$ spins possibly freeze randomly as the SRO volume fraction increases. Such a spin freezing is different form the spin freezing in zero field (mentioned in Chapter 4) [73], where only the Fe$^{3+}$ spins freeze randomly, resulting in the different nature of the SRO in the presence of field.

Now we compare the observed field induced transitions for the present compound with one of the well studied compounds of $A_3MXO_6$ family, viz. the compound
Chapter 5. Effect of Magnetic Field on the Ground State Magnetic Properties of Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ [62, 66, 106]. The compound Ca$_3$CoRhO$_6$ was reported to order in the PDA state below 90 K. However, the present compound Ca$_3$Co$_{1.8}$Fe$_{0.2}$O$_6$ orders in the SDW structure below $T_N$. Besides, for the compound Ca$_3$CoRhO$_6$, a magnetic contribution to the intensity of the (110) peak was observed in an applied field of 2 T below 90 K, which was ascribed to a field induced ferrimagnetic state. Further, a drop in the intensity of the Bragg peak (100) was observed below $\sim$ 30 K for the measurements in a field of 2 T. The observed drop in the intensity of the (100) peak was ascribed to a magnetic phase transition from the ferrimagnetic state to a frozen PDA (FPDA) state, below 30 K. In the present study for the compound Ca$_3$Co$_{1.8}$Fe$_{0.2}$O$_6$, two field induced transitions, first from the zero field SDW structure to a commensurate amplitude modulated (AM) structure, and second from the AM structure to a ferrimagnetic structure have been observed. The observed SDW structure and AM structure are very much different from the PDA and FPDA structures of the compound Ca$_3$CoRhO$_6$. The observed reduction in the intensities of the satellite peaks (in applied fields) for the present compound has been ascribed to the presence of the SRO at low temperatures.

Now we compare the observed field induced transitions in the present study with the parent compound Ca$_3$Co$_2$O$_6$. In absence of magnetic field, the parent compound Ca$_3$Co$_2$O$_6$, was reported to order in a modulated PDA structure with the propagation vector $\mathbf{k} = \{0, 0, 1.01\}$ below 25 K [86]. A field induced transition to a ferrimagnetic state was observed, in the magnetic field of 1.7 T, and then a transition to a ferromagnetic state was reported in the magnetic field of 3.6 T [62]. However, for the present compound Ca$_3$Co$_{1.8}$Fe$_{0.2}$O$_6$, we have observed a field induced incommensurate (SDW structure at $H = 0$ T) to commensurate (AM structure at $H = 2$ T) magnetic phase transition, followed by another magnetic phase transition to a ferrimagnetic state at a higher field. Further, for the parent
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compound \( \text{Ca}_3\text{Co}_2\text{O}_6 \), a SRO (of antiferromagnetic nature) along with a LRO was reported only below \( \sim 15 \) K \( (T_N = 25 \) K). Moreover, no change in the degree of antiferromagnetic disorder (SRO) was reported at magnetic fields of 1.2 and 2.4 T \[106\]. For the present compound \( \text{Ca}_3\text{Co}_{1.8}\text{Fe}_{0.2}\text{O}_6 \), in zero applied field the SRO coexists with LRO at all the temperatures below \( T_N \) \( (\sim 20 \) K). An application of magnetic field converts the SRO into the LRO above 12 K. We, therefore, conclude that the magnetic properties of the compound \( \text{Ca}_3\text{Co}_{1.8}\text{Fe}_{0.2}\text{O}_6 \) are very much different from the well studied compounds \( \text{Ca}_3\text{Co}_2\text{O}_6 \) and \( \text{Ca}_3\text{CoRhO}_6 \) of the \( A_3\text{MXO}_6 \) family.

