CHAPTER 5

Magnetic Properties and Magnetocaloric Effect in Ternary Rare Earth Intermetallic compounds

\( \text{NdMn}_{2-x}\text{Co}_x\text{Si}_2 \)

5.1 Introduction

The ternary rare earth \( RT_2X_2 \) intermetallic compounds (\( R \): rare earth, \( T \): transition metal, \( X \): Si or Ge) [125, 126] are expected to be potential candidates for their applications in magnetic refrigeration technology [127–130]. The magnetic behavior of \( RT_2X_2 \) compounds (containing manganese) is of great interest, because in this class of system, among the two magnetic sublattices i.e. \( R \) and \( T \), the transition metal sublattice orders magnetically only for the compounds with \( T = \text{Mn} \) [126, 131]. The magnetic properties of \( RMn_2X_2 \) compounds mainly depend on the intralayer Mn-Mn distance, \( d_{\text{Mn-Mn}} \). There is a critical value of \( d_{\text{Mn-Mn}} \), about 2.87 Å below which, the coupling between Mn layers is antiferromagnetic, and above this value, the coupling is ferromagnetic in nature [132–134]. In \( \text{NdMn}_2\text{Si}_2 \), the Mn sublattice is known to order antiferromagnetically below 380 K [135]. Whereas, below 33 K, the compound is ferromagnetic with ordered moments at both Nd and Mn sublattices [135]. The Mn sublattice is a canted ferromagnet at temperature below 33 K. The exchange interaction for the Nd ordering is mainly of the Ruderman-Kittel-Kasuya-Yosida (RKKY) type [135]. On the other hand, \( \text{NdCo}_2\text{Si}_2 \) is antiferromagnetic.
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below 32 K with only Nd sublattice ordering, and reported to undergo three anti-ferromagnetic transitions below this temperature [136]. It is also reported that the compound undergoes multiple metamagnetic transitions under an external magnetic field above 40 kOe at 4.2 K [136]. Thus, by replacing Mn atoms in NdMn$_2$Si$_2$ by Co, one can achieve various interesting magnetic properties in the RT$_2$X$_2$ intermetallic compounds where both R and T sublattices carry ordered magnetic moments. Besides, from the point of view of a large MCE, it is desirable to have ordered magnetic moments at both R and T sublattices.

In this chapter, we discuss magnetic properties as well as MCE in NdMn$_{2-x}$Co$_x$Si$_2$ compounds, and show that the observed magnetic properties have important roles to establish a large MCE and these compounds are potential candidates for applications in magnetic refrigeration technology. It may be mentioned here that no MCE study on these compounds has been reported yet. Here, we have observed that near the magnetic phase transition temperature (a ferromagnetic to an antiferromagnetic), NdMn$_{2-x}$Co$_x$Si$_2$ compounds show a negligible hysteresis which makes these systems important for their possible practical applications in magnetic refrigerant at low temperatures. Also for $x \sim 0.2$, the compounds undergo a metamagnetic transition as well which yields a giant MCE as a large change in magnetization is associated with the metamagnetic transition. The influence of domain wall pinning on the MCE of these compounds has also been discussed in this chapter. The results discussed in this chapter have been communicated for publication.[137]

5.2 Experimental details

Polycrystalline samples of NdMn$_{2-x}$Co$_x$Si$_2$ ($x = 0.2, 0.4, 0.6, 0.8, and 1$) were prepared by an arc melting under argon atmosphere, with constituent elements Nd (99.9 % purity), Mn (99.99% purity), Co (99.99% purity), and Si (99.9995% purity).
The samples were remelted many times for a better chemical homogeneity. After melting, the resultant ingots were annealed in a vacuum-sealed quartz tube at 1000 °C for 5 days. The powder X-ray diffraction study, carried out on all samples at room temperature using the Cu-K$_\alpha$ radiation. The dc magnetization measurements was carried out on all samples using a Physical Property Measurement System (PPMS, Quantum Design) as a function of temperature and magnetic field. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements were carried out over the temperature range of 5-330 K under 300 Oe field. Magnetization as a function of magnetic field was measured for all samples at different temperatures over a field variation of ± 80 kOe. Besides, magnetization isotherms for the $x = 0.2$ and 0.4 samples were also recorded over an applied field of 0-50 kOe at various temperatures at and around the magnetic phase transition temperatures. Neutron diffraction patterns were recorded for the $x = 0.2$ and 1 samples at various temperatures in the range 5-300 K using the powder diffractometer - II with $\lambda = 1.2443$ Å at the Dhruva reactor, Trombay, Mumbai, India. One-dimensional neutron-depolarization measurements were carried out for $x = 0.2$ and 1 samples down to 2 K using the polarized neutron spectrometer (PNS) at the Dhruva reactor ($\lambda = 1.205$ Å). FC neutron-depolarization measurements were carried out by first cooling the sample from room temperature down to 2 K in the presence of 50 Oe field (required to maintain the neutron beam polarization at the sample position) and then carrying out the measurements in warming cycle under the same field. The incident neutron beam was polarized along the -z direction (vertically down) with a beam polarization of 98.60(1)% [45].
5.3 Results and discussion

