

**DEVELOPING NEAR ROOM TEMPERATURE
MAGNETOCALORIC MATERIALS**

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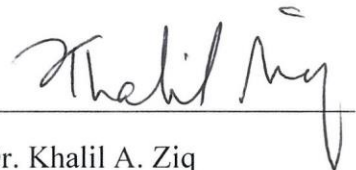


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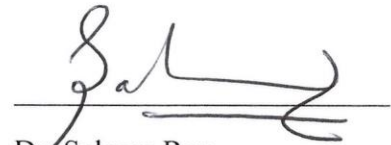
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To my compassionate parents ... Khalid Hamad and Suad Hdaib

To my soulmate ... Waed Nofal

To my sweet heart ... Suad Hamad

To my charming son ... Odai Hamad

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LIST OF ABBREVIATIONS

MCE	:	Magnetocaloric Effect
GMCE	:	Giant Magnetocaloric Effect
RCP	:	Relative Cooling Power
RC:	:	Refrigerant Capacity
CGC	:	Conventional Gas Compression
MR	:	Magnetic Refrigeration
VSM	:	Vibrating Sample Magnetometer
PM	:	Paramagnetic
FM	:	Ferromagnetic
AFM	:	Antiferromagnetic
MAP	:	Modified Arrott Plot
KF	:	Kouvel-Fisher
FOPT	:	First Order Phase Transition
SOPT	:	Second Order Phase Transition
CI	:	Critical Isotherm
RS	:	Relative Slope

ABSTRACT

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Interest in magnetocaloric effect is mainly inspired by its potential application in near room temperature refrigeration with higher efficiency than conventional gas based-systems. In this thesis, we investigated two potential magnetic-cooling materials: $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ perovskite ceramics and quasi one/two dimensional transition metal based chalcogenide $\text{CrTe}_{1-x}\text{Sb}_x$. We investigated their critical magnetic behavior, magnetocaloric and structural properties. For ceramic samples, magnetocaloric effects (MCE) show that maximum cooling power occurs close to the Curie temperatures obtained from the ac-susceptibility, where the highest obtained relative cooling power $\text{RCP} \sim 912 \text{ J/Kg}$ found in $x=0.10$ sample. The $\text{CrTe}_{1-x}\text{Sb}_x$, MCE did not show any enhancement of the cooling power near Curie temperature. Elemental substitution and short-range order and their effects on the magnetic state and magnetocaloric effect were also investigated. Moreover, the critical behaviors were investigated by measuring the initial isothermal magnetization near the paramagnetic to ferromagnetic (PM-FM) phase transition. The critical exponents β and γ were determined using a modified Arrott plot, and confirmed by Kouvel-Fisher plot whereas δ was obtained by a critical isotherms analysis at T_C . The reliability of the obtained critical exponent (β , γ , and δ) values was confirmed by the universal scaling hypothesis. Critical exponents analyses revealed that the Nd-based ceramic samples with ($x = 0.00$) is consistent with a 3D-Heisenberg-like ferromagnetic. Upon Ni substitution, the ceramic

samples follow the mean field model. In $\text{CrTe}_{1-x}\text{Sb}_x$ polycrystalline, the critical behavior analysis showed that the material does not belong to a single universality class behavior, indicating a complex competition of different magnetic interactions.

ملخص الرسالة

الاسم الكامل: مراد خالد علي حمد

عنوان الرسالة: تطوير مواد مغناطيسية حرارية عند درجات حرارة قريبة من درجة حرارة الغرفة.

التخصص: الفيزياء

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بدأ الاهتمام بتأثير المغناطيسية الحرارية عندما ظهرت بعض تطبيقاته العملية في التبريد عند درجات حرارة قريبة من حرارة الغرفة، حيث أنه من المتوقع أن نظام التبريد هذا سوف يحل محل المبردات التقليدية. إن من أهم التحديات هو تطوير مواد ذات كفاءة تعادل أو تزيد عن كفاءة المبردات التقليدية و بسعر أقل، لذلك قمنا من خلال هذا البحث بتطوير مواد جديدة تمتاز باحتوائها على عدد من الخصائص المطلوبة في المواد المغناطيسية الحرارية بحيث تكون أقل كلفة وذات استقرار كيميائي، إضافة الى ذلك يجب أن تمتلك تلك المواد قدرة عالية على التبريد وأن تكون مواد سهلة التمغنط وتمتلك مغناطيسية عالية بحيث يمكن استخدامها عند درجة حرارة الغرفة وضمن مدى واسع من درجات الحرارة. هذه المواد هي $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ الخزفية و سبائك الـ $\text{CrTe}_{1-x}\text{Sb}_x$ ، حيث قمنا بدراسة خصائصها المغناطيسية عند درجات الحرارة الحرجة باستخدام عدة طرق مثل (Critical isotherms Arrott plot, Kouvel-Fisher)، إضافة إلى خصائص تأثير المغناطيسية الحرارية الخاصة بها. أيضا قمنا بدراسة تأثير إستبدال بعض الذرات بذررات أخرى. ومن أهم النتائج التي حصلنا عليها هي أنه عند استبدال ذرات المنغنيز بذررات نيكل وبنسبة 10% فإن طاقة التبريد النسبية هي 912 جول لكل كيلوغرام، وتعتبر هذه النسبة جيدة و واعدة. أيضا وجدنا في العينات الخزفية أنها تتبع مايسمى بالـ 3D-Heisenberg-like ferromagnetic قبل الإستبدال بينما تتحول العينات الى مايسمى بالـ Mean Field Model عند إستبدال المنغنيز بالنيكل. كذلك وجدنا أن طاقة التبريد النسبية في سبائك الـ $\text{CrTe}_{1-x}\text{Sb}_x$ لا تتحسن عند إستبدال ذرات التيلوريوم بذررات الانتيوموني. إضافة الى ذلك، إن تحليل السلوك الحرج في هذه السبائك أظهر أنها لا تنتمي إلى فئة معينة بل إلى عدة فئات. وهذا يدل على انه هناك العديد من التفاعلات المغناطيسية المتنافسة في هذه العينات.

CHAPTER 1

INTRODUCTION

In this thesis work, we mainly focus on developing near room temperature magnetocaloric materials, then we investigate their critical behavior near ferromagnetic to paramagnetic (FM-PM) phase transition.

Magnetocaloric Effect (MCE) is a property of magnetic materials that refers to the variation of its temperature caused by changing applied magnetic field. When a sufficiently high magnetic field (few tesla) is applied to a magnetic material, most of its atomic magnetic moments will be aligned along the field direction. If the field is applied adiabatically (no heat or matter transfer between a thermodynamic system and its surroundings), the material's temperature will rise, and the magnetic entropy will decrease. If thermal energy is then removed from the material, and the field is reduced, the magnetic entropy will increase while the temperature will drop further and a cooling effect will occur. Such heating and cooling effect by applying and removing a magnetic field is known as the MCE [1]. In addition to the adiabatic temperature change, there are three important properties that are essential for practical applications: the magnetic entropy change, ΔS_M and its temperature width ΔT and relative cooling power, RCP (sometimes it is called the refrigerant capacity, RC), which is a measure of the amount of transferred heat between hot and cold reservoirs. If applying of the magnetic field adiabatically, rather than

removing it, causes the material to cool, and hence, increasing the entropy, then the effect is called an inverse magnetocaloric effect.

The German physicist E. Warburg [2] first discovered MCE in 1881. He reported a small but detectable temperature change in pure iron on the application of magnetic field. In the late 1920s, the origin of the MCE was explained independently by Debye [3] and Giauque [4]. They also suggested the first practical use of the MCE: the adiabatic demagnetization that can be used to reach temperatures lower than that of liquid helium (4.2K). A few years later, in 1933, the process was demonstrated for the first time by Giauque and MacDougall [5], they achieved a record low temperature of few *mK*. In 1997, it was revealed that magnetic refrigerator is a feasible and competitive cooling technology near room temperature with potential energy savings of up to 30 percent [6]. Since then, there has been an increase in research activities within this area.

1.1 Magnetic Refrigerators

Magnetic refrigeration (MR) technology, based upon the MCE [2], has several advantages over the conventional refrigeration [7]. Firstly, magnetic refrigerators have a much higher efficiency; it ranges between 30 to 60 percent of a Carnot cycle, while it does not exceed 5 to 10 percent for conventional refrigerators. Secondly, magnetic refrigerators are more compact, with no moving parts. This makes it possible to develop portable products that can be powered by batteries or solar cells. Thirdly, the MR is environment-friendly technology since it does not need gases that are harsh on the environment [1, 7].

Magnetocaloric materials are commonly paramagnetic at high temperatures and exhibit phase transition to ferromagnetic or ferrimagnetic with large saturated magnetization. The

phase transition can be either first order phase transition (FOPT), or second order phase transition (SOPT) according to the discontinuous derivative of Gibbs's potential. Materials with FOPTs show a large ΔS_M that extends over a small temperature range that results in low RCP. Hysteretic losses and a slow response time are often associated with FOPT, hence greatly limiting their usage in magnetic refrigerators. On the other hand, SOPT materials demonstrate a smaller magnitude in ΔS_M peak but extends to much wider temperature range ΔT . Consequently, such RCP are comparable or larger than its values in FOPT materials [8].

Several FOPT magnetocaloric material exhibit giant MCE (GMCE) that extends to a relatively small range of temperature. For such material to be usable in refrigeration system, they must have minimal or no thermal hysteresis. The width of the entropy peak ΔS_M can be extend over a wider range of temperature by doping the material with magnetic impurities, increasing the degree of disorder, or using a composite material consisting of several FOPT materials. Other desirable properties for FOPT material are large resistivity and large thermal conductivity that result in minimal eddy losses [8]. Thus, the following criteria should be considered to develop magnetic refrigerators:

- 1- Large ΔS_M and large ΔT_{ad} (i.e. large MCE) [9].
- 2- One should look for materials with almost no magnetic hysteresis. Hysteresis losses generate heat that is associated with increasing and decreasing magnetic field. Minimum or zero heat loss improves the working efficiency of the magnetic refrigerant materials. Consequently, MCE is reversible, and the cooling cycle is reproducible upon magnetic field cycling.

- 3- We need materials with large electric resistance that reduces the eddy current heating.
- 4- Magnetic refrigerant materials must have high chemical stability, and simple synthesis rout. Furthermore, the cost of such materials should be reasonably low.

1.2 Theoretical Background

For the characterization of the magnetocaloric response of a material, three main parameters should be understood: the isothermal magnetic entropy change (ΔS_M), the adiabatic temperature change (ΔT_{ad}), and the relative cooling power (RCP). Moreover, understanding the relation between ΔS_M and ΔT_{ad} is important since the MCE is related to these two quantities.

By applying a magnetic field (H), the change in the entropy (S) of a magnetic material is related to changes in its magnetization (M) with respect to temperature (T) through the thermodynamic Maxwell's relation:

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \quad (1.1)$$

The change of magnetic entropy, $\Delta S_M(T, H)$ can be obtained from:

$$\begin{aligned} \Delta S_M(T, H) &= S_M(T, H) - S_M(T, 0) \\ &= \int_0^H \left(\frac{\partial M(T, H)}{\partial T}\right)_H dH \end{aligned} \quad (1.2)$$

Equation (1.2) can be used to estimate the value of ΔS_M from the magnetization versus field isotherms measured at various temperatures. Experimentally, magnetization measurements are performed at discrete temperature intervals and fields. Hence, ΔS_M can be approximately calculated, at temperature intervals and discrete field by

$$\Delta S_M(T, H) = \sum_i \frac{M_{i+1}(T_{i+1}, H) - M_i(T_i, H)}{T_{i+1} - T_i} \Delta H \quad (1.3)$$

In the present thesis work, Eq. (1.3) has been used to evaluate the entropy change ΔS_M from the measured magnetization curves (see chapter 4). The commonly used unit of ΔS_M is $(J K g^{-1} K^{-1})$. Moreover; the heat capacity can be used to evaluate the entropy change $\Delta S_M(T, H)$ using:

$$\left(\frac{\partial S(T, H)}{\partial T} \right)_H = \left(\frac{C(T, H)}{T} \right)_H \quad (1.4)$$

$$\Delta S_M(T, H) = \int_0^T \frac{C(T, H) - C(T, 0)}{T} dT \quad (1.5)$$

Where $C(T, H)$ and $C(T, 0)$ are the measured heat capacity in the field (H) and in zero field ($H = 0$) respectively. The differential of the total entropy of a magnetic system (as a function of T and H) can be written as [10]

$$TdS = T \left(\frac{\partial S(T, H)}{\partial T} \right)_H dT + T \left(\frac{\partial S(T, H)}{\partial H} \right)_T dH \quad (1.6)$$

For the infinitesimal adiabatic temperature that rise for the reversible adiabatic-isobaric process, $TdS = 0$. Using Eqs. (1.1) and (1.4), one can get

$$dT = - \frac{T}{C(T, H)_H} \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH \quad (1.7)$$

By integrating Eq. (1.7) over the magnetic field, one can get ΔT_{ad} as

$$\begin{aligned}\Delta T_{ad} &= \int_0^H dT \\ &= - \int_0^H \frac{T}{C_{P,H}} \left(\frac{\partial M}{\partial T} \right)_H dH\end{aligned}\quad (1.8)$$

This suggests that for practical cooling applications at a given temperature, the heat capacity of the material $C(T, H)$ should be as small as possible, while $\left(\frac{\partial M}{\partial T} \right)_H$ should be as large as possible. The material will then have large ΔS_M and ΔT_{ad} , i.e., large MCE [1].

1.3 Relative Cooling Power

The relative cooling power (RCP) (usually expressed in J kg^{-1}), is an important parameter in determining the cooling efficiency of a magnetic refrigerant material. It is a measure of heat transfer between hot and cold reservoirs during an ideal refrigeration cycle. The RCP is defined as

$$RCP(H) \equiv \int_{T_{cold}}^{T_{hot}} \Delta S_M(T, H) dT \quad (1.9)$$

Where T_{hot} and T_{cold} are higher and lower temperatures at half maximum of the ΔS_M vs T peak (full width at half maximum *FWHM*), and can be considered as the temperatures of the hot and cold reservoirs, respectively. Currently, there are three alternate methods to define *RCP*. These correspond to different procedures in which the integral (Eq. 1.9) is

numerically evaluated (Fig. 1). A schematic representation of these methods is presented in figure 1. These are [8]:

1. Fig. 1a; RC_{FWHM} represents the approximate value of the integration as $RC_{FWHM} = \Delta S_M^{pk} \delta T_{FWHM}$.
2. Fig. 1b; RC_{Area} corresponds to properly calculating the area under the peak within that δT_{FWHM} temperature range.
3. Fig. 1c; RC_{WP} proposed by Wood and Potter [11], corresponds to the area of the largest rectangle which can be inscribed into the $\Delta S_M(T)$ curve.