5.4 Summary and Conclusion

The author has studied the effect of an external magnetic field on the nature of the magnetic ordering in the compounds \( \text{Ca}_3\text{Co}_{2-x}\text{Fe}_x\text{O}_6 \) \( (x = 0, 0.1, 0.2, \text{and} 0.4) \) using dc magnetization and neutron diffraction techniques. For all compounds, the high temperature magnetic susceptibility obeys the Curie-Weiss law. The values of paramagnetic Curie temperature decrease as the concentration of iron increases \( (\theta_p = 27.8 \text{ for } x = 0 \text{ compound}) \) and it becomes negative \( (-1.6 \text{ K for } x = 0.4) \) for higher concentration of iron. From the dc-magnetization study, we have derived the values of the intrachain (positive) and interchain (negative) exchange constants for the compounds \( \text{Ca}_3\text{Co}_{2-x}\text{Fe}_x\text{O}_6 \) \( (x = 0.0, 0.1, 0.2, \text{and} 0.4) \). The values of intrachain exchange constant \( J \) derived by fitting the high temperature \( \chi T \) vs \( T \) curves with the theoretical model indicates that as the concentration of iron increases, \( J \) decreases and for higher concentration of iron \( (x > 0.2) \) it becomes negative. These results can be understood by considering the formation of pairs of \( \text{Fe}^{3+} \) ions along the chain for higher concentration of iron \( (x = 0.4) \) and negative exchange interaction between \( \text{Fe}^{3+} \) ions along the chain (via oxygen). A coexistence of the SRO and
LRO (for the $x = 0.2$ and $0.4$ compounds), has been confirmed from the zero field neutron diffraction study (Chapter 4). It is observed that the correlation lengths for both SRO and LRO do not differ very much for the $x = 0.2$ and $0.4$ compounds, indicating that Fe ions in a chain are located preferentially very close to each other for higher concentration of iron ($x = 0.4$). A field induced ferri-to-ferromagnetic like transition is found in the $M$ vs $H$ study. An estimate of the interchain exchange constant $J'$, derived from the ferri-to-ferromagnetic like transition under field, indicates that $J'$ increases with increasing the Fe concentration. This indicates that the strength of negative exchange interaction for Co2/Fe-O-Co2/Fe pathway is greater than that of the Co2-O-Co2 which can be ascribed to the different spin nature of Co$^{3+}$ and Fe$^{3+}$ ions. Deviation from $\Delta M/M_S = \delta H^{-3/2}$ behavior with increasing iron concentration indicates the deviation from quasi-1D character of spins for higher Fe substituted compounds. The observed results (in the dc magnetization study) have been ascribed to a breaking of the ferromagnetically ordered linear spin-chains along the crystallographic $c$ axis with iron substitution and strengthening of antiferromagnetic exchange interaction between Fe$^{3+}$ ions.

Neutron diffraction study has been carried out to study the spin-spin correlations in the compound Ca$_3$Co$_{1.8}$Fe$_{0.2}$O$_6$, by directly investigating the evolution of the magnetic structures as a function of applied magnetic field (0, 2 and 4 T) and temperature (1.5 - 100 K). At low temperatures, in the zero field, the magnetic structure corresponds to the SDW structure with an incommensurate propagation vector $[k = \{0, 0, 1.0182(9)\}]$. An application of magnetic field up to 4 T does not change the number of the additional magnetic Bragg reflections in the neutron diffraction patterns, it only affects their intensities and positions. A change in the propagation vector from an incommensurate $[k = \{0, 0, 1.0182(9)\}]$ to a commensurate $[k = \{0, 0, 1\}]$ is found, when the magnetic field is increased to 2 T. In an
applied field of 2 T, the magnetic structure corresponds to an amplitude modulated structure with \( k = \{0, 0, 1\} \). The observed change in the propagation vector, from the incommensurate to the commensurate, indicates a reduction of the spin frustration on the triangular lattice in an applied field of 2 T. A further increase of the magnetic field \( (H = 4 \text{ T}) \) leads to a magnetic phase transition from the amplitude modulated structure to a ferrimagnetic structure. In the ferrimagnetic phase, intensities of the satellite peaks \((100), (200), \text{ and } (210)\) are low compared to the SDW and the AM structures, indicating that the AFM correlations between spin chains are weakened or broken, before the system reaches to a fully polarized ferromagnetic phase at higher magnetic fields \( (> 5 \text{ T}) \). The application of magnetic field affects the SRO volume fraction as well as the spin-spin correlation length. The applied magnetic field also converts the SRO (which was present in zero field) into LRO above 12 K, however, below 12 K, the SRO still persists. In the magnetic fields of 2 and 4 T, the observed reduction in the intensities of the peaks \((100), (200), \text{ and } (210)\) \([\text{below } \sim 12 \text{ K}]\) has been attributed to an increase in the volume fraction of the SRO (different from the zero field SRO). This is in contrast with the zero field neutron diffraction study, where a SRO coexists with LRO in a constant volume ratio of 13:7 at all temperatures below \( T_N \). The derived results would be useful to understand the effect of an external magnetic field on the nature of the magnetic ordering in other geometrically frustrated triangular lattice spin systems. The results would also be useful to develop theoretical models to describe the effect of magnetic field on the degenerate magnetic ground states of such quasi-1D spin-chain systems. However, a single crystal neutron diffraction study would be required for a complete elucidation of a magnetic phase diagram of the compound \( \text{Ca}_3\text{Co}_{1.8}\text{Fe}_{0.2}\text{O}_6 \) in the temperature-magnetic field plane.