Chapter 3

Magnetocaloric Effect and Critical Behavior Study in TbCo$_{2-x}$Fe$_x$

3.1 Introduction

Cubic Laves phase compounds $R$Co$_2$, where $R$ is a rare earth, have become potential candidates for magnetocaloric effect (MCE) as they show a large change in magnetic entropy ($\Delta S_M$) around their magnetic ordering temperatures [33]. They are of great interest since their discovery because of their interesting magnetic and electronic properties [51–54]. These compounds with the light rare-earth elements such as Pr, Nd, Sm, Gd and Tb are reported to show second-order magnetic phase transitions while, with heavy rare-earth elements such as Dy, Ho and Er, first-order metamagnetic transitions are reported [55]. It is known that in these $R$Co$_2$ compounds, the magnetic moments of the Co atoms align antiparallel to those of the rare earth atoms [51]. In such compounds, the observed magnetic moments of the $R$ atoms are close to their theoretically expected large moment values from their free ionic states [51]. Hence, a large MCE is expected for $R$Co$_2$ compounds. The magnetic state of Co depends on the induced moment at Co site due to 4f-3d exchange interactions and also on the lattice parameter in the $R$Co$_2$ compounds [55].

For TbCo$_2$ compound, the paramagnetic to ferrimagnetic second-order phase transition temperature $T_C$ (231 K) lies well below the room temperature [33, 55]. It is also known to undergo a structural transition near $T_C$. Below $T_C$, it has a
rhombohedral crystal structure with a space group $R\bar{3}m$ and above $T_C$ it has a cubic crystal structure with a space group $F\bar{d}3m$ [56, 57]. Here, in this chapter, we have shown that an appropriate (Fe) chemical substitution not only tunes the paramagnetic to ferrimagnetic transition temperature to around room temperature but also increases the operating temperature range of magnetic refrigeration without significant reduction in the $\Delta S_M$ value. We have also performed the temperature-dependent neutron diffraction study on $\text{TbCo}_{2-x}\text{Fe}_x$ to investigate the effect of Fe substitution on the structural phase transition and correlated that with the MCE. Generally, a structural phase transition is associated with a first-order magnetic phase transition, [58–60] but $\text{TbCo}_2$ is reported to undergo a second-order magnetic phase transition [61, 62]. This further motivated us to investigate the nature of the order of magnetic phase transition in detail in these $\text{TbCo}_{2-x}\text{Fe}_x$ compounds by carrying out dc magnetization and neutron-diffraction studies. Fe substitution at the Co site in $\text{TbCo}_2$ also provides an opportunity to investigate whether this transition can be tuned by a quenched disorder i.e., by chemical substitution. A critical exponent analysis in the vicinity of the magnetic phase transition is a powerful tool to investigate the details of the magnetic interaction responsible for the transition [63]. There are reports in literature that a quenched disorder can tune a first-order phase transition to a second-order phase transition [64, 65]. Fe substitution at the Co site in $\text{TbCo}_2$ also provides an opportunity to investigate whether this transition can be tuned by a quenched disorder i.e. by chemical substitution. In this chapter, the critical exponent study deals with a case where the effect of quenched disorder is investigated for a second-order magnetic phase transition. The nature and dimensionality of the magnetic interaction responsible for the transition have also been brought out from the critical exponent study. It is also shown that $\Delta S_M(H)$ curves are unique for each universality class. The results discussed in this chapter
have been published [66, 67].

3.2 Experimental details

The polycrystalline TbCo$_{2-x}$Fe$_x$ samples ($x = 0$, 0.06, 0.08 and 0.1) with constituent elements of 99.9 % purity were prepared by an arc melting under argon atmosphere. An excess of Tb (3 wt %) was added to the starting compositions to prevent the formation of Co-rich phases. For better chemical homogeneity, the samples were remelted many times. After melting, they were annealed in vacuum-sealed quartz tube at 850 °C for 7 days. The powder X-ray diffraction (XRD) using the Cu-K$_\alpha$ radiation in the 2$\theta$ range of 10 – 90° with a step of 0.02° was carried out on all the samples at room temperature. Magnetization ($M$) measurements were carried out using a commercial (Oxford Instruments) vibrating sample magnetometer. For dc magnetization measurements, the samples were field-cooled (FC) under 200 Oe field down to 5 K. The measurements were then carried out in the warming cycle from 5 to 320 K under the same field. The magnetization isotherms were recorded at various temperatures with an interval of 5 K up to a maximum applied magnetic field of 50 kOe. For critical exponent study, magnetization isotherms were measured for $x = 0$ and 0.1 samples up to a maximum field of 50 kOe over a temperature range of $T_C \pm 10$ K with an interval of 1 K. Neutron diffraction patterns were recorded at various temperatures for $x = 0$ and 0.1 samples using the powder diffractometer - II ($\lambda = 1.249$ Å) at the Dhruva Research Reactor, Trombay, Mumbai, India. Differential scanning calorimetry (DSC) measurements were carried out using Mettler Toledo DSC 822, with an empty aluminum pan as a reference. The measurements were carried out in the heating as well as cooling cycles with a scanning rate 5 K/min for the $x = 0$ and 0.1 samples.
3.3 Results and discussion