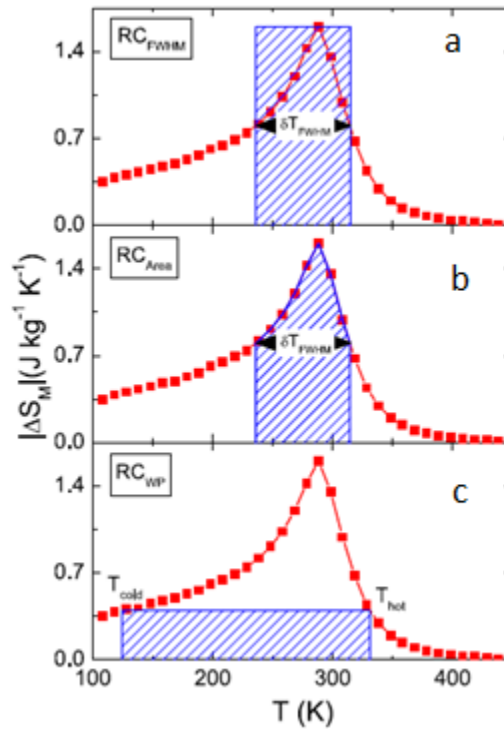


Figure 1: Definition of the RCP in different ways [8].

The common feature in all previous methods is that they are easy to apply; however, they under estimate the area under the curve and hence under estimate RCP. One may propose alternate methods that better estimate RCP as shown in figure 2. This method corresponds

to the area of the triangle with its height corresponds to the maximum $\Delta S_M(T)$ value and its base determined by the extension of two lines joining the $\Delta S_M(T)$ maximum and the two points at half maximum. This procedure provides better estimate for the area under the peak than the previous definitions.

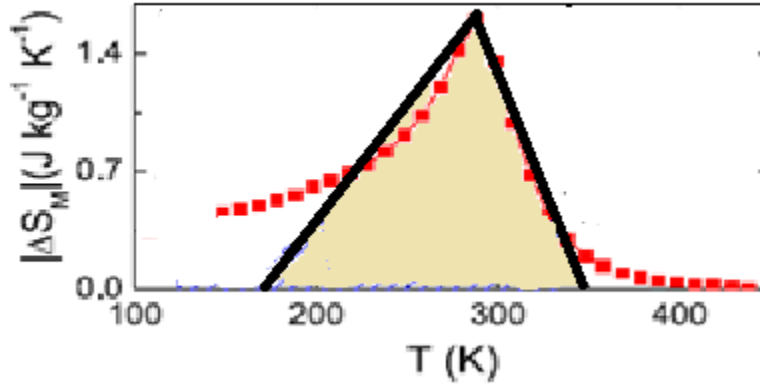


Figure 2: a new proposed method to calculate the RCP.

Ferromagnetic materials, such as Perovskite Manganite, have a high RCP than other magnetic materials. Those materials have high spontaneous magnetization and high transition temperature T_c .

In semiconducting and insulating materials, their electrons are (bounded d charge and magnetic moment) hence affecting the atomic magnetic moment. This can be achieved through direct or super-exchange interaction [12].

Perovskite Manganite are generally represented as $R_{1-x}A_xMnO_3$, where R is a rare-earth element such as $Nd, La, and Ce$, and A is a divalent alkaline earth metal like $Sr, Ca, Ba, and etc.$ These materials undergo two kinds of transitions: electric; metal-insulating, and several magnetic transitions paramagnetic phase: ferromagnetic, ferrimagnetic, antiferromagnetic and spin-glass. Upon cooling a manganite below its

transition temperature, there are several combinations of transitions between these states such as: paramagnetic-insulator to ferromagnetic/antiferromagnetic-metal transition depending on the substitution level x . Variations of these transitions with substitution level is the key idea behind constructing the material phase diagram (Fig.3) [13]. The level of substitution in these strongly correlated electronic systems is a critical factor in determining the different phases that can coexist or dominate the structure. These phase variations lead to huge changes in many physical properties such as the MR and MCE [14].

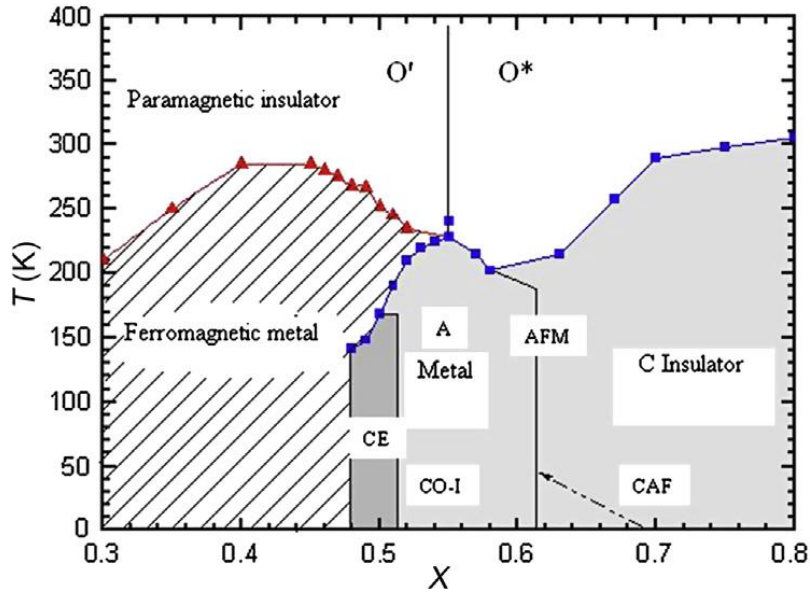


Figure 3: $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ electronic phase diagram (CO-charge ordering, AFM - antiferromagnetism, CO-I-charge ordering insulator, CAF-canted antiferromagnetism [13]).

Neodymium based perovskite manganite $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ (NSMO) is a good candidate for possible practical application in near room temperature MR [15]. The magnetic ground state in these materials is sensitive to variations of Sr contents, $\text{Mn}-\text{O}$ bond length, $\text{Mn}-\text{O}-\text{Mn}$ bond angle and $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio [16]. These parameters can be used to tune the ferromagnetic state with high spontaneous magnetization with T_c near room

temperature. The reported MCE in these manganites and the ability to control their Curie temperature by chemical substitutions opened doors to produce new candidates for non-polluting magnetic refrigerants over a wide temperature range. In addition, the magnetic behavior and magneto-transport properties of these materials are commonly ascribed to the ferromagnetic (FM) double exchange (DE) interactions predominating in the hole-doped (Mn^{3+} -rich) manganites [17, 18]. However, according to Millis *et al.* [19], the DE is not sufficient to explain the experimental data. To explain the problem, they suggest that the polaron effect due to the strong electron–phonon interaction arising from Jahn–Teller splitting of the Mn^{3+} ion. This effect is confirmed theoretically by Roder *et al.* [20].

In the current thesis work, we investigated two sets of samples. The first family is hole-doped mixed-valent manganite [21]. The second family is the van der Waals quasi-one/two dimensional semiconductor $\text{CrTe}_{1-x}\text{Sb}_x$. The material is relatively a new candidate that can be used in spintronic devices.

To get a deeper understanding of the magnetic FM-PM phase transition of a magnetic material, one needs to investigate its critical behavior around T_c . The values of critical exponents (β, γ , and δ) associated with the transition are different from model to model (see Table 1) [22]). These exponents are commonly used to classify the material in a certain universality class reflecting a wide range of magnetic interaction. The values of β, γ can experimentally be determined by analyzing the Arrott plot [23] at temperatures around T_c , and Kouvel-Fisher plot [24]. The exponent δ can be calculated from the Widom scaling relation according to [25, 26]

$$\delta = 1 + \frac{\gamma}{\beta} \quad (1.10)$$

More details will be given in chapter 6 and 7.

Table 1: Critical exponents (β , γ , and δ) for different universality classes.

Model	β	γ	δ
Mean Field	0.5	1	3
3D Heisenberg	0.365	1.336	4.66
3D Ising	0.325	1.24	4.82
Tricritical mean field	0.25	1	5

1.4 Landau Theory

In 1936, Lev Landau (1908 – 1968) developed his theory of phase transitions that manages to give a phenomenological description of both first order and second order phase transitions and their interplay. According to Landau theory, the Gibbs free energy can be expanded in a power series of the order parameter M , where the only constraint is the underlying symmetries of the system that should be respected. For example, an inversion symmetry of the system implies that only even powers of the order parameter may appear. This is often known as the mean field theory.

In the absence of the external magnetic field (i.e $H = 0$), the free energy should not depend on the sign of M

$$G(T, M) = G(T, -M) \quad (1.11)$$

Therefore, in the free energy expansion; odd powers of M should not appear because time reversal symmetry requires that the energy is unchanged on reversing the magnetization and the expansion becomes as

$$G(T, M) = G_0 + a(T)M^2 + bM^4 + cM^6 + \dots - \mu_0 HM \quad (1.12)$$

At a second order phase transition, the order parameter increases continuously from zero starting at the critical temperature of the phase transition. An example of this is the continuous increase of the magnetization at a $FM - PM$ phase transition. Since the order parameter is small near the phase transition, to a good approximation the free energy of the system can be approximated by the first few terms of the expansion of the free energy in the order parameter.

$$G(T, M) = G_0 + a(T)M^2 + bM^4 - \mu_0 HM \quad (1.13)$$

Where G_0 and b are constants, (*with* $b > 0$), and $a(T)$ is temperature dependent and expressed as $a(T) = a_0(T - T_c)$ where a_0 is a positive constant. For $T < T_c$, energy minima at $M = \pm M_s$ imply $a < 0$ and $b > 0$. For $T > T_c$, an energy minimum at $M = 0$ implies $a > 0$ and $b > 0$. It follows that $a(T)$ must change sign at T_c (Fig.4).

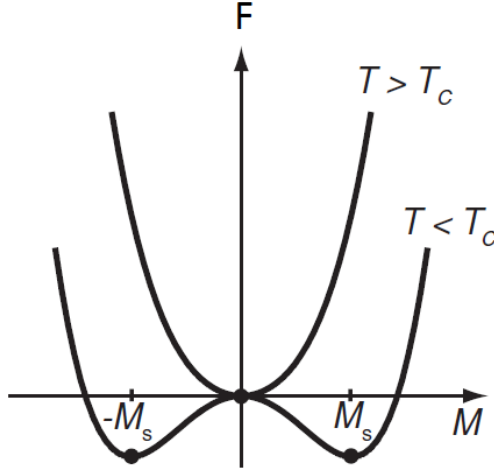


Figure 4: The Landau free energy for a ferromagnet close to T_c . There are two energy minima at $\pm M_s$ for $T < T_c$, but a single minimum at $M=0$ for $T > T_c$.

To find the ground state of the system, one can minimize the free energy (near T_c) with respect to M (using the equilibrium condition $\frac{\partial G(T,M)}{\partial M} = 0$), the equation can be written as

$$\frac{\mu_0 H}{M} = 2a_0(T - T_c) + 4bM^2 \quad (1.14)$$

In the absence of applied magnetic field ($H = 0$), $2a_0(T - T_c) + 4bM^2 = 0$, which implies

$$M = \pm \left[\frac{a_0(T_c - T)}{2b} \right]^{\frac{1}{2}} \quad (1.15)$$

The Curie-Weiss susceptibility $\chi = M/H$ (for low H and M) and using Eq. 1.14, the second term (M^2) goes to zero; we have:

$$\chi = \frac{M}{H} \approx \left(\frac{\mu_0}{2a_0} \right) (T - T_c)^{-1} \quad (1.16)$$

When the system is at a temperature exactly equal to T_c , $a(T) = 0$ and Eqn. (1.14) gives the critical isotherm

$$M = \left(\frac{\mu_0}{4b} \right)^{1/3} H^{1/3} \quad (1.17)$$

In critical behavior analysis, the magnetization curves are $M(H)$ curves at different temperatures are commonly presented as M^2 vs. H/M (known as the Arrott plots), the curves should appear as parallel straight lines for all temperatures above and below T_c . Linear extrapolation of the high-field region intercepts M^2 axis at the spontaneous magnetization M_s , and the H/M axis at χ_0 values. At $T = T_c$ the line passes through the origin.

The critical exponents near T_c are summarized in Table 2. The values of the static critical exponents β, γ , and δ are common to all mean field theories.

Table 2: The critical exponents of the mean field theory for ferromagnetic phase transition.

Magnetization	Susceptibility	Critical isotherm
$M_s \sim (T_c - T)^\beta$	$\chi \sim (T - T_c)^{-\gamma}$	$M_s \sim H^{1/\delta}$
$\beta = \frac{1}{2}$	$\gamma = 1$	$\delta = 3$

1.5 Objectives

The main objectives in this thesis work is to develop near room temperature magnetocaloric materials. Two possible candidates have been investigated $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ manganite with $0.00 \leq x \leq 0.20$ and the van der Waals quasi-one/two dimensional semiconductor $CrTe_{1-x}Sb_x$. Two-fold approaches is used to develop these material; first: we propose to use transition metal substitutions and to change the degree of short range order-disorder in these material.

The second objective of the thesis is to investigate the critical behavior, the critical exponents, and how they are affected upon substitutions.

CHAPTER 2

EXPERIMENTAL TECHNIQUES: SYNTHESIS AND CHARACTERIZATIONS

2.1 Samples Preparations

All investigated samples have been prepared in the superconductivity lab at the KFUPM campus using standard solid-state reaction method.

2.1.1 Preparation of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ Ceramic

In standard solid-state reaction method, high purity (4N) oxides (Nd_2O_3 , SrCO_3 , MnO_2 , and NiO) were used to prepare various $\text{Nd}_{0.60}\text{Sr}_{0.40}\text{Ni}_x\text{Mn}_{1-x}\text{O}_3$ polycrystalline samples with $0.00 \leq x \leq 0.20$. Stoichiometric ratios of these elements (Table 3) were mixed and grinded in an agate mortar and pestle for about 30 minutes. The resulting powder was pressed into pellets, and calcinated in the air for 24 hours at 1000°C in a programmable furnace using a heating cycle as shown in Fig.5 (a). The samples were re-grinded, pressed and re-annealed at 1000°C and 1300°C for another 10 hours at each temperature. Finally, the samples were furnace cooled to room temperature. (Fig.5 (b)).