5.3.1 X-ray diffraction study

Figure 5.1 shows the XRD patterns at room temperature for $x = 0.2$, 0.4, 0.6, 0.8, and 1 samples. The XRD patterns confirm that all samples are in single phase.

Figure 5.1: X-ray diffraction patterns for $x = 0.2$, 0.4, 0.6, 0.8 and 1 samples at room-temperature. The ($hkl$) values corresponding to Bragg peaks are marked.
with ThCr$_2$Si$_2$-type crystal structure and space group $I4/mmm$. Nd and Si atoms occupy the (0, 0, 0) and (0, 0, z) (with $z \sim 0.38$) sub lattices, respectively, while Mn/Co occupy the (0, 1/2, 1/4) position. In this structure, Nd, Mn and Si atoms are stacked in layers along the $c$-axis in Nd-Si-Mn-Si-Nd sequence. The crystal structure of NdMn$_{2-x}$Co$_x$Si$_2$ series is shown in Fig. 5.2. The present XRD study shows that the lattice constants $a$ and $c$ decrease with increasing Co substitution (Fig. 5.3), similar to that reported for NdMn$_{2-x}$Fe$_x$Si$_2$, [138] NdMn$_{2-x}$Fe$_x$Ge$_2$, [139] and NdMn$_{2-x}$Co$_x$Ge$_2$ compounds [140].

![Crystal structure of NdMn$_{2-x}$Co$_x$Si$_2$ at room temperature.](image)

**Figure 5.2: Crystal structure of NdMn$_{2-x}$Co$_x$Si$_2$ at room temperature.**

### 5.3.2 Magnetization study

Figure 5.4 shows the ZFC and FC magnetization ($M$) vs temperature ($T$) curves under an applied field of 300 Oe for the $x = 0.2$, 0.4, 0.6, 0.8, and 1 samples in the temperature range of 5 to 330 K. It is seen that a magnetic phase transition occurs around 45 K for all samples. It will be evident from our detailed magnetization and neutron diffraction investigations (described later) that, this magnetic phase transition ($T_C \sim 45$ K) corresponds to a transition from an antiferromagnetic state...
Figure 5.3: Variation of lattice constants and unit cell volume with Co concentration. The error bars are within the symbols.

Figure 5.4: Temperature dependence of FC and ZFC magnetization $M$ for $x = 0.2$, 0.4, 0.6, 0.8, and 1 samples at 300 Oe applied field. Inset shows the enlarged view of the FC and ZFC magnetization for the $x = 0.8$ and 1 samples.

to a canted-ferromagnetic state with decreasing temperature. At all temperatures below $\sim T_C$, there is a branching of the ZFC and FC curves for all samples, and the ZFC curves show a down turn below this temperature, the reason for which will be
discussed later. At lower temperatures, a negative magnetization is observed in the ZFC curves due to a small negative magnetic field trapped in the superconducting magnet of the PPMS magnetometer [141]. Figure 5.5 depicts the temperature dependence of the real part of the ac susceptibility $\chi'_{ac}$ at various frequencies for the $x = 0.2$ and 1 samples. The peak of $\chi'_{ac}$ denotes the magnetic transition temperature. There is no shift in the peak position of $\chi'_{ac}$ vs temperature curves with frequency indicating that there is no glassy behavior present in these samples. However, for the $x = 1$ sample, a sluggish nature of magnetic ordering (as compared to that for the $x = 0.2$ sample) is evident.