3.3.1 X-ray diffraction study

Figure 3.1 shows the XRD patterns for all samples at room temperature. The XRD patterns at room temperature confirm that all samples are in single phase with the C15 cubic MgCu$_2$-type crystal structure and space group $Fd3m$. The structural analysis, carried out using the Rietveld refinement method, confirms that Tb is at...
8a(1/8, 1/8, 1/8) and Co/Fe are at 16d (1/2, 1/2, 1/2) crystallographic sites. The crystal structure of the parent compound TbCo$_2$ at room temperature is shown in Fig. 3.2.

![Crystal structure of TbCo$_2$ at room temperature.](image)

**Figure 3.2: Crystal structure of TbCo$_2$ at room temperature.**

### 3.3.2 Magnetization and magnetocaloric effect

The FC magnetization versus temperature curves are shown in Fig. 3.3 for all samples. The paramagnetic to ferrimagnetic transition temperature $T_C$ is derived from the minima of the $dM/dT$ vs $T$ curves. $T_C$ has been found to increase with Fe substitution (231, 275, 290 and 303 K for $x = 0, 0.06, 0.08$ and 0.1, respectively). The observed increase in $T_C$ on substitution of Fe at the Co site is due to an enhanced exchange interaction between the 3$d$ transition metal ions [68]. The increase in $T_C$ is associated with the density of states at the Fermi level and on the splitting energies of the 3$d$ sub bands [69, 70]. Figure 3.4 shows the $M$ vs $H$ curves at 5 K over a field range of ± 50 kOe (covering all four quadrants) for the $x = 0, 0.06$, and 0.1 samples.
Figure 3.3: Temperature dependence of normalized magnetization for various compositions at 200 Oe applied field, where $M_{5K}$ is observed magnetization at 5 K.

Figure 3.4: $M$ vs $H$ curves over all the four quadrants for the $x = 0$, 0.06, and 0.1 samples of the TbCo$_{2-x}$Fe$_x$ series at 5 K.

Figure 3.5 shows a series of magnetization isotherms measured at various temperatures for the samples with $x = 0$, 0.06 and 0.1. Here the hysteresis effect is negligibly small. The magnetic entropy change $\Delta S_M$ was estimated from the magnetization isotherms using Eq. (1.9). Figure 3.6 shows the variation of $-\Delta S_M$ with temperature for the $x = 0$, 0.06 and 0.1 samples. The maxima in the $-\Delta S_M$ vs $T$ curves are found to be around $T_C$, and $-\Delta S_M$ increases with the increase in the
applied magnetic field. The peak of the $- \Delta S_M(T)$ curve also shifts towards room temperature on Fe substitution. The inset of Fig. 3.6 marks the area under the $- \Delta S_M(T)$ curve corresponding to RCP for the $x = 0.06$ sample. The RCP has been calculated by using Eq. (1.15). The $- \Delta S_M$, $T_{Cold}$, $T_{Hot}$, and RCP values of various compositions at field values of 10 and 50 kOe are given in Table 3.1. For $x = 0.1$ sample, due to experimental limitation we could not perform magnetization measurements above 320 K. So we extrapolated the $- \Delta S_M(T)$ curve to derive RCP.
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It can be seen (from Fig. 3.6) that by substituting Fe at the Co site, the width of the $-\Delta S_M(T)$ curve increases. This is because the magnetic transition spreads over a wide temperature range. This may be attributed to the presence of some magnetic randomness (disorder) at low temperature in the Tb sublattice on substituting Fe at the Co site. A similar kind of broadening was reported in TbNi$_2$ on substituting Fe at the Ni site by Singh et al. [71] which was due to the magnetic randomness in the

Figure 3.6: Magnetic entropy change $-\Delta S_M$ vs temperature for $\Delta H = 50$ kOe for $x = 0$, 0.06 and 0.1 samples. The inset shows the $-\Delta S_M$ vs T curve for $\Delta H = 50$ kOe for $x = 0.06$ sample. The shaded area corresponds to the relative cooling power.

Table 3.1: The magnetic entropy change $-\Delta S_M$, $T_{hot}$, $T_{cold}$, and the relative cooling power (RCP) values of various compositions at field values of 10 and 50 kOe.