Table 3: Calculated masses of each constituent of 1g of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Mn}_{1-x}\text{O}_3$ polycrystalline.

x	$\text{Nd}_2\text{O}_3(\pm 0.1\text{mg})$	$\text{SrCO}_3(\pm 0.1\text{mg})$	$\text{MnO}_2(\pm 0.1\text{mg})$	$\text{NiO}(\pm 0.1\text{mg})$
0.00	0.4496	0.2630	0.3872	0
0.05	0.4492	0.2628	0.3675	0.0166
0.10	0.4488	0.2626	0.3479	0.0332
0.15	0.4484	0.2623	0.3283	0.0498
0.20	0.4481	0.2621	0.3087	0.0663

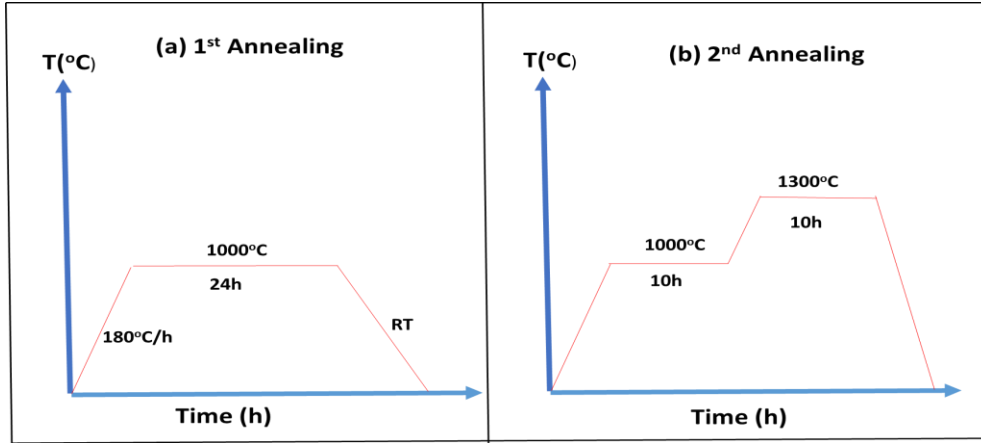


Figure 5: Schematic diagram illustrates the two annealing processes of the samples in the furnace.

2.1.2 Preparation of $\text{CrTe}_{1-x}\text{Sb}_x$ Alloys

To prepare $\text{CrTe}_{1-x}\text{Sb}_x$ (with $x=0.0, 0.1, 0.2, 0.3, 0.4$, and 0.5) samples, high purity (4N to 5N) *Cr*, *Te*, and *Sb* were used. All samples were grinded and pressed in a 5mm diameter disk and about 2 mm thick pellets. The pellets were encapsulated in evacuated quartz tubes flushed several times with high purity argon, filled partially with high purity argon gas,

and then sealed. All sealed samples were annealed at 800-1000 °C for 10 hours. Stoichiometric ratios of these elements are shown in Table 4.

Table 4: Concentration of each constituent for 1 gram of $\text{CrTe}_{1-x}\text{Sb}_x$ polycrystalline.

x	Cr	Te	Sb
0.0	0.2895	0.7105	0
0.1	0.2905	0.6415	0.0680
0.2	0.2914	0.5721	0.1365
0.3	0.2924	0.5022	0.2054
0.4	0.2933	0.4319	0.2748
0.5	0.2943	0.3611	0.3446

All samples were initially characterized by different techniques:

- 1- X-ray diffraction (XRD) were used to study the structural properties.
- 2- Magnetic measurements using both, AC-susceptibility (χ_{ac}), and magnetization.

2.2 Materials Characterization

2.2.1 X-ray Diffraction

X-ray diffraction (XRD) analysis was performed on both series: $\text{Nd}_{0.60}\text{Sr}_{0.40}\text{Ni}_x\text{Mn}_{1-x}\text{O}_3$ and $\text{CrTe}_{1-x}\text{Sb}_x$ polycrystalline powder samples by using Shimadzu (LabX XRD-600) and Bruker XRD (Phaser D2 2nd G) [27] with $\text{Cu } K_\alpha$ - line ($\lambda = 1.5406 \text{ \AA}$). The diffracted x-

ray beams were recorded in the range 10-80°. X-ray structural analysis is based on Bragg's law [28]:

$$2d_{hkl}\sin\theta_{hkl} = n\lambda \quad (2.1)$$

Where d is the distance between two parallel planes, hkl are the Miller indices, θ is the Bragg angle, n is an integer, and λ is the wavelength of the X-ray.

The phase purity and crystallite sizes in the synthesized samples were checked by x-ray diffraction, and Rietveld refinements of the patterns were carried out using FULLPROF software to determine the refined crystal parameters, relative abundance of secondary phases, and the cationic distributions in the lattice [29].

2.2.2 AC-Susceptibility

A homemade ac susceptometer was developed to investigate the quality and the properties of the prepared samples for a wide range of temperatures (5 to 320K). The ac susceptibility technique provides several important information such as the transition temperature, energy losses and the magnetization lag angle.

The susceptometer was fitted directly on the cooled head of a closed cycle refrigerator (Model SHI-4T). Real and imaginary parts of the susceptibility were measured using SR850 lock-in-amplifier. The temperature was monitored using Lake Shore 336 temperature controller along with LABVIEW software to control all measuring systems. The susceptometer is made of two pairs of coils; primary (with 370 turns each, $R \sim 12 \Omega$), and two secondary coils (with 535 turns each, $R \sim 24 \Omega$). According to the data in Table.5

and using $B = \left(\frac{L}{\sqrt{d^2 + L^2}}\right) \mu_0 n I$, the calculated magnetic field in the primary coil was 0.5 Oe/mA . where $n = N/L$ is the number of turns per unit length (N is the number of turns in the primary coil, and L is the total length of the coil. I is the current and d is the average diameter of the primary coil.

Table 5: Specifications of the primary and secondary coils

	Secondary Coil		Primary Coil	
	Coil 1	Coil 2	Coil 1	Coil 2
Wire Diameter(mm)	0.1007	0.1007	0.1270	0.1270
Number of turns	535	535	~370	~370
Resistivity (Ω)	23.3	23.8	12	11.4
Number of layers	12	12	10	10

When a constant ac current source is connected to the primary coil, it generates the alternating magnetic field at the position of the sample. The secondary coils are connected in opposite winding to cancel the electromagnetic force (emf) produced by the varying field in the primary empty coils. The configuration of the susceptometer is depicted in figure 6. The primary coil generates an ac-magnetic field which induces an ac-voltage in the secondary coils. Since the secondary coils are connected in opposite direction, the net voltage will be zero. The sample is introduced in one coil to change the inductance of one coil and creates unbalance induced emf in the secondary coils. A lock-in-amplifier is used to measure the net voltage across the secondary coils. The measured voltage depends on

the magnetic properties of the sample, frequency and amplitude of the driving field. This measuring technique allows measuring the magnetization response without the need to move the sample.

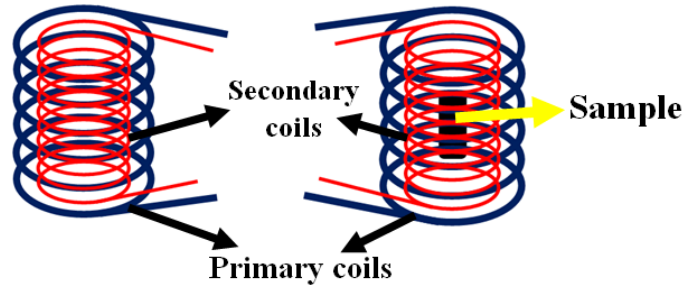


Figure 6: Coil configuration of the AC Susceptometer.

2.2.3 Magnetization Measurements Using Vibrating Sample Magnetometer (VSM)

The VSM technique is called the induction technique, which was first designed by S. Foner [30]. In this technique, the sample is set to vibrate in a magnetic field. The magnetized vibrating sample generates varying magnetic flux. The sample is vibrating at the middle of two coils connected in opposition to double the induced voltage generated by the varying flux. According to Faraday's Law of Induction, and if the sample vibrates along the z -direction, the emf is given by the rate of change of the magnetic flux

$$emf = -2N \frac{d\phi_B}{dz} \frac{dz}{dt} \quad (2.2)$$

Here, N is the number of turns in the coil, ϕ_B is the magnetic flux in the coil, and t is the time. The induced emf is doubled because of the oppositely connected coils. Since

generated *emf* in coils depends on the amplitude a , and frequency w of vibration, the wave equation is then described as

$$z = a e^{iwt}$$

$$\frac{dz}{dt} = a i w e^{iwt} \quad (2.3)$$

Therefore

$$emf = -2N a i w \frac{d\phi_B}{dz} e^{iwt} \quad (2.4)$$

The value of the magnetization can be deduced from the *emf* upon proper calibrations. A standard *Ni* sample was used for the calibration before each run.

Magnetization measurements were performed using a computer controlled PAR-Lakeshore (Model 4500/150A) variable temperature vibrating sample magnetometer (VSM). This system combines from VSM with a superconducting magnet generates a high magnetic field up to 9 *Tesla* and a variable temperature cryostat in range of 1.8K to 325K. The VSM system consists, mainly, of the vibrating head and sample holder, variable temperature cryostat, temperature controller, VSM controller, power supply and controller of the magnet, in addition to PC with GPIB-PC-II interface card which is connected to all controllers of the system. For detailed description of the system see [31].

The experimental procedure for magnetization measurements can be described by the following: at first at a given measuring temperature, the magnetic field is swept between 0 to 5T. Measurements are repeated at several temperatures in range 4K to 320K with small temperature intervals ($\Delta T \sim 2K$) around the critical temperature for each sample. The result

at each temperature is a hysteresis loop which is a plot of the ascending and descending branches of the magnetization versus magnetic field. We used the initial ascending magnetization curve to study and calculate various magnetic properties such as MCE, and critical behavior.

CHAPTER 3

X-RAY DIFFRACTION (XRD)

In this Chapter, we investigate the structural properties for all samples using FULLPROF software, which is based on Rietveld refinement technique.

The original perovskite mineral (CaTiO_3) is named after a Russian mineralogist, Count Lev Aleksevich von Perovski. It was discovered by Gustav Rose in 1839 from samples found in the Ural Mountains [32]. Ever since, enormous attention has been paid to the perovskite family of compositions. The general stoichiometry of the perovskite structure is ABX_3 with the ideal cubic structure with space group $Pm\bar{3}m$ (221) [33]. Both ‘A’ and ‘B’ are cations, whereas ‘X’ is an anion. In addition, the A cation is divalent such as La^{3+} , Nd^{3+} , Sm^{3+} , etc., while the B cation is tetravalent like Al^{3+} , Cr^{3+} , Sc^{3+} , etc., and X can be O. The perovskite lattice consists of small B cations that sits on (0, 0, 0) position within the oxygen octahedral, and larger A cations sits at the center of the cubic structure (1/2, 1/2, 1/2), while the oxygen atoms is at the face center positions (1/2, 1/2, 0), (1/2, 0, 1/2), and (0, 1/2, 1/2) [33].

The rare earth perovskites have been widely studied using X-ray diffraction. The first study was carried out in 1927 by Goldshmidt [34] which focused on YAlO_3 and LaFeO_3 [35]. Several investigations reported that the perovskites showed mainly cubic or pseudo-cubic structure, but as work on these systems proceed, many proposed non-cubic symmetries appeared. For example, there are two main non-cubic phases; these are the tetragonal and the orthorhombic structures. These new structures could appear due to increasing internal

pressure that is commonly achieved by substitutions. On top of that, new phases can be created after substitutions as well as prolonged heat treatment [36].

X-ray diffractions patterns for $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ at room temperature with Rietveld refinement [37, 38] are shown in Fig.7 through Fig. 9.

The results of the refinement demonstrated that there are two phases in all samples. The main phase in all samples ($Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$) was consistent with the standard pattern for perovskite manganites, which is orthorhombic with space group $Pnma$ (62). The secondary phase ($Nd(Sr)MnO_3$) is cubic perovskite with space group $Pm\bar{3}m$ (221). The refined lattice parameters, unit cell volume, and reliability (R) factors are shown in Table.6.

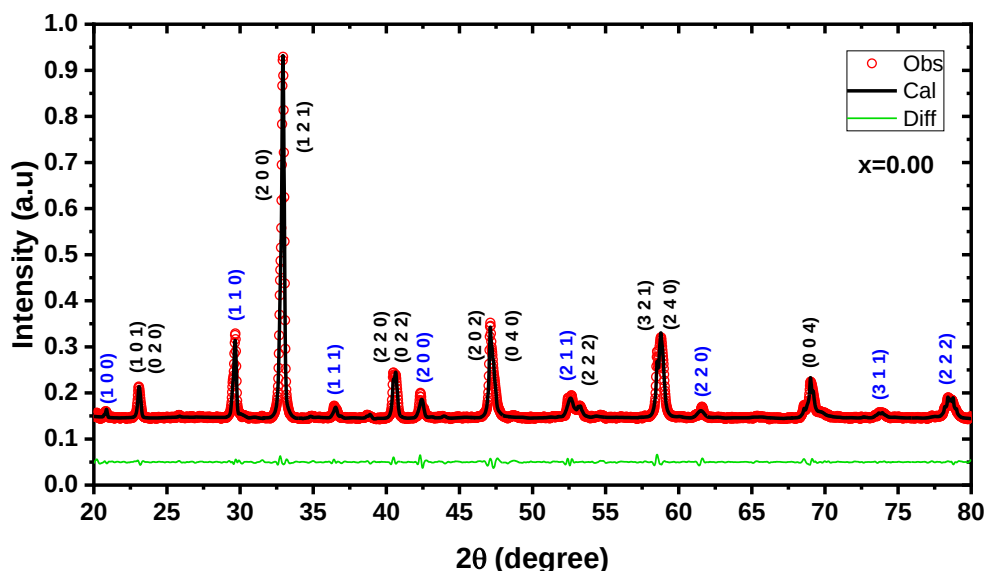


Figure 7: X-ray diffraction patterns (red circles) for $x = 0.00$ sample at room temperature. The (hkl) values corresponding to Bragg peaks of primary (in black) and secondary (in blue) phases are marked. The best-fit line is shown in black color while the difference between the observed data and fitting is in green.