![Figure 5.5: Temperature dependence of the real part of the ac susceptibility $\chi'_{ac}$ at various frequencies with an ac field of 5 Oe for the $x = 0.2$ and 1 samples.](image)

Figure 5.6 shows the $M$ vs applied field ($H$) curves for all samples at 5 K over a field range of ± 80 kOe (i.e. over all four quadrants). No saturation in magnetization is found even up to a field of 80 kOe, indicating the presence of a high magnetic
anisotropy in these samples. The presence of a strong uniaxial anisotropy was reported for the parent compound NdMn$_2$Si$_2$ [135]. There is a step like increase in the $M$ vs $H$ curves for all present samples at 5 K, indicating a metamagnetic-like (magnetic field-induced transition from an antiferromagnetic state to a ferromagnetic-like state) transition. The importance of the observed metamagnetic transition to establish a large MCE is discussed later. The value of magnetization ($M_S$) at the maximum applied field (80 kOe) decreases with an increase in the Co concentration (shown in Fig. 5.7) indicating that the substitution of Mn by Co dilutes the magnetism in the NdMn$_{2-x}$Co$_x$Si$_2$ series. This is due to the fact that Co atoms do not carry any magnetic moment in the $RT_2X_2$ compounds [126, 131]. Similar behavior was observed for NdMn$_{2-x}$Cr$_x$Si$_2$ [142] as well as NdMn$_{2-x}$Fe$_x$Si$_2$ [138] compounds where both Cr and Fe are known to be non magnetic. The coercivity increases with an increase in Co concentration (Fig. 5.7).
5.3.3 Magnetocaloric effect

The magnetic entropy change $\Delta S_M$ has been derived from the magnetization isotherms (Fig. 5.8) using the Eq. (1.9). For the present NdMn$_{2-x}$Co$_x$Si$_2$ compounds, a field induced magnetic transition is observed [Fig. 5.8]. For such a first order type phase transition, the magnetization is not a continuous function of temperature and magnetic field. Therefore, the usage of the Maxwell relation [Eq. (1.9)], for the calculation of magnetic entropy change, is not correct in principle. However, the transition is not discontinuous under a finite value of applied magnetic field, rather a quasi-continuous in nature; hence Eq. (1.9) (derived from the Maxwell relation) can be used [7, 143]. The variations of $-\Delta S_M$ with temperature for the $x= 0.2$ and 0.4 samples at various fields are depicted in Figs. 5.9 (a) and 5.9 (b), respectively. The maximum value of $-\Delta S_M$ is found to be around the magnetic transition temperature and it increases with an increase in the applied magnetic field. At a field variation of 50 kOe, $-\Delta S_M$ values are found to be 14.4 and 12.4 J kg$^{-1}$ K$^{-1}$ at 47.5 K for the $x = 0.2$ and 0.4 samples, respectively. The value of $-\Delta S_M$ decreases as Co concentration increases because magnetization decreases with an increase in Co concentration,
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Figure 5.8: Magnetization isotherms at various temperatures below and above $T_C$ for the $x = 0.2$ and 0.4 samples. The isotherms are at an interval of 5 K.

and $\Delta S_M$ depends on the change in magnetization with temperature. The $x = 0.2$ and 0.4 samples show a giant MCE, and these values are comparable with that reported for some of the best known giant MCE materials such as Gd$_5$Ge$_2$Si$_2$ [27] and MnFeP$_{0.45}$As$_{0.55}$ [28] around room temperature. When compared over the similar lower temperature region, these observed values are nearly equal [144, 145] or even larger than some of the potential magnetic refrigerant materials such as DyMn$_2$Ge$_2$ [130]. It is observed that the field-hysteresis reduces significantly near the $T_C$, which makes these materials important for practical applications. $-\Delta S_M$ acquires both positive and negative values corresponding to normal and inverse MCE, respectively. Due to both positive ($T > 32$ K) and negative ($T < 32$ K) MCEs, the studied materials can be used for both magnetic cooling and heating, respectively.
Since the magnetic anisotropy is quite large in these studied samples, the use of a single crystal can give a larger value of $-\Delta S_M$ because the change in magnetization across the magnetic transition region is expected to be quite sharper for a single crystal. Fig. 5.10 marks the area under the $-\Delta S_M(T)$ curves corresponding to RCP for the $x = 0.2$ and 0.4 samples, for a field variation of 50 kOe. The RCP values for the $x = 0.2$ and 0.4 samples are found to be 154 and 89 J kg$^{-1}$, respectively.