<table>
<thead>
<tr>
<th>TbCo$_{2-x}$Fe$_x$</th>
<th>$\Delta H$ (kOe)</th>
<th>$-\Delta S_M$ (J kg$^{-1}$ K$^{-1}$)</th>
<th>$T_{cold}$ (K)</th>
<th>$T_{hot}$ (K)</th>
<th>RCP (J kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>10</td>
<td>2.5</td>
<td>217</td>
<td>239</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6.9</td>
<td>205</td>
<td>255</td>
<td>357</td>
</tr>
<tr>
<td>$x = 0.06$</td>
<td>10</td>
<td>1.1</td>
<td>253</td>
<td>286</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3.9</td>
<td>216</td>
<td>305</td>
<td>299</td>
</tr>
<tr>
<td>$x = 0.1$</td>
<td>10</td>
<td>1.0</td>
<td>269</td>
<td>315</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3.7</td>
<td>245</td>
<td>340</td>
<td>271</td>
</tr>
</tbody>
</table>
Tb sublattice. It was shown that this randomness occurred from the Tb sublattice and not from the Ni or Fe sublattices. For the $x = 0.06$ sample, the operating temperature range (defined as a difference between $T_{Hot}$ and $T_{Cold}$) is over 216 - 305 K i.e. $\sim 89$ K at $H = 50$ kOe, and for the $x = 0.1$ sample, the operating temperature range is over 245 - 340 K, i.e. $\sim 95$ K, while for the $x = 0$ sample it was only 50 K temperature range. The values of $-\Delta S_M$ and the operating temperature range for the present $x = 0.1$ sample and other reported materials showing giant MCE close to room temperature are given in Table 3.2. It is evident that the operating temperature range for the $x = 0.1$ sample is much broader than that for other reported giant MCE materials in the same temperature range (see Table 3.2). Such a broad operating temperature range is important for practical applications.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$T_C$ (K)</th>
<th>$\Delta H$ (kOe)</th>
<th>$-\Delta S_M$ (J kg$^{-1}$ K$^{-1}$)</th>
<th>$(T_{hot} - T_{cold})$ (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TbCo$<em>{0.9}$Fe$</em>{0.1}$</td>
<td>303</td>
<td>50</td>
<td>3.7</td>
<td>95</td>
<td>This work</td>
</tr>
<tr>
<td>Gd</td>
<td>292</td>
<td>50</td>
<td>9.5</td>
<td>70</td>
<td>[27]</td>
</tr>
<tr>
<td>Gd$_5$Ge$_2$Si$_2$</td>
<td>276</td>
<td>50</td>
<td>18.6</td>
<td>25</td>
<td>[27]</td>
</tr>
<tr>
<td>MnFeP$<em>{0.45}$As$</em>{0.55}$</td>
<td>300</td>
<td>50</td>
<td>18.0</td>
<td>23</td>
<td>[28]</td>
</tr>
<tr>
<td>Ni$<em>{55}$Mn$</em>{20}$Ga$_{25}$</td>
<td>313</td>
<td>50</td>
<td>86.0</td>
<td>1</td>
<td>[72]</td>
</tr>
</tbody>
</table>

Thus, by substituting Fe in TbCo$_2$, we not only tuned the $T_C$ from 231 K towards room temperature but also increased the operating temperature range for the MCE. To further increase the operating temperature range, composites of these alloys with different Fe concentrations can be made. A series of such compositions can be used in a cascaded way for magnetic cooling over a broad temperature range. Another important factor to be considered for magnetic refrigerant material is the hysteresis
loss. It has been already pointed out that the hysteresis in the $M(H)$ curves (shown in Fig. 3.5) in the operating temperature range is negligible for the Fe substituted samples, thus increasing the working efficiency of the material. This is important for a reversibility of the MCE of refrigerant materials.

### 3.3.3 Neutron diffraction study

The neutron diffraction study has been performed on the parent sample as well as on the $x = 0.1$ sample to find whether the structural phase transition is coupled with the magnetic phase transition. Neutron diffraction patterns were measured at various temperatures in magnetically ordered and paramagnetic states for both $x = 0$ and 0.1 samples. The patterns measured at 22 K and 300 K for both $x = 0$ and 0.1 samples are shown in Fig. 3.7. The diffraction patterns were analyzed by the Rietveld refinement technique using the FULLPROF program [41, 42].

The starting values of the atomic positions and lattice constants for the parent sample were taken from literature [57]. The analysis of the room temperature diffraction pattern for the $x = 0$ sample reveals that it has cubic crystal structure with a space group $Fd\bar{3}m$. The refinement of the diffraction pattern at 22 K shows that the low temperature phase is rhombohedral with a space group $R\bar{3}m$. This is in agreement with the neutron [57, 73] and X-ray powder diffraction [56] results reported earlier. The refinement of the diffraction pattern at 22 K for $x = 0.1$ sample reveals that the low temperature phase is rhombohedral, whereas at 300 K there is a coexistence of both rhombohedral and cubic phases. From the analysis of the diffraction patterns, measured at various temperatures [Figs. 3.8 (a) and (b)], we find that near the magnetic transition temperature $T_C$, there is also a structural phase transition associated with magnetic phase transition.