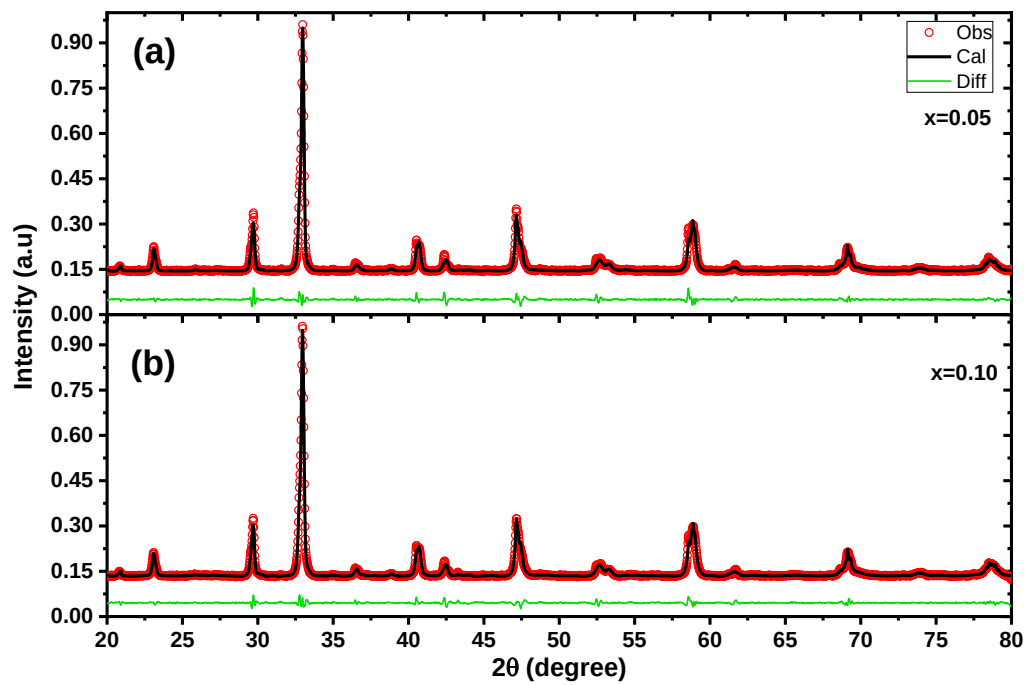


Figure 8: X-ray diffraction patterns for (a) $x = 0.05$, and (b) $x = 0.10$, at room temperature.

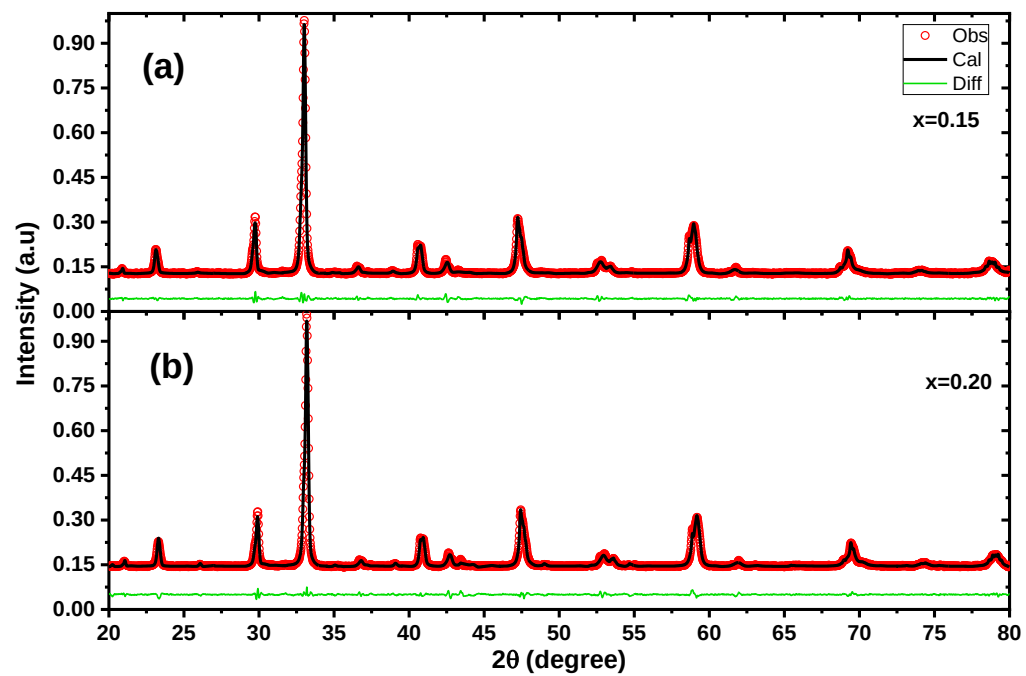


Figure 9: X-ray diffraction patterns for (a) $x = 0.15$, and (b) $x = 0.20$, at room temperature.

The values of both, filling reliability factors (R_F), and Bragg-reliability factor (R_B) are also shown. These values indicate reliable fits and refined parameters as they were lower than those reported by [30] and by [40]. The results in Table 6 indicates almost linear reduction in the lattice parameters (a , b , and c), and the unit cell volume (V) with increasing Ni concentration (Fig. 10). This is consistent with the observed shifts of the positions of the diffraction peaks shown in figure 11. To illustrate the peaks' shift tracking, Fig. 12 depicts the mapping of the peaks shift with increasing Ni concentration, where the red color represents the maximum intensities, whereas the blue color is for the minimum intensities. This shift could be due to the smaller ionic radius of Ni^{2+} ($r(Ni^{2+}) = 0.72\text{\AA}$) as compared to Mn^{2+} ionic radius ($r(Mn^{2+}) = 0.80\text{\AA}$) [41]. This behavior (change in lattice parameters) leads to change in the bond lengths ($Mn-O$), and hence the bonds angles ($O-Mn-O$) as shown in Table 7 and figure 13. VESTA software [42] was used to draw the unit cell and Diamond software [43] was used to determine the distances ($Mn-O$) between Mn ions and the nearest neighbors of oxygen ions as well as the ($Mn-O-Mn$) bond angles.

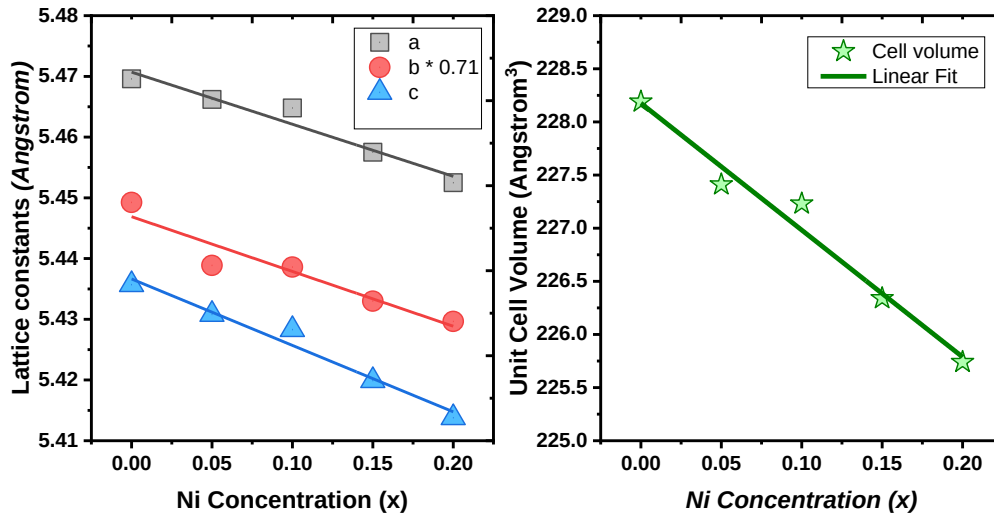


Figure 10: Change of lattice constants and unit cell volume with increasing the Ni fraction.

Table 6: Summary of the refinement of XRD patterns of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ manganites.

Concentration (x)	0	0.05	0.10	0.15	0.20
<i>Phase 1: $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ Space group: $Pnma$ (62) - orthorhombic</i>					
$a(\text{\AA})$	5.47(0)	5.46(6)	5.46(5)	5.45(8)	5.45(3)
$b(\text{\AA})$	7.67(5)	7.66(0)	7.66(0)	7.65(2)	7.64(7)
$c(\text{\AA})$	5.43(6)	5.43(1)	5.42(8)	5.42(0)	5.41(4)
$V(\text{\AA}^3)$	228.19	227.41	227.23	226.34	225.74
R_B	1.91	2.04	1.5	1.15	2.53
R_F	3.18	2.47	2.27	1.71	2.68
Wt. ratio (%)	81.48	84.04	82.65	80.99	82.24
<i>Phase 2: $\text{Nd}(\text{Sr})\text{MnO}_3$ Space group: $Pm\bar{3}m$ (221) - cubic</i>					
$a(\text{\AA})$	4.26(3)	4.25(8)	4.25(7)	4.25(1)	4.24(7)
$V(\text{\AA}^3)$	77.45	77.20	77.15	76.82	76.61
R_B	2.38	1.71	2.6	1.94	1.89
R_F	1.87	1.32	1.78	1.28	1.10
Wt. ratio (%)	18.52	15.96	17.35	19.01	17.76

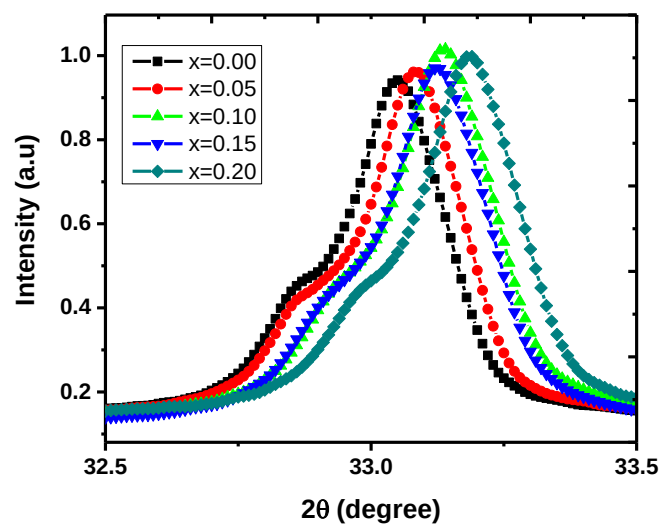


Figure 11: Diffraction peaks shifted upon increasing Ni concentration.

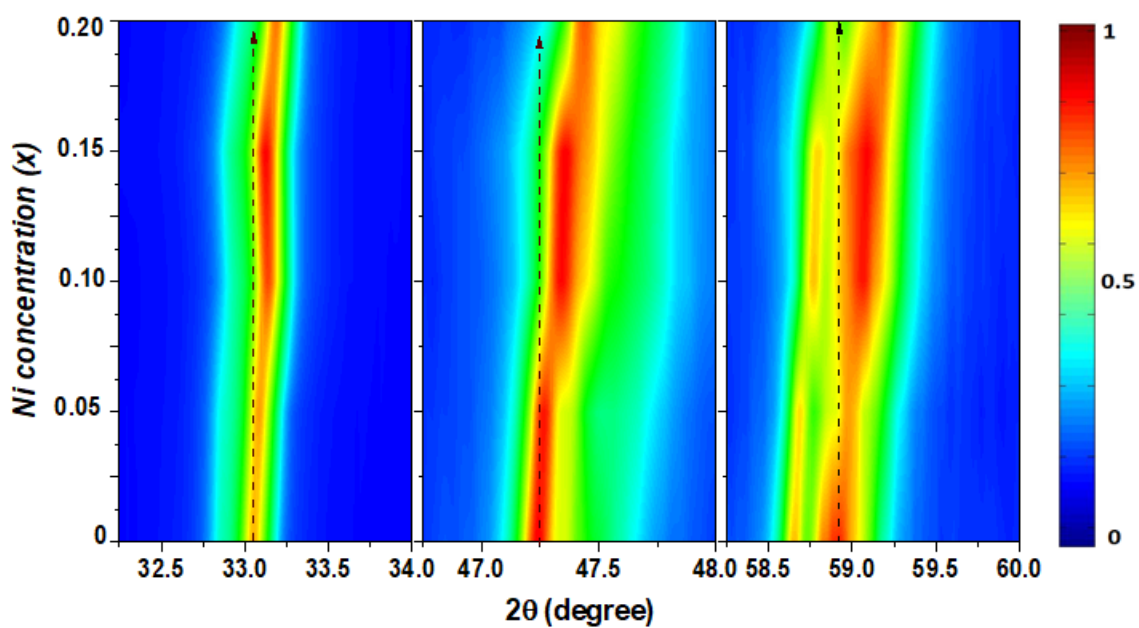


Figure 12: XRD intensity mapped with respect to diffraction angle, 2θ , for selected peaks. With increasing Ni concentration, the peaks position shifted to higher angles.

Table 7: Bonds length and bonds angles of of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ manganites.

x	Mn-O1 (Å)	Mn-O2(A)	Mn-O2(A)	$\text{O1-Mn-O1(}^\circ\text{)}$	$\text{O2-Mn-O2(}^\circ\text{)}$
0.00	1.9482	1.9575	1.9889	180	90.975
0.05	1.9313	1.9241	1.9931	180	90.367
0.10	1.9455	1.9489	1.9663	180	90.056
0.15	1.9516	1.9299	1.9573	180	89.765
0.20	1.9274	1.9168	1.9718	180	89.540

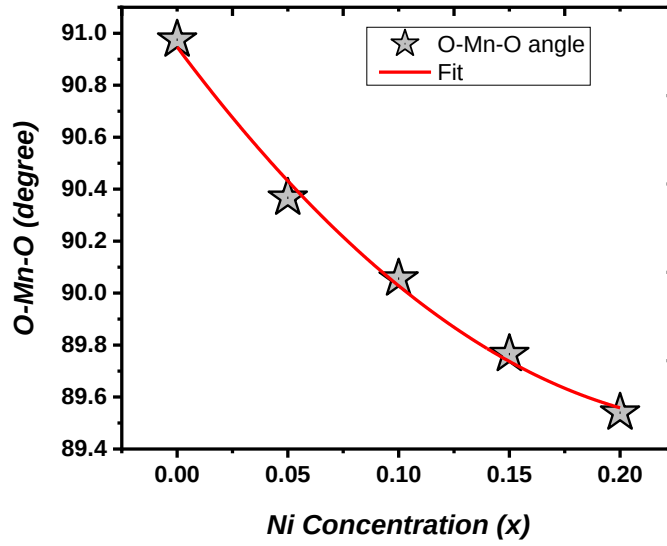


Figure 13: Change of bond angles of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ upon Ni concentration.

The crystal structure of the unsubstituted $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ compound along with $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ compound, and the coordination polyhedral of Mn are depicted in Figs. 14 and 15 respectively.

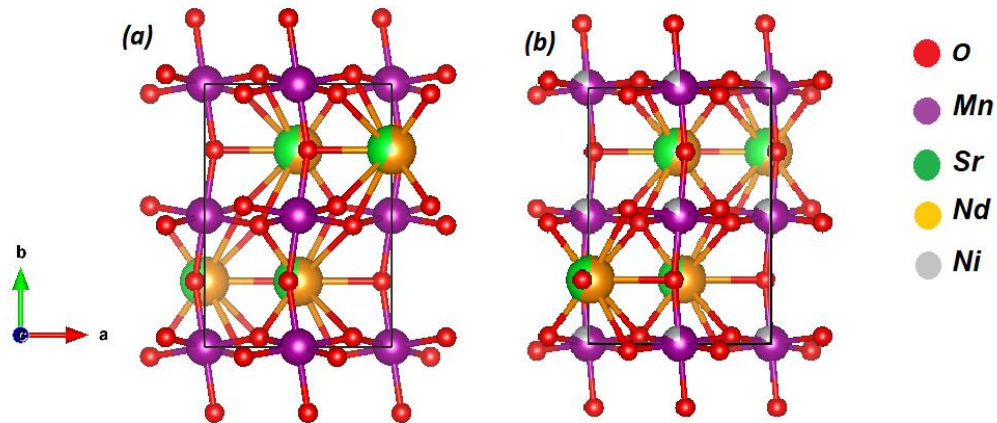


Figure 14: Crystal structure of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ were (a) for $x=0.00$, and (b) for $x=0.20$. (the c-direction is out of page.)