### 5.3.4 Detailed magnetization study

In order to understand the observed MCE, we have carried out further dc magnetization study. Figure 5.11 depicts $M$ vs $H$ curves at various temperatures above 5 K over all four quadrants for the $x = 0.6$ sample. The coercive field $H_C$ sets-in only below $\sim 40$ K, and then increases with decreasing temperature [inset of Fig. 5.11]
Figure 5.10: $-\Delta S_M$ vs $T$ curve for $x = 0.2$ and 0.4 samples, respectively, for $\Delta H = 50$ kOe. The shaded area corresponds to the relative cooling power.

(b)]. For $x = 0.2$ and 0.8 samples, the $M$ vs $H$ curves at different temperatures are shown in Figs. 5.12 (a) and 5.12 (b), respectively. The hysteresis loops are found to almost collapse at higher temperature when compared with that at 5 K, shown in Fig 5.6. The significant reduction of hysteresis near the $T_C$, makes these materials important for practical applications in magnetic refrigeration. $H_C$ is a measure of the magnetic field required to displace the domain wall over the largest potential energy barrier on its path. The observed large coercivity at lower temperatures has two contributions, one is the intrinsic and the other is the extrinsic. System with a large magnetocrystalline anisotropy has a narrow domain wall because the width of the domain wall is inversely proportional to its anisotropy constant [146]. Broeck et al.[147] showed that there is a difference in the domain wall energy when domain wall centre coincides with the atomic plane, and when it is located between planes.
This energy difference causes the intrinsic domain wall pinning. Hilzinger and Kronmiller [148, 149] showed that the intrinsic coercivity is larger for narrow domain walls, and intrinsic domain wall pinning dominates at low temperatures. Whereas, the extrinsic pinning arises from various kinds of impurities and defects. The parent compound NdMn$_2$Si$_2$ is also reported to shows a large $H_C$ of 1.4 kOe at 4.2 K [135]. In the present compounds, the Co atoms are nonmagnetic, as confirmed by neutron diffraction study (presented later), and could act as defects causing an increase in the extrinsic domain wall pinning, thus resulting in overall increase in coercivity.
Figure 5.12: $M$ vs $H$ curves over all the four quadrants for (a) $x = 0.2$, and (b) $x = 0.8$, samples at various temperatures.

(Fig. 5.7). Stronger domain wall pinning, results in a slow rise of magnetization as a function of magnetic field. However at higher temperatures, the domain walls are relatively more mobile resulting in a faster raise of magnetization as a function of field. This behavior results in a cross-over of virgin magnetization curves as seen for the $x = 0.2$ and 0.4 samples in Figs. 5.13 (a) and 5.13 (b), respectively. The inverse MCE occurs in the temperature region where there has been a crossover of $M$ vs $H$ curves due to the domain wall pinning. The crossover of $M$ vs $H$ curves is more prominent for the $x = 0.4$ sample, therefore, this sample acquires a higher value of negative $-\Delta S_M$. The peak in the $M$ vs $T$ curves in ZFC condition (shown in Fig. 5.4) can also be explained on the basis of the domain wall pinning. Below
Figure 5.13: Magnetization isotherms (a) and (b) at temperatures below $T_C$ and low fields for the $x = 0.2$ and 0.4 samples, respectively.

$T_C$, in the ferromagnetic state, the magnetization is expected to have a higher value at low temperature due to the ordering of spins within the domain. The magnetic hardness also increases due to domain-wall pinning at $T < T_C$. These two effects are opposite in nature, and results in the appearance of peak in the ZFC magnetization curves. In case of FC magnetization, when the sample is cooled under a magnetic field, it would favor the growth of domains in the direction of the applied magnetic field resulting in a higher value of magnetization as compared to the ZFC magnetization. Other intermetallic compounds with high magnetic anisotropy are also reported to show such type of domain-wall pinning [146, 150, 151].