For both samples, we find that there is an increase in the $a$-axis lattice parameter
Figure 3.7: Neutron diffraction patterns of $x = 0$ and $0.1$ samples at 22 and 300 K of the TbCo$_{2-x}$Fe$_x$ series. The open circles show 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 curve by solid lines. The vertical bars indicate the position of the allowed Bragg peaks.
Figure 3.8: Temperature dependent neutron diffraction patterns for (a) $x = 0$ and (b) $x = 0.1$ samples. (a) The pattern at 22 K shows the rhombohedral phase. The patterns from 210-240 K show the region of coexistence of both rhombohedral and cubic phases. The pattern at 300 K shows the cubic phase. (b) The pattern at 22 K shows the rhombohedral phase, whereas the patterns from 270-300 K show the region of coexistence of both rhombohedral and cubic phases. The patterns are shifted with respect to neutron counts for better clarity.

and, a decrease in the $c$-axis lattice parameter with increasing temperature [Fig. 3.9 (a)]. A relatively larger change in the lattice parameters is found near the magnetic transition temperature, indicating that the structural phase transition is coupled with the magnetic transition. Figure 3.9 (b) shows the variation of the "unit-cell" volume with temperature for $x = 0$ and 0.1 samples. For the cubic unit cell, the lattice constant $a$ is used to calculate the unit-cell volume ($a^3$). For the rhombohedral phase, the quantities $\sqrt{2}a$ and $c/\sqrt{3}$ ($a$ and $c$ are the lattice parameters of the rhombohedral phase) are equivalent to the cubic lattice. These quantities
Figure 3.9: Temperature dependence of (a) lattice constants and (b) unit cell volume of the rhombohedral (equivalent to cubic lattice) and cubic phases for the $x = 0$ and 0.1 samples. The error bars are within the symbol. Inset shows variation of the Co-Co average bond length with temperature for the samples $x = 0$ and 0.1.

are, therefore, used to calculate the “unit-cell” volume of the rhombohedral phase.

The continuous change in the “unit-cell” volume across the phase transition temperatures indicates that the structural phase transition is of second-order in nature. There is an increase in the average Co-Co bond length on substituting Fe at the Co site, shown in the inset of Fig. 3.9 (b).

For the $x = 0.1$ sample, the structural transition also shifts towards a higher
temperature along with the magnetic transition temperature. The structural phase transition occurs near the same temperature as that of the magnetic transition temperature, indicating that there is a strong magnetoelastic coupling for both $x = 0$ and 0.1 samples. Here, a quantitative phase analysis of the rhombohedral and cubic phases has been made as a function of temperature across the structural/magnetic (magnetostructural) phase transition for both $x = 0$ and 0.1 samples and the derived phase fractions are plotted in Fig. 3.10. For the $x = 0.1$ sample, with increasing temperature, it is found that the growth of the cubic phase (at the expense of the rhombohedral phase) spreads over a wide temperature range (260 K to beyond room temperature) indicating that the structural transition is broadened on Fe

Figure 3.10: Quantitative phase analysis of the rhombohedral and cubic phases as a function of temperature across the magnetostructural phase transition for both the (a) $x = 0$ and (b) 0.1 samples. The dashed line above 300 K is the extrapolation of the data obtained below 300 K. Region between the vertical dotted lines shows the temperature range in which both the phases co-exist.
substitution. This is in good agreement with the results obtained from the dc magnetization studies, where we observe that the width of the $-\Delta S_M(T)$ curve increases on Fe substitution. The cubic and rhombohedral crystallographic phases coexist over the temperature ranges of around (205 K - 285 K) and (265 K - 365 K) for $x = 0$ and 0.1 samples, respectively. While the width of the magnetic transition, estimated from the temperature dependence of magnetic entropy change curve, is about 50 K and 95 K at 50 kOe field, for $x = 0$ and 0.1 samples, respectively. The second-order nature of the structural phase transition can be due to the soft phonons associated with the structural phase transition [74, 75]. Thus the structural transition coupled with the magnetic transition enhances the magnetocaloric effect.

The refinement of the neutron diffraction pattern at 22 K for the $x = 0$ sample shows a ferrimagnetic ordering of the Tb and Co moments along the $c$-axis of the rhombohedral structure as reported in literature [57]. The magnetic structure for the TbCo$_{2-x}$Fe$_x$ at 22 K is shown in Fig. 3.11. For the $x = 0$ sample, Tb has an

![Figure 3.11: Magnetic structure of TbCo$_{2-x}$Fe$_x$ at 22 K. Tb and Co/Fe moments are antiparallel to each other with ferrimagnetic ordering.](image-url)
ordered moment of $8.49 \pm 0.17 \, \mu_B$ per Tb ion, while Co has an ordered moment of $1.07 \pm 0.02 \, \mu_B$ per Co ion which are consistent with the values reported earlier [57]. The saturation moment is calculated to be $6.34 \, \mu_B$/f.u. For the $x = 0.1$ sample also, the Rietveld refinement of the neutron diffraction pattern at 22 K shows that there is a ferrimagnetic ordering of Tb with Co and Fe. Tb has an ordered moment of $8.44 \pm 0.02 \, \mu_B$ per Tb ion, Co has an ordered moment of $1.12 \pm 0.01 \, \mu_B$ per Co ion, while Fe has an ordered moment of $1.84 \pm 0.03 \, \mu_B$ per Fe ion. The saturation moment is calculated to be $6.13 \, \mu_B$/f.u. Figs. 3.12 (a) and (b) show the variation in magnetic moment as a function of temperature for both $x = 0$ and 0.1 samples.