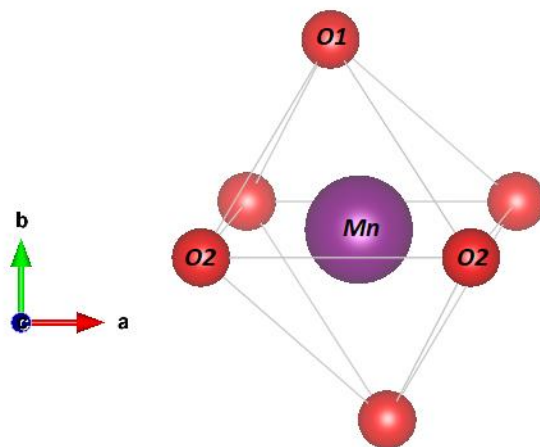


Figure 15: The coordinate of polyhedral of Mn in $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ compound. (the c-direction is out of page.)

Distortion of the ideal perovskite structure is very important parameter since it correlates with magnetic properties. The obtained distortion index (D) was calculated using VESTA software and the results are summarized in Table 8.

Table 8: Distortion index and quadratic elongation of Mn polyhedral of Mn in Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO₃

x	<i>Polyhedral volume</i> ($\text{\AA}^3$)	<i>Distortion index</i> (bond length)	<i>Quadratic</i> <i>elongation</i>	<i>Bond angle variance</i> (deg^2)
0.00	9.99	0.0081	1.0087	29.99
0.05	9.79	0.0149	1.0065	21.26
0.10	9.86	0.0043	1.0056	19.71
0.15	9.72	0.0057	1.0076	26.58
0.20	9.67	0.0113	1.0036	11.85

CHAPTER 4

AC-SUSCEPTIBILITY

Alternating current ac-susceptibility is a significant tool for characterizing materials. Applying an ac-field to a sample, enables investigating the dynamics of the magnetization and its response to several varying parameters.

The main idea of the *ac*-susceptibility is based in measuring the response of the magnetization of the sample to a small *ac*-field. The magnetization can be monitored upon sweeping the temperature, the amplitude and the frequency of the applied magnetic field. The induced magnetization of the sample is given by

$$M_{AC} = \frac{dM}{dH} H_{AC} \sin(\omega t) \quad (4.1)$$

Where H_{AC} refers to the amplitude of the field, $\omega = 2\pi f$ is the angular frequency, and $\chi = \frac{dM}{dH}$ is the “dynamic” susceptibility which is the initial slope of the $M(H)$ curve at a given temperature. At any given frequency, the magnetization of the sample lags the driving field which may cause an irreversible behavior and energy losses because of Eddy currents. These currents lead to increase in temperature due to increase in internal energy. In each loop, the magnitude of the current depends on the frequency, and is proportional to the strength of the magnetic field, the area of the loop, and the rate of change of flux, and inversely proportional to the resistivity of the material. It can be reduced by having small isolated particles.

The *ac*-magnetic susceptibility (χ) measurement gives both components of the susceptibility, the real (χ') (in-phase) and the imaginary component χ'' . The angle between both components is known as the phase shift(ϕ) of the magnetization relative to the driving field. The imaginary part is related to the energy loss. Both components are given as:

$$\chi' = \chi \cos \phi \quad (4.2)$$

$$\chi'' = \chi \sin \phi \quad (4.3)$$

Which leads to

$$\chi_{tot} = \sqrt{\chi'^2 + \chi''^2} \quad (4.4)$$

$$\text{and, } \phi = \tan^{-1} \frac{\chi''}{\chi'} \quad (4.5)$$

In this chapter, we characterize the two sets of polycrystalline samples, $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ ceramics, and $CrTe_{1-x}Sb_x$ alloys by using *ac*-susceptibility technique. The effect of frequency change was investigated in the ceramic samples.

4.1 AC-SUSCEPTIBILITY OF $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$

Figure 16 shows both χ' and χ'' vs. temperature in the range between 5 K and 320 K for the un-substituted $Nd_{0.6}Sr_{0.4}MnO_3$ polycrystalline. From this figure, one can investigate many magnetic properties such as the Curie temperature; the ferromagnetic to paramagnetic (*FM – PM*) phase transition temperature. The susceptibility shows almost linear increase in the region between $T = 5K$ and $260 K$ reflecting the ferromagnetic

behavior with some disorder effect. Typical ferromagnetic susceptibility shows almost constant behavior below its ferromagnetic transition. Spin disorder effect causes an increase in the susceptibility due to softening of the exchange interaction with increasing temperature. The imaginary part of the susceptibility reveals a broad hump near 100K, while the real part shows a broad minimum. These features may be caused by weak antiferromagnetic exchange interactions at low temperature (see chapter 6). Above $T \sim 280\text{K}$, the behavior is paramagnetic.

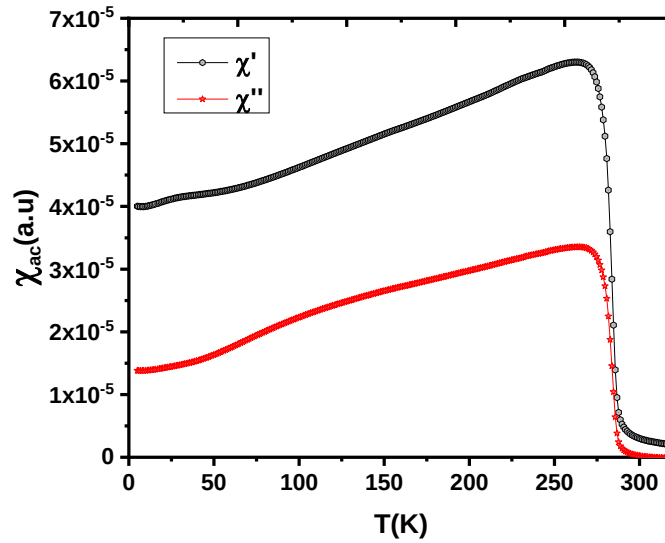


Figure 16: The in-phase and out-of-phase components of the AC susceptibility of the un-substituted $\text{Nd}_{0.65}\text{Sr}_{0.4}\text{MnO}_3$ sample at 887Hz.

The Curie temperature (T_c) can be simply obtained by specifying the inflection point of the total ac-susceptibility. The first derivative of the susceptibility is shown in Figure 17. The position of the sharp minima (the red color) in this figure indicates the $FM - PM$ phase transition. In addition, the (T_c) in this compound is found to be around 270K (see Fig.17). For the low-frequency limits, ac -susceptibility resembles the dc -susceptibility. The in-phase component (χ') is the slope of the $M(H)$ curve while the out-of-phase component

(χ'') indicates dissipative processes in the sample which is due to irreversibility in the magnetization behavior and eddy currents losses in conductive samples. Moreover, both (χ') and (χ'') are very sensitive to thermodynamic phase changes, and are often used to measure transition temperatures [44].

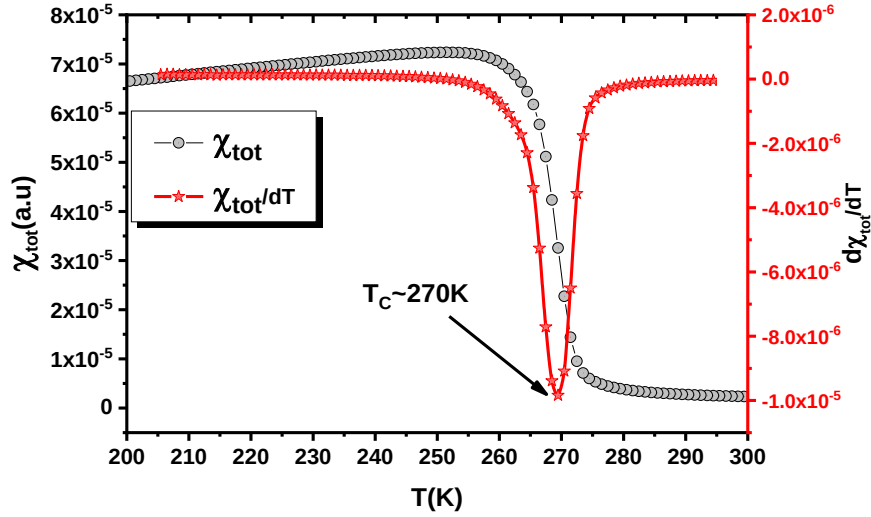


Figure 17: Total ac-susceptibility for un-substituted $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ polycrystalline (black circles) and its first derivative (red stars).

To investigate the $FM - PM$ phase transition in the parent sample $x = 0.00$, we studied the effect of Ni substitution in the range ($0 \leq x \leq 0.20$) on the $Mn - site$. The measured χ_{tot} for all samples are depicted in figure 18 (a), whereas the full-width at half maximum ($FWHM$) decreases. In addition, a significant reduction in the peak temperature T_p , and hence reduction in the Curie temperature T_c , was detected upon increasing the amount of Ni (Fig.19). This reduction is associated with the reduction of ferromagnetic exchange interaction, and strengthening of the antiferromagnetic exchange interaction. In addition, it is quite evident that Curie temperature curve lies above the peak temperature curve (Fig.

19.) So, on the one hand, there is a ferromagnetic insulating regime where double exchange along with metallic behavior is expected for ferromagnetism to occur. On the other hand, it is in insulating state where double exchange model is not valid. Moreover, the transition width broadens as shown in figure 18 (b). All these features indicate an increase in magnetic-disorder with the decrease of cell volume (see chapter 3) which is an improvement in magnetic properties where a large distribution of magnetic exchange interaction is present. Table.9 summarizes information obtained from figures 18.

It is well known that the *Sr* is divalent, which exists as Sr^{2+} , and *Nd* is trivalent that exists as Nd^{3+} . This implies that a fraction $Sr_{0.4}$ of the *Mn* ions are Mn^{4+} and $Nd_{0.6}$ are Mn^{3+} . The Ni^{2+} substitution competes the *Mn* ions to interact with *Nd* and/or *Sr* ions. This mechanism enhances the antiferromagnetic behavior since both $NdMnO_3$ and $SrMnO_3$ are pure antiferromagnetic insulators, as would be expected for an oxide material in which the magnetism is mediated by super exchange through the oxygen [44]. This is an indirect exchange interaction between non-neighboring magnetic ions which is mediated by a non-magnetic ion that is placed in between the magnetic ions. This exchange interaction depends on the degree of overlap of orbitals, and thus it is strongly dependent upon the angle of the $Mn - O - Mn$ bond, where the *3d* electrons delocalized over this bond, and consequently lowering the kinetic energy. This bond is strongly depending upon substitution (see chapter 3) since it affected by changing of Mn^{4+}/Mn^{3+} ratio and hence interruption of $Mn - O - Mn$ double exchange interaction.

Table 9: Effect of Ni substitution on the Mn site in the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ polycrystalline.

Concentration (x)	$T_p(K)$	$T_c(K)$	$FWHM(K)$
0.00	~252	~270	263.61
0.05	~209	~240	234.29
0.10	~156	~195	186.26
0.15	~113	~138	115.60
0.20	~78	~91	59.70

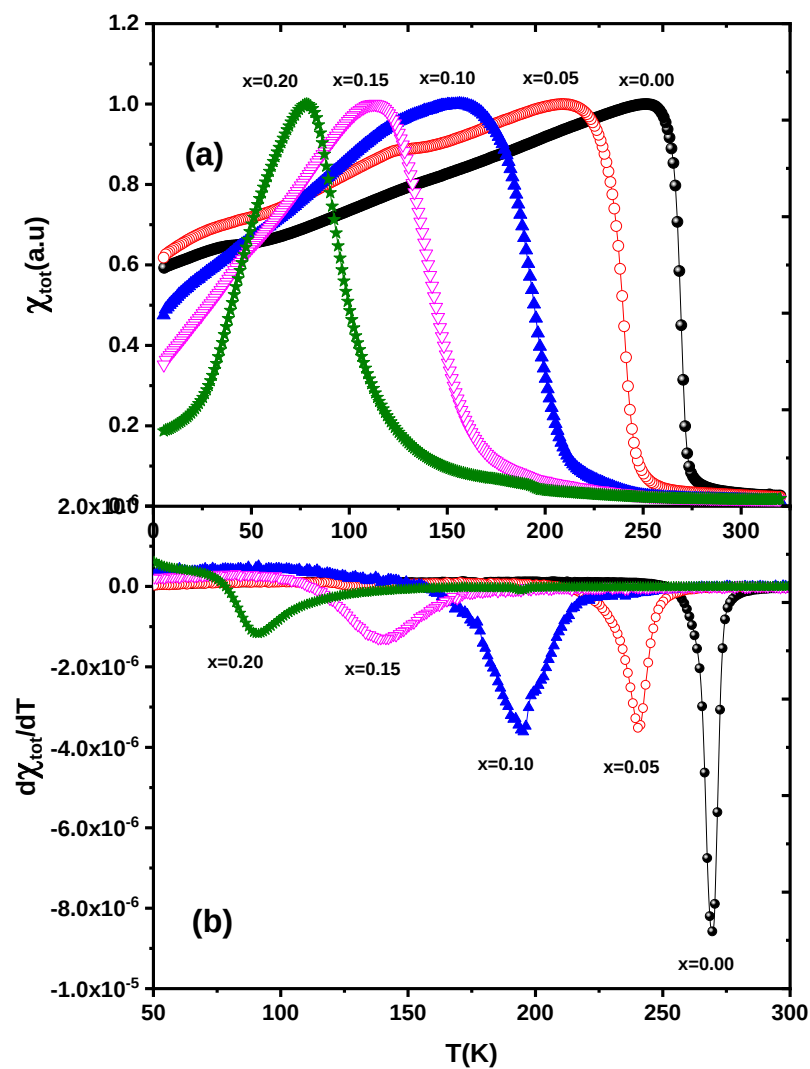


Figure 18: (a) Normalized total ac-susceptibility for $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ ($0 \leq x \leq 0.2$) polycrystalline, (b) their first derivative.