The magnetic field dependence of magnetization for the $x = 0.2$ and 0.4 samples at different temperature (under ZFC condition) is shown in Fig. 5.8. For both $x$
= 0.2 and 0.4 samples above 45 K, i.e. in the antiferromagnetic region (confirmed from our neutron diffraction study, described later for the $x = 0.2$ sample), there is a signature of a metamagnetic-like transition (field induced antiferromagnetic to a ferromagnetic-like transition) in the $M$ vs $H$ curves, similar to that observed in other intermetallic compounds with same crystal structure [127, 152]. When the applied field is less than a certain critical value $H_{Crt}$, the magnetization increases (almost) linearly with increasing field as expected for an antiferromagnet. However, when $H > H_{Crt}$, the increase in magnetization is initially faster and then shows a tendency of saturation at higher fields. Significantly, the value of $H_{Crt}$ increases with an increasing temperature. In an antiferromagnetic ground state, one expects that the magnetic field required for a metamagnetic transition (if exists) should increase with decreasing temperature. The observed contrary behavior of the metamagnetic transition just above $T_C$ indicates that either, the ferromagnetic correlation of Nd sublattice extends above $T_C$ (up to a certain temperature) under an external magnetic field or that the Mn sublattice is at the verge of a ferromagnetic transition even above $T_C$ (up to a certain temperature). In fact, it is known in literature that a ferromagnetic ordering of the Nd sublattices induces a ferromagnetic ordering of the Mn sub-lattices. For example, Welter et al [135]. have postulated that the ferromagnetic ordering in Nd sublattice (below $T_C$) results in switching of the antiferromagnetic to ferromagnetic phase in the Mn sub lattice in NdMn$_2$Si$_2$. Thus for the present system, under an applied field, once the Nd sub-lattices order ferromagnetically at $T > T_C$, it induces a ferromagnetic ordering of the Mn sub-lattices. This leads to the observed metamagnetic transition. For the $x = 0.2$ sample, a metamagnetic transition is quite prominent (Fig. 5.8), while with an increasing Co concentration i.e. for the $x = 0.4$ sample, the metamagnetic transition is weakened. The metamagnetic transition, which occurs near the antiferromagnetic to ferro-
magnetic transition for $x = 0.2$ and $0.4$ samples, results in a giant MCE in these materials. Following the metamagnetic transition, when the applied field is reversed (decreased), a hysteresis behaviour is observed [Figs. 5.11(b) and 5.12]. However, when field is lowered further (i.e. $H < H_{Cr1}$), the hysteresis disappears as expected in an antiferromagnetic state. When the sample temperature is increased above $T_C$ (e.g. $T \geq 100$ K), the $M$ vs $H$ curves show a linear behavior corresponding to a pure antiferromagnetic state at these higher temperatures.

### 5.3.5 Neutron diffraction study

We have performed the neutron diffraction study on the $x = 0.2$ sample at various temperatures in order to gain a microscopic understanding of the nature of the magnetic ordering (discussed later in this section) viz. the canted-ferromagnetic state at lower temperatures ($< 45$ K), and a collinear antiferromagnetic state at higher temperatures ($> 45$ K, up to room temperature). The measured diffraction patterns were analyzed using the Rietveld refinement technique (FULLPROF [41, 42]). The reported values of the atomic positions and lattice constants for NdMn$_2$Si$_2$ were used as the starting values for the refinement [135]. The analysis reveals that the crystal structure is body centered tetragonal ThCr$_2$Si$_2$-type structure (space group: $I4/mmm$) for the $x = 0.2$ sample. The observed and Rietveld calculated diffraction patterns are shown in Fig. 5.14. The variation in values of $a$-axis and $c$-axis lattice constants with temperature is shown in Fig. 5.15. The variation of $d_{Mn-Mn}$ with temperature is also depicted in Fig. 5.15. Both lattice constants and $d_{Mn-Mn}$ increase with increasing temperature with a distinct enhancement near $T_C$. Here we would like to mention that $d_{Mn-Mn}$ is found to be less than the critical value (2.87 Å [132–134]) at all temperature (Fig. 5.15). This results in an antiferromagnetic coupling between Mn layers (discussed later) as described in
Figure 5.14: (a), (b) and (c): Neutron diffraction patterns for the $x = 0.2$ sample at 5, 50 and 300 K, respectively. The open circles represent the observed patterns. The solid lines represent the Rietveld refined patterns. The difference between observed and calculated patterns is also shown at the bottom of each panel by solid lines. The vertical bars indicate the allowed Bragg peaks position for chemical (top row) and magnetic (bottom row) phases. (d) The temperature dependence of the antiferromagnetic (111) Bragg peak.
Figure 5.15: Variation of lattice constants and $d_{\text{Mn-Mn}}$ with temperature for the $x = 0.2$ sample. The solid lines are guide to eye. The dotted line separates the canted ferromagnetic (CFM) and antiferromagnetic (AFM) regions.