![Figure 3.12](image-url)
3.3.4 Nature of magnetic phase transition

The nature of the magnetic phase transition in TbCo$_{2-x}$Fe$_x$ has been studied by the Arrott plot ($M^2$ vs $H/M$ curves) method as well as by employing the Inoue-Shimizu model. According to the Banerjee criteria [16], a positive slope in the $M^2$ vs $H/M$ curves indicates a second-order magnetic transition, while a negative slope indicates a first-order transition. Only positive slopes of the $M^2$ vs $H/M$ curves have been observed, for both $x = 0$ and 0.1 samples (shown in Fig. 3.13). It indicates that the paramagnetic to ferrimagnetic transition is of second order in nature.

![Figure 3.13: Arrott Plots for $x = 0$ and 0.1 samples of the TbCo$_{2-x}$Fe$_x$ series. The isotherms are at a temperature interval of 5 K.](image)

Another way to determine the nature of transition is by using the Inoue-Shimizu model [76]. The magnetic free energy, $F(M,T)$ can be expressed as per the Landau expansion

$$F(M,T) = \frac{a_1(T)}{2} M^2 + \frac{a_3(T)}{4} M^4 + \frac{a_5(T)}{6} M^6 + ... \ - \mu_0 H M$$ (3.1)

The Landau coefficients are accessible through the equation of state linking $M$ and the magnetic field, $\mu_0 H$

$$\mu_0 H = a_1(T)M + a_3(T)M^3 + a_5(T)M^5$$ (3.2)
The temperature dependence of the Landau coefficients $a_1(T)$ and $a_3(T)$ allows us to distinguish between first and second-order magnetic transitions. The susceptibility must be positive and exhibits a maximum at $T_C$, therefore the (positive) minimum in $a_1(T)$ marks $T_C$. $a_3(T)$ crosses zero at a second temperature, $T_0$. If $T_0 = T_C$, then the transition is second-order in nature, whereas $T_0 > T_C$, implies a first-order transition. The coefficients $a_1(T)$ and $a_3(T)$ are obtained by fitting the $M$ vs $H$ isotherms using Eq. (3.2). Figure 3.14 shows the variation of the coefficients $a_1(T)$ and $a_3(T)$ with temperature for both $x = 0$ and 0.1 samples. For

The $x = 0$ sample, the value of $T_C$ ($= T_0$) is 230 K and for the $x = 0.1$ sample, the value of $T_C$ ($= T_0$) is 299 K. Thus, $T_0 = T_C$ is found for both $x = 0$ and 0.1 samples, indicating the magnetic transition is of second order in nature. From the magnetization measurements, the magnetic transition temperature for the $x = 0$ and 0.1 samples are 231 K and 303 K, respectively.
3.3.5 Critical exponent study

To study the magnetic phase transition in detail, we have carried out critical exponent study near the Curie temperature $T_C$ for the $x = 0$ and 0.1 samples. According to the scaling hypothesis [77], for a second-order phase transition around $T_C$, the critical exponents $\beta$ (associated with the spontaneous magnetization), $\gamma$ (associated with the initial susceptibility), and $\delta$ (associated with the magnetization isotherm) are related as

$$M_S(T) = M_0(-\varepsilon)^\beta, \varepsilon < 0$$

$$\chi_0^{-1}(T) = \frac{h_0}{M_0}(\varepsilon)^\gamma, \varepsilon > 0$$

At $T_C$, the exponent $\delta$ relates magnetization $M$ and applied magnetic field $H$ by

$$M = DH^\frac{1}{\delta}, \varepsilon = 0$$

Here $M_S(T)$ is the spontaneous magnetization; $\chi_0^{-1}(T)$ is the inverse of susceptibility; $\varepsilon$ is the reduced temperature $(T - T_C)/T_C$; and $M_0$, $h_0/M_0$, and $D$ are the critical amplitudes. According to the scaling hypothesis [78], $M(H, \varepsilon)$ is a universal function of $T$ and $H$, and the experimental $M(H)$ curves are expected to collapse into the universal curve

$$M(H, \varepsilon) = \varepsilon^\beta f_\pm(H/\varepsilon^{\beta+\gamma})$$

with two branches, one for temperatures above $T_C$ and the other for temperatures below $T_C$. Here $f+$ for $T > T_C$ and $f-$ for $T < T_C$, are regular functions.
Figure 3.15 (a) shows the Arrott plot \(M^2 \text{ vs } H/M\) for the \(x = 0\) sample near \(T_C\). According to the mean field theory, such curves should give a series of straight lines for different temperatures and the isotherm at \(T = T_C\) should pass through the origin [77]. But in our case, we find that the curves of the Arrott plot are nonlinear showing that the mean field theory is not applicable in this case. Therefore, we tried to analyze the data using the modified Arrott plots (MAPs), based on the Arrott-Noakes equation of state [79]. According to the MAPs method, the \(M^{1/\beta}\) versus \((H/M)^{1/\gamma}\) plots at various temperatures are parallel to each other at high magnetic fields. The critical isotherm at \(T = T_C\) is the line which passes through