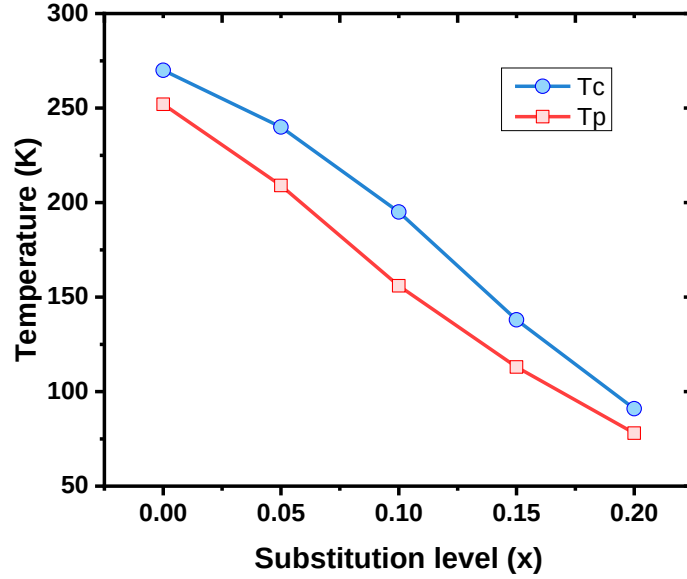


Figure 19: Effect of Ni substitutions on critical temperature (blue circles), and peak temperature (red squares) in $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ compounds

4.1.1 The Frequency Effects

In this section we investigate the effect of frequency of the ac-susceptibility in all ceramic samples. The main panels in Fig.20 depict the temperature dependence of ac-susceptibility of the $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ for $x=0.00$, $x=0.10$, and $x=0.20$ respectively in the presence of different applied frequencies (300- 5000 Hz). The *FWHM* has been increased upon increasing the frequency, indicating that the ferromagnetic exchange interaction is sensitive to the applied frequency. This behavior is usually interpreted to originate from the disordered or short-range nature of the ferromagnetism in the sample. The broadening of the ac-susceptibility can be in samples with higher frequency. Moreover; there is small but detectable shift in the peak temperatures (see the insets in Fig. 20). This shift in the peak temperature is a characteristic of the spin disorder clearly seen spin-glass systems. This

suggests that the $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ has certain degree of spin-disorder, and the disorder increases with increasing Ni-substitutions. Spin disorder may arise from conflicting exchange interactions such as FM and AFM interactions, structural disorder, geometrical disorder and frustrated interactions.

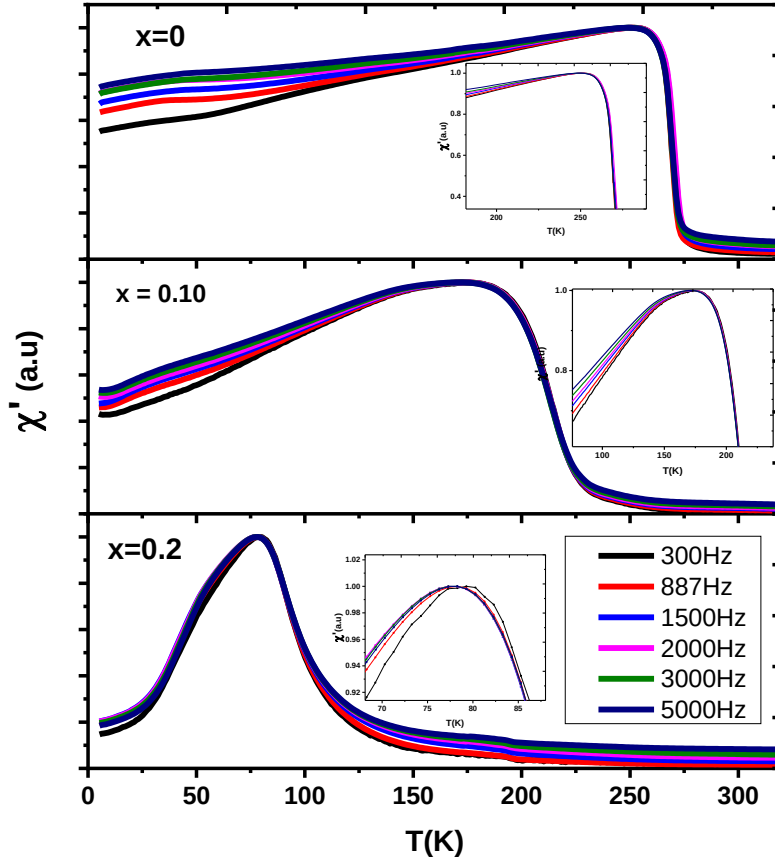


Figure 20: Effect of changing frequency on ac-susceptibility for $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ where (a) is for $x=0.00$, (b) is for $x=0.10$, and (c) is for $x=0.20$. The insets show the enlarged view for the peaks.

4.2 AC-SUSCEPTIBILITY OF $\text{CrTe}_{1-x}\text{Sb}_x$

The *Cr-based* chalcogenide have attracted scientists for their possible applications in spintronics technologies. These materials known to be van der Waals bonded magnetic materials. Telluride (such as *CrTe*) are ferromagnetic conductors [46], while *CrSb* is predominately antiferromagnetic [47]. Accordingly, substituting of *Sb* on the *Te* site will change the magnetic state of the solid solution $\text{CrTe}_{1-x}\text{Sb}_x$ due to double exchange interaction [48] (see chapter 7 for more details).

The temperature dependence of the total ac-susceptibility of $\text{CrTe}_{1-x}\text{Sb}_x$ is shown in Fig. 21 to Fig. 26. It is worth mentioning that this system is quasi-two dimensional system, and many features of magnetic state is not fully understood. More details about the critical behavior of the ferromagnetic state is discussed in chapter 7.

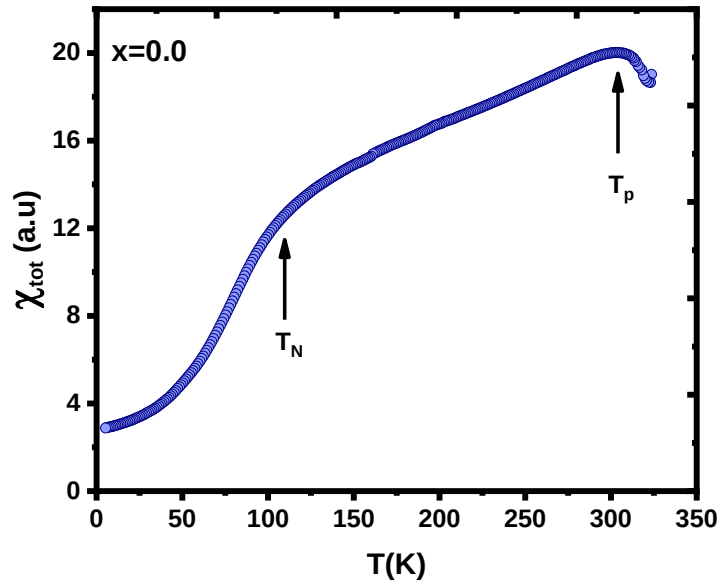


Figure 21: Temperature dependence of total ac-susceptibility of CrTe polycrystalline.

Figure 21 reveals a large plateau in the susceptibility that extend between T_N ($\sim 120\text{K}$) and T_p ($\sim 300\text{K}$). The peak temperature T_p which corresponds to the freezing temperature T_f in spin glass system. However, in some ferromagnetic materials it develops into a sharp peak that represents the ferromagnetic phase transition. In the unsubstituted *CrTe* sample, the FM transition peak is located near $T_c = 360\text{ K}$ [49]. The drop in the susceptibility near $T_N = 120\text{ K}$ indicates that the magnetization is decreasing with lowering the temperature.

At low temperatures, competing exchange interaction like AFM causes frustrated interactions and disorder in the spin configuration, hence the observed reduction in the susceptibility. The temperature drop marks the Néel temperature T_N . The reported value of the Curie temperature for *CrTe* is $T_c \sim 360\text{ K}$ [49] obtained from the linear extrapolation of χ^{-1} in the paramagnetic state. This is almost 60K higher than the observed peak in the susceptibility.

In Figure 22 we present the *ac*-susceptibility of *CrTe_{0.9}Sb_{0.1}* sample. The figure reveals that the antiferromagnetic transition temperature T_N has increased to $T_N \sim 213\text{ K}$. This shift is due to the fact that *CrTe* is pure ferromagnetic material while *CrSb* is pure antiferromagnetic [50]. On the other hand, the peak temperature T_p is reduced to $T_p \sim 285\text{ K}$ (Fig.22 (a)). The width of the plateau decreases to $\sim 60\text{K}$. The Curie temperature is found to be $T_c \sim 312\text{ K}$, and another minor peak is found at $T \sim 310\text{ K}$ (Fig.22 (b)).

In Figure 23, the fraction of *Sb* is increased to be $x=0.20$, which lead to increase $T_N \sim 185\text{ K}$, and the peak temperature has lowered to reach $T_p \sim 275\text{ K}$ (Fig.23 (a)). The Curie temperature reduced to $T_c \sim 278\text{ K}$ (Fig.23 (b)) indicating that there is extra antiferromagnetic exchange interaction. It is worth mentioning that the T_p matches with the

minor peak shown in Fig.23 (b), and its corresponding χ_{tot} becomes lower than the χ_{tot} of the T_N . This is because of complex competition of different magnetic interactions (see chapter 7).

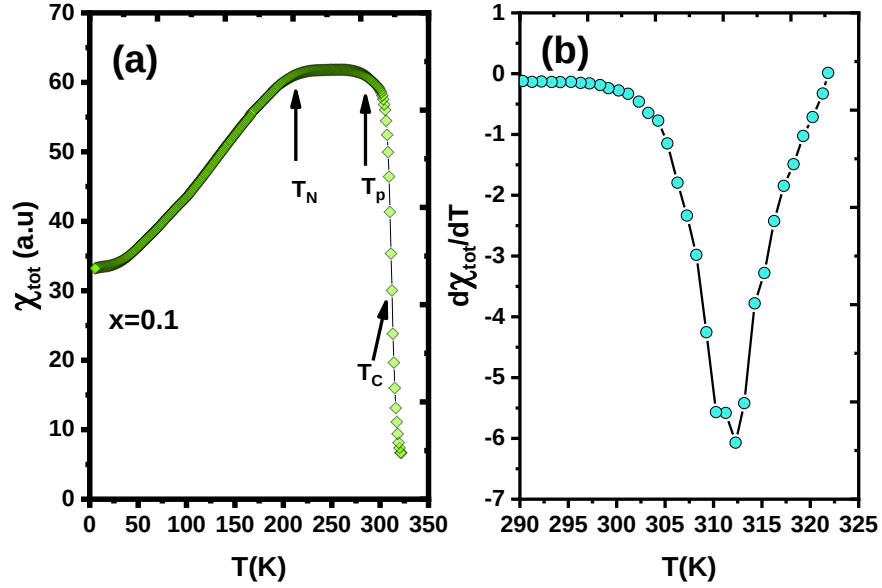


Figure 22: (a)Temperature dependence of total ac-susceptibility of $\text{CrTe}_{0.9}\text{Sb}_{0.1}$ polycrystalline, (b) Its first derivative to find the T_c .

In Figure 24, the peaks are still shifting upon increasing the fraction of $\text{Sb} = 0.3$, where $T_p \sim 250$ K, $T_N \sim 205$ K, and $T_c \sim 258$ K. Clearly, there are some magnetic interaction joining around the peak temperature. This interaction could be either another antiferromagnetic exchange interaction, or spin-glass phase transition.

The peak temperature becomes more dominant when the fraction of $\text{Sb} = 0.4$ (see Fig. 25) and behaves like an antiferromagnetic material with phase transition around $T_p \sim 215$ K. In addition, both T_N and T_p shifted toward each other.

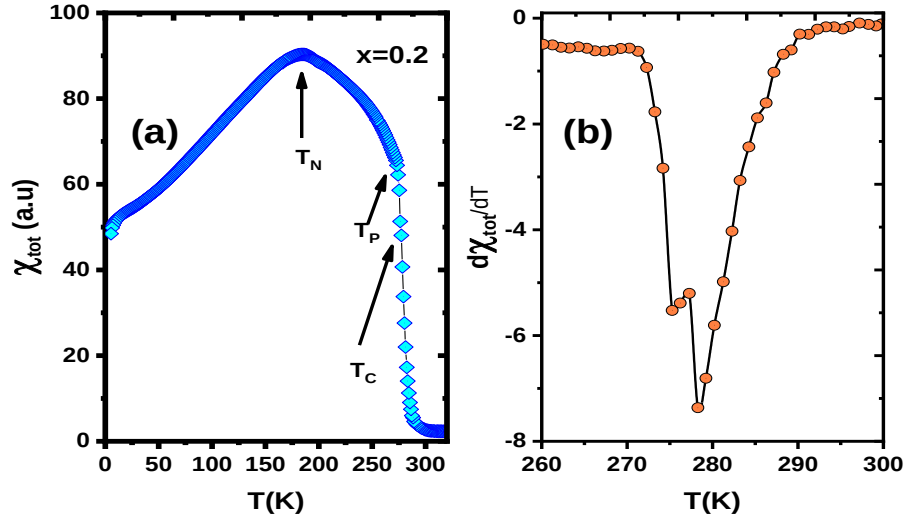


Figure 23: (a)Temperature dependence of total ac-susceptibility of CrTe_{0.8}Sb_{0.2} polycrystalline, (b) Its first derivative to find the T_c.

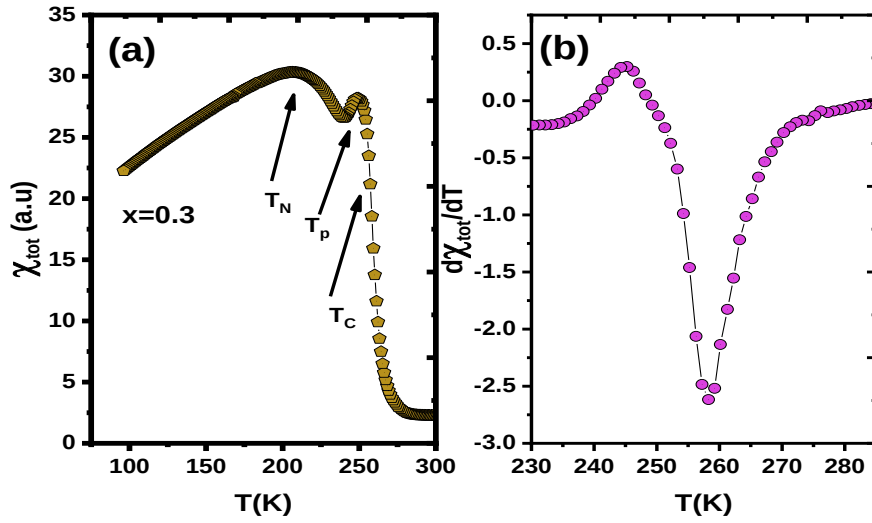


Figure 24: (a)Temperature dependence of total ac-susceptibility of CrTe_{0.7}Sb_{0.3} polycrystalline, (b) Its first derivative to find the T_c.

Similar behavior is seen for the sample with $Sb = 0.5$. The sample exhibits a pure antiferromagnetic behavior, with phase transition near $T_p \sim 140K$ (see Fig.26). Table 10 summarizes all data related to T_N , T_p , and T_c .