literature [132–134]. At 5 K, the neutron diffraction pattern shows an additional Bragg peak (001) and an enhancement in the intensities of the (101) and (112) nuclear Bragg peaks [Fig. 5.14 (a)] when compared with 50 or 300 K diffraction patterns [Figs. 5.14 (b) and 5.14 (c)]. The analysis of the diffraction pattern at 5 K shows that the Nd moments are aligned along the crystallographic c-axis, and the Nd layers are stacked ferromagnetically along the c-axis. The Mn moments are ferromagnetically coupled (parallel) to each other within a given Mn-layer, however, canted at an angle of $+30(1)^\circ$ (clockwise) and $-30(1)^\circ$ (counter clockwise) to the c-axis for two consecutive layers. Such bi-layers of Mn are stacked along the c-axis forming a part of the Nd-Si-Mn-Si-Nd-Si-Mn sequence along the c-axis. The canting results in a ferromagnetic component of the Mn moments along the c-axis and an antiferromagnetic component in the ab plane. The ferromagnetic component of the Mn moments (aligned along the c-axis) is parallel to the Nd moments, and gives an enhancement in the intensities of the fundamental (nuclear) Bragg peaks over the lower scattering region. For instance, the increase in the intensity of (101) Bragg
peak at 5 K is due to the ferromagnetic ordering of Nd sublattice, whereas, (112) fundamental peak gets a magnetic contribution from both Nd and Mn sublattices. While the antiferromagnetic component of Mn moment lies in the (001) plane, and gives rise to the additional (001) Bragg peak, which is purely of magnetic origin. We, therefore, refer the low temperature (5K) magnetic phase as a canted-ferromagnetic state. The derived values of Nd and Mn net moments are 2.95(6) (along the c-axis) and 2.29(5) $\mu_B$ (at an angle of 30° with respect to the c-axis) at 5 K, respectively. The magnetic structure at 5 K is shown in Fig. 5.16 (a). No ordered magnetic moment of the Co atoms could be refined satisfactorily leading to the conclusion that the Co atoms do not order. This is in agreement with the literature reports that the transition metal atoms other than Mn in $RT_2X_2$ compounds do not carry any magnetic moment [126, 131]. The resulting magnetic moment (considering Nd moment and the ferromagnetic component of Mn moment along c-axis to be 2.95 and 1.98 $\mu_B$, respectively) for the $x = 0.2$ sample is $\sim 6.9 \, \mu_B$ per formula unit at 5 K, which is quite higher than that obtained from dc magnetization measurements.

Figure 5.16: Magnetic structure at (a) 5 K and (b) 50 K for the $x = 0.2$ sample.
(4.24 µB per formula unit). This is due to the non saturation tendency shown by the $M$ vs $H$ curve even at 80 kOe field.

At temperatures 50 K and above (i.e. 100, 200 and 300 K), the (001) Bragg peak disappears with a simultaneous decrease in the intensities of (101) and (112) nuclear Bragg peaks. However, an additional reflection (111), which is purely of magnetic origin [Fig. 5.14 (d)] appears. This suggests that there is a reorientation of the Mn moment above $T_C$ with respect to its direction below $T_C$. This leads to a different kind of antiferromagnetic ordering above $T_C$ as compared to the antiferromagnetic ordering (which appeared due to the canting of the Mn moment) observed in the canted-ferromagnetic state below $T_C$. The analysis of the diffraction patterns at 50, 100, 200 and 300 K suggests an antiferromagnetic structure based on the stacking of ferromagnetic (001) Mn planes in a + - + - sequence along the $c$-axis. This type of magnetic ordering is usually referred to as type-I antiferromagnetic [126]. The magnetic structure at 50 K is shown in Fig. 5.16 (b). The reorientation of Mn moment is supported by the fact that the Nd sub-lattice does not order at this temperature ($T > T_C$). The variations of the net Mn moments with temperature (for both $T < T_C$, and $T > T_C$) are shown in Fig. 5.17. The Mn moment at 5 K i.e. in the canted-ferromagnetic state is slightly less than the moment at 50 K i.e in the antiferromagnetic state. Similar behavior was observed in pure NdMn$_2$Si$_2$ [135].