![Figure 3.15: Isotherms \(M^2 \text{ vs } H/M\) at different temperatures close to the Curie temperature for (a) \(x = 0\) and (b) \(x = 0.1\) samples.](image)

the origin. The initial values of $\beta$ and $\gamma$ are chosen in such a way that they give straight lines in the MAPs. The values of $M_S(T)$ and $\chi_0^{-1}(T)$ are obtained from a linear extrapolation of MAPs at fields above 0.1 T to the intercept with the $M^{1/\beta}$ and $(H/M)^{1/\gamma}$ axes, respectively. Only the high-field linear region is used for the analysis because MAPs deviate from linearity at low field due to the mutually misaligned magnetic domains [80]. In each stage of the fitting, we first plot the values of $M_S(T)$ and $\chi_0^{-1}(T)$ as a function of temperature. Then by fitting these plots with Eqs. (3.3) and (3.4), we get the new values of $\beta$ and $\gamma$. By using these new values of $\beta$ and $\gamma$, new MAPs are constructed. In an iterative process, we get the stable values of $\beta$, $\gamma$ and $T_C$. In Fig. 3.16 the $M_S(T)$ and $\chi_0^{-1}(T)$ curves are plotted. The continuous curve shows the power law fits of Eqs. (3.3) and (3.4)

Figure 3.16: Temperature dependence of the spontaneous magnetization $M_S(T)$ and the inverse initial susceptibility $\chi_0^{-1}(T)$. The solid lines are the fitted curves obtained from Eqs. (3.3) and (3.4), respectively for $x = 0$ sample. The $M$ vs $H$ on a log-log scale at $T = 225$ K for $x = 0$ sample is shown as an inset. The straight line is the linear fit with Eq. (3.5).

to $M_S(T)$ and $\chi_0^{-1}(T)$, respectively. Eq. (3.3) gives the value of $\beta = 0.380(4)$ with $T_C = 224.83(7)$ K and, Eq. (3.4) gives the value of $\gamma = 1.407(8)$ with $T_C = 224.67(1)$ K for the $x = 0$ sample. These values of $\beta$ and $\gamma$ are close to the values
predicted for a short-range Heisenberg model ($\beta = 0.368$ and $\gamma = 1.396$) [81]. To find the value of $\delta$, the $M_S (225 \text{ K}, H)$ versus $H$ isotherm is plotted on the log-log scale [inset of Fig. 3.16]. According to Eq. (3.5), this should be a straight line with a slope $1/\delta$. From the linear fit of the straight line, we obtain $\delta$ and is derived to be $4.85(3)$. The value of $\delta$ can also be calculated from the Widom scaling relation [82]

$$\delta = 1 + \frac{\gamma}{\beta} \quad (3.7)$$

The calculated value of $\delta$ is 4.70. The value of $\delta$, calculated from the magnetization isotherm, is in agreement with the scaling hypothesis within the experimental errors. The critical exponent analysis can be justified by the $M\varepsilon^{-(\beta+\gamma)}$ vs $H\varepsilon^{-(\beta+\gamma)}$ plot. According to Eq. (3.6) all the data should fall on one of the two curves. The scaled data are plotted on a log scale as shown in Fig. 3.17 (a). It can be clearly seen that all the data fall on either of the two branches of the universal curve, one for temperatures above $T_C$ and the other for temperatures below $T_C$.

![Figure 3.17: Logarithmic scaling plot of $M|\varepsilon|^{-\beta}$ verses $H|\varepsilon|^{-(\beta+\gamma)}$ in the critical region. All the experimental data fall on either of the two branches of the universal curve for (a) $x = 0$ and (b) $x = 0.1$ samples of the TbCo$_{2-x}$Fe$_x$ series.](image_url)