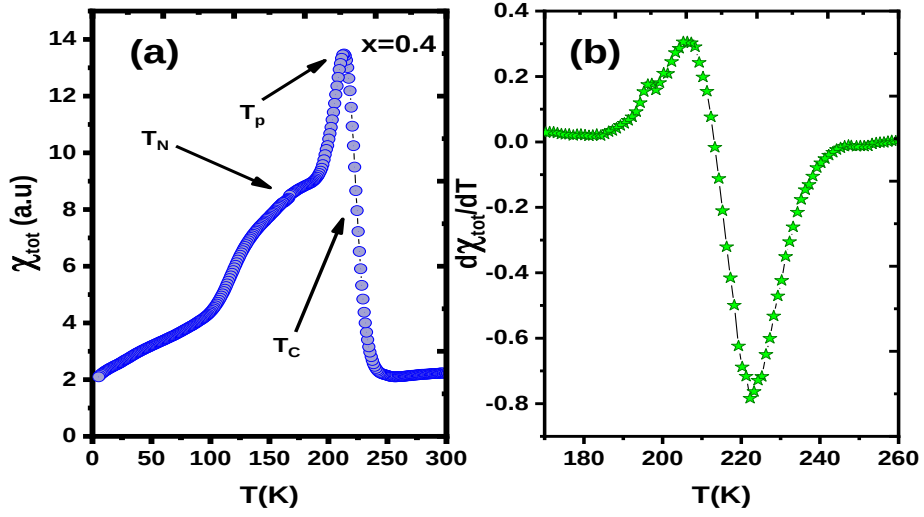


Figure 25: (a)Temperature dependence of total ac-susceptibility of CrTe0.6Sb0.4 polycrystalline, (b) Its first derivative to find the T_c .

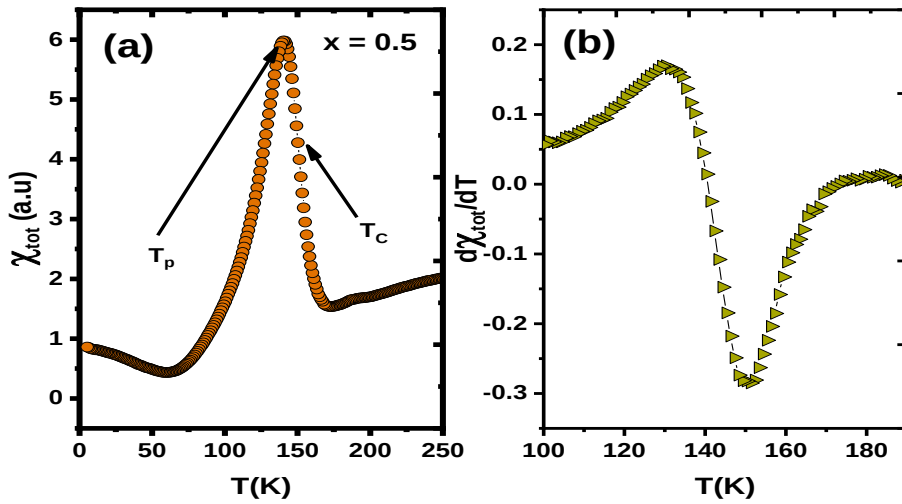


Figure 26: (a)Temperature dependence of total ac-susceptibility of CrTe0.5Sb0.5 polycrystalline, (b) Its first derivative to find the T_c .

Table 10: Change of T_N , T_p , and T_c with Sb concentration in $\text{CrTe}_{1-x}\text{Sb}_x$.

<i>Concentration (x)</i>	<i>$T_N(\text{K})$</i>	<i>$T_p(\text{K})$</i>	<i>$T_c(\text{K})$</i>
0.0	150	305	360
0.1	213	285	312
0.2	185	275	278
0.3	205	250	258
0.4	167	215	221
0.5	140	140	150

CHAPTER 5

MAGNETOCALORIC EFFECT AND RELATIVE COOLING POWER

Magnetic refrigeration MR, based on MCE, has recently received increased attention as an alternative to the conventional gas compression (CGC) refrigeration technology near room temperature in use today. Magnetic materials contain two energy reservoirs; the normal phonon excitations connected to lattice degrees of freedom, and magnetic excitations connected to spin degrees of freedom which can be strongly affected by an external applied magnetic field. These two reservoirs are generally coupled by the spin-lattice coupling that ensures loss-free energy transfer within millisecond timescales. Figure 27 shows the magnetic refrigeration cycle. According to this figure, the randomly oriented magnetic moment will be aligned by applying a magnetic field leading to heat the magnetic material. This heat can be expelled out to the surrounding due to heat transfer. Upon removing the magnetic field, the magnetic moment will be randomized again, which resulting in cooling the material below the surrounding temperature.

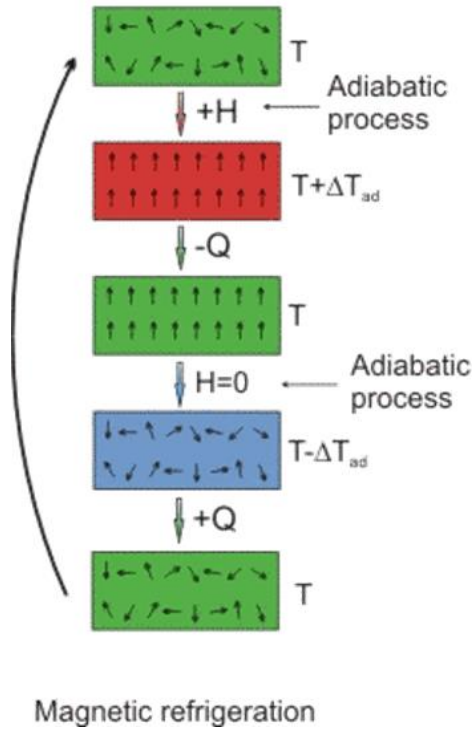


Figure 27: Schematic diagram of magnetic refrigeration that shows the two basic processes (isothermal magnetization and adiabatic demagnetization) of a magnetic system when a magnetic field is applied or removed.

5.1 MAGNETOCALORIC EFFECT IN $\text{Nd}_{0.60}\text{Sr}_{0.40}\text{Ni}_x\text{Mn}_{1-x}\text{O}_3$ POLYCRYSTALLINE

The magnetization isotherms (M vs. H curves) for $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Mn}_{1-x}\text{O}_3$ ($x=0.00$) over a magnetic field ranged from 0 all the way to $5T$ is depicted in figure 28. In this figure, at very low temperatures, say at $T = 20\text{ K}$, the compound is in its ferromagnetic state, and the magnetization is rapidly increasing by increasing the magnetic field from zero to about $0.5T$. when the field reaches $1T$, the magnetization tends to be saturated all the way to $5T$. Moreover, by increasing the temperature, the magnetization starts to decrease, and the compound moves from the ferromagnetic (FM) toward the paramagnetic (PM) region

around the room temperature (300K). In this region, (i.e. PM), the magnetization is linearly increasing from 0 up to 5T, and it will never saturate. Such a figure is rich in information that can be extracted. For example, investigate the critical behavior through its critical exponents, β , γ , and δ values which can be calculated using Arrott plot, Kouvel-Fisher plot, and critical isotherms as discussed later in chapter 6. On top of that, figure 28 is essential to study the relative cooling power (RCP), and the change in magnetic entropy ΔS_M to assess the magnetocaloric effect of our compounds.

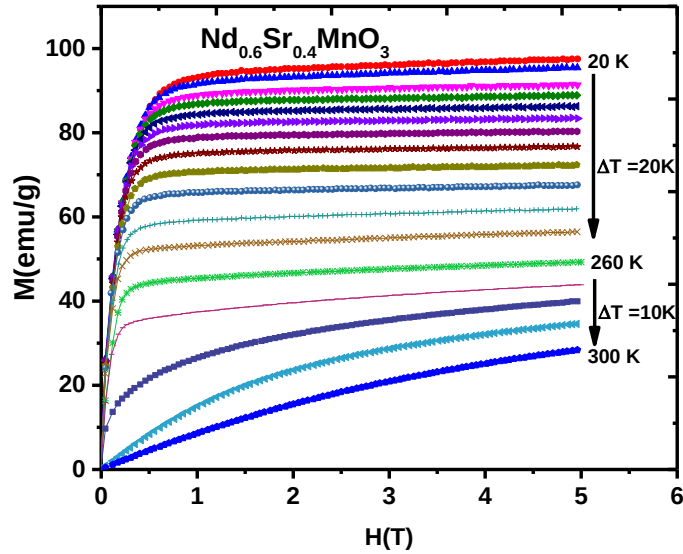


Figure 28: M vs H for $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ ($x=0.00$).

5.1.1 The magnetic entropy change ΔS_M and Relative cooling power (RCP)

The magnetic entropy change ΔS_M was determined through the magnetization isotherms (Fig. 28) using Eq. (1.3).

$$\Delta S_M(T, H) = \sum_i \frac{M_{i+1}(T_{i+1}, H) - M_i(T_i, H)}{T_{i+1} - T_i} \Delta H \quad (1.3)$$

For this purpose, we analyze the temperature dependence of $(-\Delta S_M)$ for each sample. The magnitude of $(-\Delta S_M)$ for the sample showed a peak at a temperature near its PM–FM transition temperature at all applied fields. For instance, Figure 29 shows $-\Delta S_M$ vs. T for the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ sample, resulting from different changes of the applied field (from 0 to $H = 1$ to 5T).

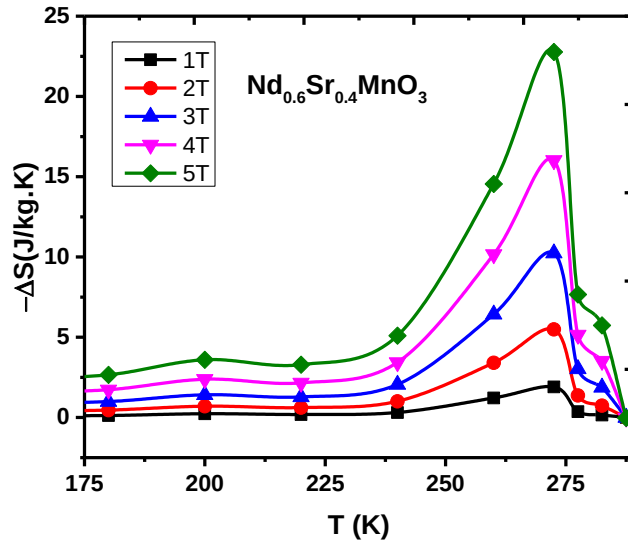


Figure 29: Temperature dependence of the negative magnetic entropy change of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ ($x=0.00$).

In figure 29, the peak position due to $-\Delta S_M$ is found to be 272.5K . Besides, upon increasing the magnetic field, there is a minor peak emerges around 292.5K . This peak is due to a secondary phase confirmed by XRD analysis of this compound shown in chapter 3. In addition, there is a considerable increasing in the amplitude of $(-\Delta S_M)$ around the peak with increasing the magnetic field. Table 11 shows the values of the amplitude upon changing the magnitude of applied magnetic field. Furthermore, the RCP which is a measure of the amount of transferred heat between hot and cold reservoirs were measured and recorded in table 11. This quantity, (i.e RCP), depends on both the maximum value of

the magnetic entropy change (ΔS_M^{max}) and the full-width at half-maximum (ΔT_{FWHM}) of the peak profile based on the following equation [51]

$$RCP = -\Delta S_M^{max} \times \Delta T_{FWHM} \quad (5.1)$$

Figure 30 depicted the values of RCP vs H for the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ compound.

Table 11: Effect of changing magnetic field on the entropy change for $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ ($x=0.00$).

<i>Magnetic field (T)</i>	<i>Amplitude (ΔS_M^{max}) (J/kg.K)</i>	<i>FWHM (K)</i>	<i>RCP(J/kg)</i>
1	1.91	21.40	40.87
2	5.50	21.34	117.37
3	10.24	22.03	225.59
4	16.02	22.58	361.73
5	22.77	22.96	522.80

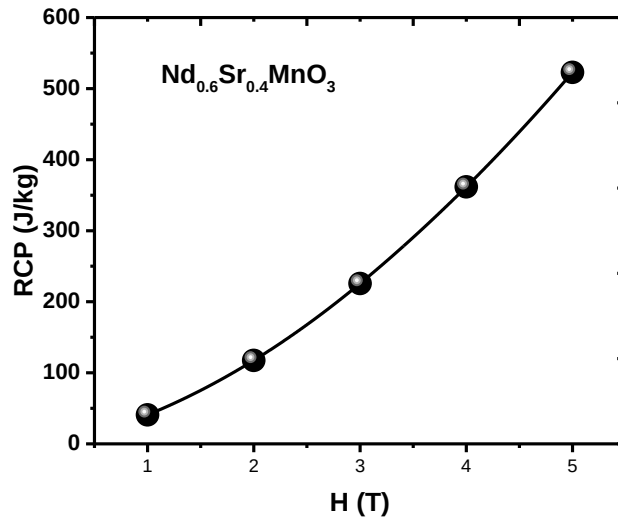


Figure 30: the RCP vs H in $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ ($x=0.00$).

5.2 Effect of *Ni* substitution on MCE and RCP in $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Mn}_{1-x}\text{O}_3$ polycrystalline

To enhance the MCE in the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ manganite, we investigate the substitution of *Ni* at the *Mn* site to broadening the magnetic transition as discussed earlier. Figure 31 shows the temperature dependence of the entropy change for the parent compound ($x=0$) along with the substituted compounds ($x=0.10$, and 0.20) at a magnetic field of $5T$. In this figure, the maximum value of the magnetic entropy change (ΔS_M^{max}) is significantly reduced by increasing *Ni* substitutions. However, the peak positions are shifted downward, and the curves are broadened with the *Ni* substitutions. This broadening provides an opportunity to fabricate a useful compound for the practical applications in a wide range of temperature. The minor peak at $x=0.20$ curve is due to a secondary phase shown by XRD analysis in chapter 3. A summary shows the results of maximum entropy change and relative cooling power for the investigated samples is depicted in Table 12. The deviation at $x=0.05$, and 0.15 in the FWHM and (ΔS_M^{max}) could be due to the magnetic properties of this compound. Figure 32 shows the temperature dependence of the negative magnetic entropy change of those two samples (i.e $x=0.05$, and $x=0.15$). From this figure, the behavior of samples is quite similar indicating that there is no abnormality in either samples.