### 5.3.6 Neutron depolarization study

We have also carried out the one dimensional neutron depolarization study [48, 119–122] for the $x = 0.2$ and 0.4 samples. Figure 5.18 shows the temperature dependence of the transmitted neutron beam polarization $P$ for an external field of 50 Oe applied parallel to the incident neutron beam polarization. For both samples, $P$ shows a continuous decrease from $\sim 48$ K and attains a constant value below $\sim 30$ K.
Figure 5.17: Temperature dependence of the net full magnetic moment of Mn [oriented at an angle of +30(1)° (clockwise) and -30(1)° (counter clockwise) to the \(c\)-axis for two consecutive layers in the canted ferromagnetic phase (CFM) and in a + - + - sequence along the \(c\)-axis in antiferromagnetic phase (AFM)] for the \(x = 0.2\) sample. The dotted line separates the CFM and AFM regions.

Figure 5.18: Temperature dependent of the transmitted neutron beam polarization \(P\) at an applied field of 50 Oe for \(x = 0.2\) and 0.4 samples.

Above 48 K the samples are in the collinear antiferromagnetic state (confirmed by neutron diffraction study for the \(x = 0.2\) sample), therefore no depolarization is observed. The temperature at which the value of \(P\) starts decreasing can be considered as the canted-ferromagnetic (CFM) transition temperature \(T_C\). Below \(T_C\),
the ferromagnetic component of the CFM state gives rise to the observed significant depolarization. The observed lower value of \( P \) for the \( x = 0.4 \) sample (as compared to that for the \( x = 0.2 \) sample) indicates a less ferromagnetic character with increasing Co-concentration. This is consistent with the observed lower \( M_S \) for the \( x = 0.4 \) sample compared to that for the \( x = 0.2 \) sample (Fig. 5.7). This is due to the fact that Co atoms do not carry any moment in this system.

### 5.4 Summary and conclusion

Here, in this chapter, we have studied the MCE as well as magnetic properties of the intermetallic compounds NdMn\(_{2-x}\)Co\(_x\)Si\(_2\). These compounds undergo a series of magnetic transitions from paramagnetic to antiferromagnetic to canted-ferromagnetic states with lowering of temperature. Neutron diffraction study at 5 K for the \( x = 0.2 \) sample shows that the Nd moments are aligned along the crystallographic \( c \)-axis and the Mn moments are canted at an angle of 30(1)\(^\circ\) to the \( c \)-axis. The canted Mn moments are coupled ferromagnetically along the \( c \)-axis and antiferromagnetically in the \( ab \) plane. Co does not carry any moment. Above \( T_C \) (\( \sim 45 \) K for the \( x = 0.2 \) sample), Nd sublattice does not order but Mn sublattice orders antiferromagnetically with full moment i.e. without any canting. The lattice constants as well as Mn-Mn bond distance show a distinct variation near \( T_C \). We observe that magnetization (\( M_S \)) decreases with increase in the Co concentration indicating that substitution of Mn by Co dilutes the magnetism in the NdMn\(_{2-x}\)Co\(_x\)Si\(_2\) series due to the fact that Co is non magnetic in this system. The coercivity increases with increase in Co concentration which is attributed to the domain wall pinning due to the defects created by Co substitution. The crossover of virgin magnetization curves in field dependent dc magnetization study and the observed peak in the ZFC curve in temperature dependent dc magnetization study have been explained on the basis
of domain wall pinning. Metamagnetic transition (from the antiferromagnetic to the ferromagnetic) is observed above $T_C$ for all samples. Due to the metamagnetic transition, a giant MCE is observed with $-\Delta S_M$ values of 14.4 and 12.4 J kg$^{-1}$ K$^{-1}$ for $x = 0.2$ and 0.4 samples, respectively, at 47.5 K under a field variation of 50 kOe. An inverse MCE is observed at temperatures below which there is a crossover of $M$ vs $H$ curves due to the domain wall pinning. Also due to the substitution, the hysteresis reduces significantly at $T \geq T_C$, which makes these materials important for magnetic refrigeration at low temperature.