Now for the $x = 0.1$ sample, Fig. 3.15 (b) shows the Arrott plot or $M^2$ vs $H/M$ curves. From the Arrott plot we can find that the curves are almost linear,
suggesting that the system is close to the mean-field theory. By choosing initial values of $\beta$ and $\gamma$, we did the same analysis for the $x = 0.1$ sample. In Fig. 3.18, the $M_S (T)$ and $\chi_0^{-1} (T)$ verses temperature curves for the $x = 0.1$ sample are shown. Equation (3.3) gives the value of $\beta = 0.541(1)$ with $T_C = 304.48(7) \text{ K}$, and Eq. (3.4) gives the value of $\gamma = 1.023(2)$ with $T_C = 304.27(3) \text{ K}$ for the $x = 0.1$ sample. These values of $\beta$ and $\gamma$ are close to the values predicted from the mean-field theory ($\beta = 0.5$ and $\gamma = 1$) [77]. The value of $\delta$ obtained from the fitting of the $M_S (304 \text{ K}, H)$ versus $H$ isotherm plotted on the log-log scale, as shown in inset of Fig. 3.18 is 2.75(4). From the Widom scaling relation, the value of $\delta$ is calculated to be 2.89, which is in agreement with value of $\delta$ derived from the magnetization isotherm within the experimental errors. $M \varepsilon^{-\beta}$ vs $H \varepsilon^{-(\beta+\gamma)}$ plot on a log scale is shown in Fig. 3.17 (b). It can be clearly seen that all the data fall on either of the two branches of the universal curve, one for temperatures above $T_C$ and the other for temperatures below $T_C$. Physically, $\beta$ describes how the

Figure 3.18: Temperature dependence of the spontaneous magnetization $M_S (T)$ and the inverse initial susceptibility $\chi_0^{-1} (T)$. The solid lines are the fitted curves obtained from Eqs. (3.3) and (3.4), respectively for $x = 0.1$ sample. The $M$ vs $H$ on a log-log scale at $T = 304 \text{ K}$ for $x = 0.1$ sample is shown as an inset. The straight line is the linear fit with Eq. (3.5).
ordered moment grows below $T_C$. The smaller the value of $\beta$, faster is the growth of the ordered moment. $\gamma$ describes the divergence of the magnetic susceptibility at $T_C$. Smaller values yield a sharper divergence, and $\delta$ describes the curvature of $M (H)$ at $T_C$, with smaller values reflecting less curvature and slower saturation. The value of $\beta$ increases for the $x = 0.1$ sample reflecting a slower growth of the ordered moment with decreasing temperature. This is consistent with the neutron diffraction study (Figs. 3.10 and 3.12), where we found that the magnetostructural transition broadens on Fe substitution, which results in broadening of the width of the $\Delta S_M(T)$ curve (Fig. 3.6), indicating a slow magnetic phase transition on Fe substitution. On substituting Fe, the value of $\delta$ decreases, indicating a less curvature and a slower saturation in the $M (H)$ curves. This can be observed from the $M$ vs $H$ curves of both $x = 0$ and 0.1 samples (shown in Fig. 3.5).

A phenomenological universal curve for the field dependence of $\Delta S_M$ has been proposed by Franco et al. [83]. The major assumption is based on the fact that if an universal curve exists, then the equivalent points of the $\Delta S_M(T)$ curves measured at different applied fields should collapse onto the same universal curve. It is also shown that these curves are unique for each universality class [84]. The MCE data of different materials of same universality class should fall onto the same curve, irrespective of the applied magnetic field. The field dependence of $\Delta S_M$ is given by the following equation:

$$\Delta S_M|_{T=T_C} \propto H^n \text{ where } n = 1 + 1/\delta(1 - 1/\beta)$$  \hspace{1cm} (3.8)

Using the values of $\beta$ and $\gamma$ obtained above, the values of $n$ are calculated to be 0.653 and 0.707 for $x = 0$ and 0.1 samples, respectively. The values of $n$ obtained from fitting of Eq. (3.8) are 0.65(1) and 0.76(2) for $x = 0$ and 0.1 samples, respectively,
which are in good agreement with that obtained from the critical exponents using MAPs. From Fig. 3.19, it is clear that \( x = 0 \) and 0.1 samples belong to two different universality classes. This shows that for materials with same universality class, there exists an universal curve for the magnetic entropy change. This existence of a universal curve helps us to predict the response of a particular material under different experimental conditions in the magnetic field-temperature plane.

### 3.3.6 Differential scanning calorimetry study

In general a structural transition is associated with a first-order magnetic transition [58–60]. In case of TbCo\(_2\), we find that there is a structural phase transition coupled with a magnetic phase transition but the nature of the magnetic phase transition is of second order. Magnetostructural transition with second order has been observed earlier also [85]. The second-order nature of the structural phase transition can be due to the soft phonon modes \([74, 75]\). To further confirm the nature of the magnetostructural phase transition, we have performed the DSC measurements on
the $x = 0$ and $0.1$ samples in the heating as well as cooling cycles [Figs. 3.20 (a) and (b)]. For the $x = 0$ sample, the DSC scan [Fig. 3.20 (a)] shows a phase transition at 230 K close to its magnetic phase transition temperature (231 K) obtained from the magnetization measurements. A negligible thermal hysteresis of $\Delta T < 1$ K (at a scanning rate of 5K/min) is observed between the heating and cooling scans. The transition has a long tail on the lower temperature side indicating a second-order nature of the phase transition. For the $x = 0.1$ sample, the DSC scan [Fig. 3.20 (b)] shows a phase transition at 304 K, close to its magnetic phase transition temperature (303 K). Here also a second-order phase transition is evident from the observed negligible thermal hysteresis ($\Delta T < 1$ K) and a long tail on the lower temperature side.

On substituting Fe, we find that not only the magnetic transition remains coupled with the structural transition and the magnetic phase transition remains second-order as in the case of the parent TbCo$_2$ compound, but the transition spreads over a wide temperature range. On substituting Fe, we find that the value of $\beta$ increases and value of $\gamma$ decreases. Change in the values of critical exponents with quenched disorder is a general trend observed in amorphous ferromagnets [86]. There, the
change in the values of critical exponents is due to the formation of finite magnetic clusters in the infinite ferromagnetic network. For the \( x = 0.1 \) sample, the value of \( \beta \) is greater than the value predicted by the mean-field theory. In \( \text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) single crystal, the value of \( \beta \) and \( \gamma \) are found to be 0.57(1) and 1.16(3), respectively, which is due to the formation of ferromagnetic clusters above \( T_C \) [87]. For the \( x = 0.1 \) sample, the paramagnetic to ferrimagnetic transition takes place over a wide temperature range indicating a possible existence of ferromagnetic clusters [88]. For the \( x = 0 \) sample, the critical exponents are close to the Heisenberg model, while for \( x = 0.1 \) sample, the exponents are close to the mean-field theory, indicating that there is a crossover from short-range interaction to long-range interaction on substituting Fe. The increase in the value of \( \beta \) and decrease in the value of \( \gamma \) with increasing Fe concentration were also evident in \( (\text{Fe}_x\text{Mn}_{1-x})_{75}\text{P}_{16}\text{B}_6\text{Al}_3 \) alloys [89]. There, the value of \( \delta \) decreases and \( T_C \) increases with Fe concentration as observed for \( \text{TbCo}_{2-x}\text{Fe}_x \) in the present study. A possible reason for the dominance of long-range interactions could be Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions in these intermetallic compounds. In amorphous ferromagnets, the deviation from the Heisenberg model has been attributed to the RKKY interactions found in such systems [86]. In rare-earth based intermetallics, the interaction is mainly of RKKY type. On substituting Fe, the RKKY interactions dominate and the exchange interaction extends beyond the nearest neighbors leading to a long-range interaction which enhances the exchange interaction and an enhancement in \( T_C \) is observed.

3.3.7 Summary and conclusion

Here, in this chapter, the effect of Fe substitution at the Co site on the magnetocaloric effect in \( \text{TbCo}_2 \) has been investigated. It is observed that the substitution of Fe at the Co site causes an increase in \( T_C \), which could be due to an enhancement
in the exchange interaction between 3d transition metal ions. For $\Delta H = 50$ kOe, the maximum reversible magnetic entropy change of 3.7 J kg$^{-1}$ K$^{-1}$ for the $x = 0.1$ sample has been observed near the magnetic transition temperature (303 K). Substitution of Fe at the Co site not only tunes the $T_C$ towards room temperature but also causes an increase in the MCE operating temperature range ($\sim 95$ K for $x = 0.1$ sample). The magnetostructural transition spreads over a wide temperature. This is confirmed by the temperature dependent neutron diffraction experiments. Thus, the broad operating temperature range with high values of both $-\Delta S_M$ and RCP, and a negligible hysteresis make TbCo$_{0.9}$Fe$_{0.1}$ a potential candidate for magnetic refrigeration near room temperature. The temperature dependent neutron diffraction study on the magnetostructural transitions has given understanding of their coupled magnetic and structural properties. The results are useful to explore their implications on large magnetocaloric effect shown by these compounds across the magnetostructural phase transition. The DSC measurements show the absence of thermal hysteresis for both $x = 0$ and 0.1 samples indicating the second-order nature of the magnetostructural phase transition. The critical exponents $\beta$, $\gamma$ and $\delta$ are obtained using the MAPs and the Widom scaling relation. The field and temperature dependent magnetization behavior follows the scaling theory, and all the data points fall on the two distinct branches, one for $T < T_C$ and the other for $T > T_C$. The values of critical exponents obtained are used to show that the equivalent points of the $\Delta S_M (T)$ curves measured at different applied fields collapse onto the same universal curve; i.e., these curves are unique for each universality class. The critical exponents obtained from MAPs agree fairly well with the $\Delta S_M (H)$ curve. For the $x = 0$ sample, the values of critical exponents are close to that of three-dimensional Heisenberg model with a short-range interaction. For the $x = 0.1$ sample, the values of critical exponents are close to that of the mean-field theory
with a long-range interaction, indicating that on substituting Fe, there is a crossover from short-range interaction to long-range interaction and an enhancement in $T_C$. 