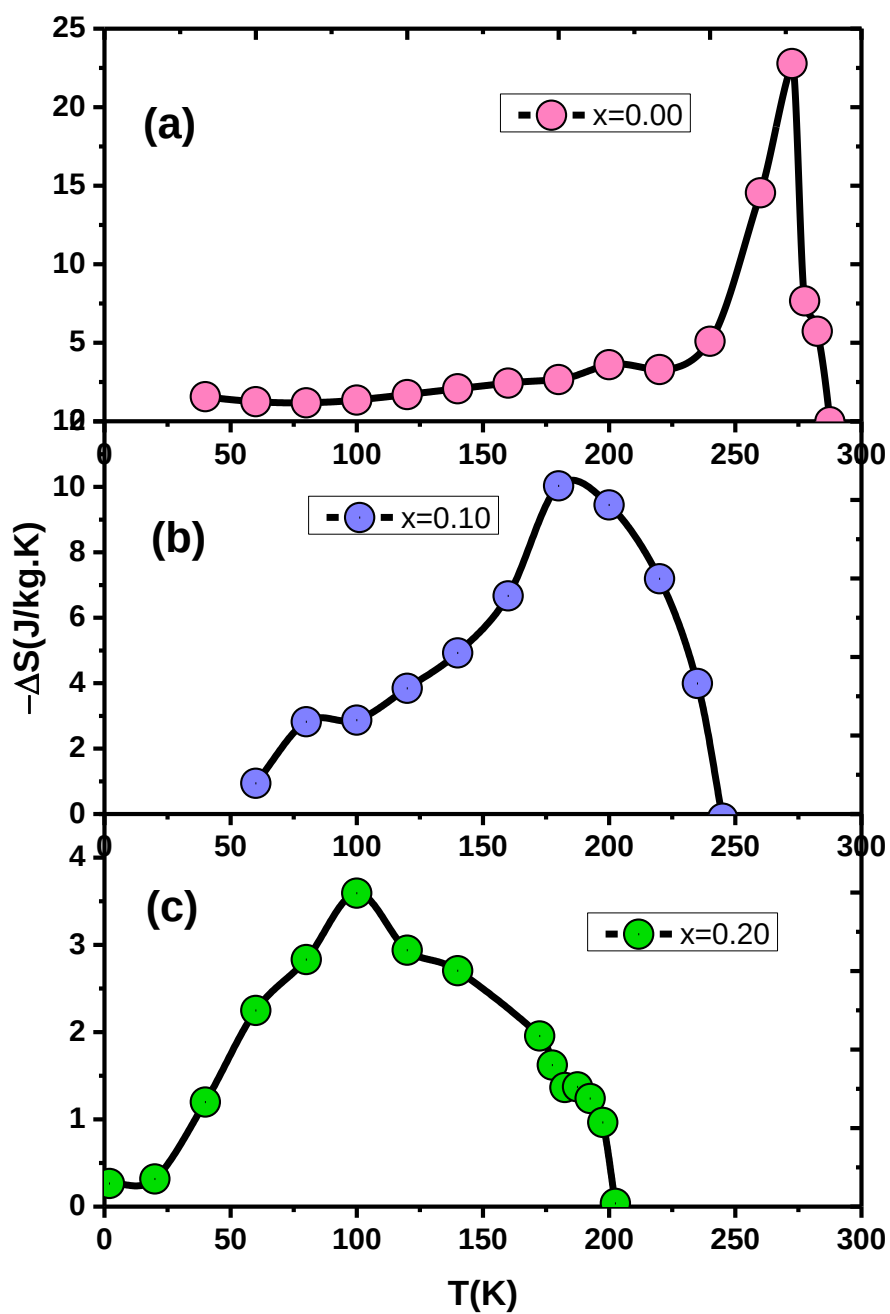


Figure 31: Temperature dependence of the negative magnetic entropy change of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ ($x=0.00, 0.10$, and 0.20).

Table 12: Maximum entropy change and RCP value at one tesla for $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ compounds.

Concentration (x)	Amplitude ($\Delta S_M^{\max}$) (J/kg.K)	FWHM	RCP(J/kg)
0.00	22.77	22.96	522.80
0.05	44.99	12.21	549.19
0.10	10.23	89.15	912.01
0.15	15.54	33.33	517.91
0.20	3.59	144.02	517.03

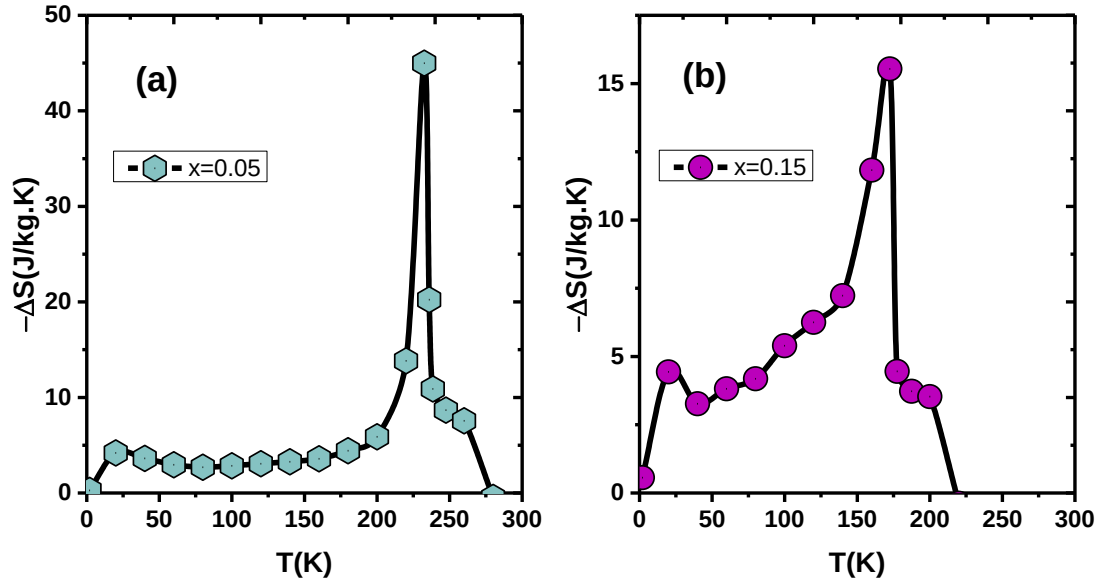


Figure 32: Temperature dependence of the negative magnetic entropy change of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Ni}_x\text{Mn}_{1-x}\text{O}_3$, (a) $x=0.00$, and (b) $x=0.15$.

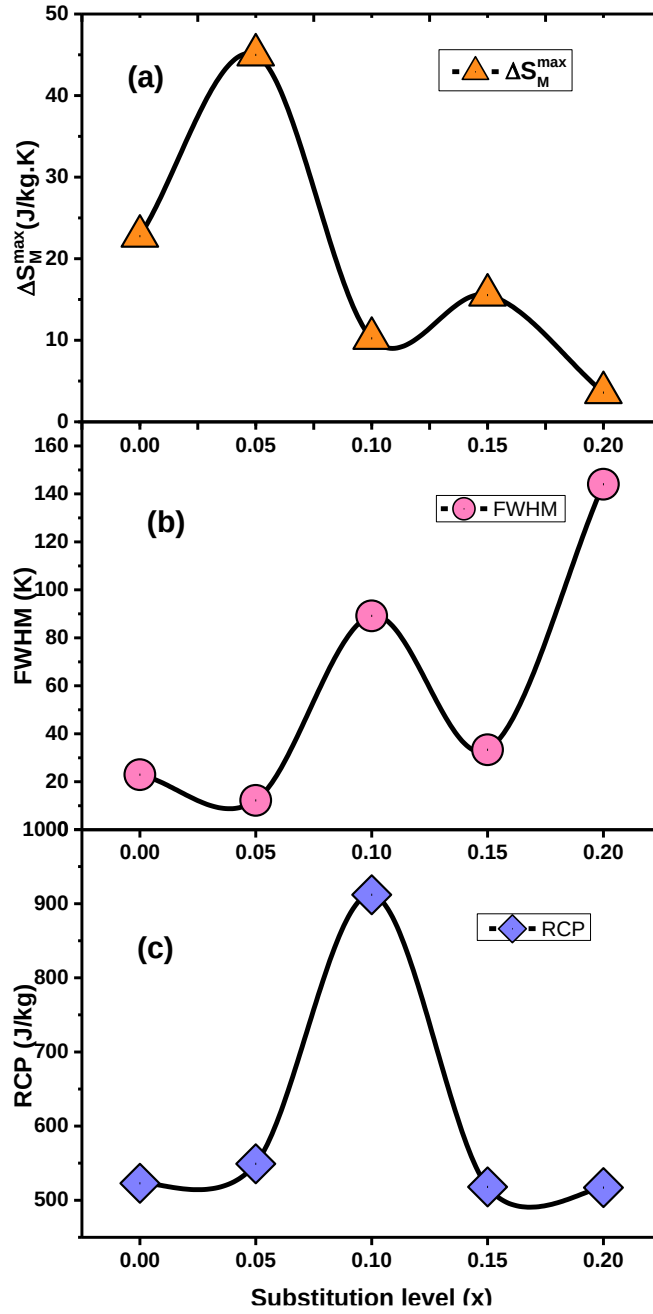


Figure 33: Effect of Ni substitution in $Nd_{0.6}Sr_{0.4}Ni_xMn_{1-x}O_3$ on: (a) Maximum amplitude ($\Delta S_M^{\max}$), (b) Full-width at half-maximum (FWHM), and (c) Relative cooling power.

To sum up, the maximum amplitude is obtained in $x=0.05$ sample, while the minimum one is related to $x=0.20$ (Fig. 33 (a)). Oppositely, the wider full-width at half-maximum

(FWHM) is due to $x=0.20$, and the thinner one is related to $x=0.05$ (Fig.33 (b)). Moreover, when $x=0.10$, we get the maximum relative cooling power (RCP) (Fig.33 (c)), indicating that $Nd_{0.6}Sr_{0.4}Ni_xMn_{1-x}O_3$ is a flexible promising candidate that could be used in a wide range of practical applications such as magnetic refrigerators.

CHAPTER 6

CRITICAL BEHAVIOR NEAR FERROMAGNETIC TO PARAMAGNETIC PHASE TRANSITION IN $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ MANGANITE

Toward a microscopic understanding of the magnetocaloric effect of $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ polycrystalline, we study the critical phenomena near its *FM* – *PM* phase transition. This transition is characterized by a set of critical exponents in the critical region (see Table 13). Upon choosing T_c accurately, the mentioned critical exponents will be associated with magnetic phase transition that allows classification of these material in a certain universality class.

Table 13: Critical exponents that characterize the FM-PM phase transition.

Critical exponent	Related physical quantity
β	spontaneous magnetization M_s
γ	initial susceptibility χ_0^{-1}
δ	Critical isotherms
α	Heat capacity

The exponents are defined as [53]:

$$M_S = m_0 |\varepsilon|^\beta; \quad T < T_c \quad (6.1)$$

$$\chi_0^{-1} = \frac{h_0}{m_0} |\varepsilon|^\gamma; \quad T > T_c \quad (6.2)$$

$$H = DM^\delta; \quad T = T_c \quad (6.3)$$

here $\varepsilon = \frac{T-T_c}{T_c}$ is the reduced temperature, m_0 , h_0 and D are the critical amplitudes. The critical exponent of the heat capacity (α) is by convention set to $\alpha = 0$. The exponent identities are given as:

$$\alpha + 2\beta + \gamma = 2 \text{ (Rushbrooke's Identity) and } \delta - 1 = \gamma/\beta \text{ (Widom's Identity)}$$

The reported values for the critical parameters of numerous perovskite manganites are controversial, covering the range between those corresponding to short-range Heisenberg model ($\beta = 0.365$, $\gamma = 1.336$, and $\delta = 4.66$) and those corresponding to long-range mean-field theory ($\beta = 0.5$, $\gamma = 1$, and $\delta = 3$) [53].

In the current chapter work, we study the critical phenomena in $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ compound, where $0.00 \leq x \leq 0.20$, near its $FM - PM$ phase transition. The corresponding critical exponents are determined from the Arrott plots [23], and are confirmed then by Kouvel-Fisher method [24]. The range and dimensionality of magnetic exchange interaction are also ascertained from the scaling analysis of $\ln(M)$ vs. $\ln(H)$ of isothermal magnetization.

6.1 Modified Arrott plot (MAP) and critical isotherm

The conventional method to determine the critical exponents and transition temperature involves the use of Arrott plot [54]. In this procedure, the magnetization isotherms are plotted in the form of M^2 vs. H/M . This form leads to a set of parallel straight lines around T_c which can accurately be defined since the isotherm at T_c passes through the origin. This method is based on the mean field free energy and its expansion near T_c . The critical exponents are those of mean-field theory ($\beta = 0.5$, $\gamma = 1$, $\delta = 3$). Hence, linear behavior of high field isotherms indicates the presence of mean-field interactions. In addition to finding T_c accurately, one can obtain the inverse of the initial susceptibility χ_0^{-1} , as a function of temperature, directly from an intercept of the parallel lines with the H/M axis. Moreover, the temperature dependence of spontaneous magnetization M_S can be determined from the intercept of the parallel lines with the M^2 axis. To illustrate the procedure, we present the Arrott-plot of the unsubstituted sample ($Nd_{0.6}Sr_{0.4}MnO_3$) is presented in figure 34.

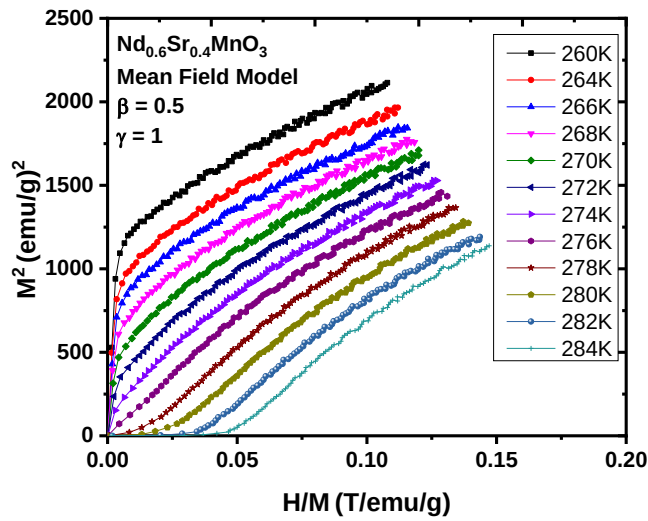


Figure 34: Arrott-plot for $Nd_{0.6}Sr_{0.4}MnO_3$ compound. Representative isotherms are shown for clarity.

According to this figure, all curves yield, in the low field region, nonlinear lines with concave downward curvature below T_c and concave up, above T_c . Slight non-linearity persists at the high-field regions. This curvature clearly indicates second-order phase transition according to the criterion suggested by Banerjee [55], which also indicates that the mean-field model is not valid. Consequently, the magnetization isotherms need to be analyzed by what is commonly known as the modified Arrott-plot (MAP), or sometimes called the Arrott-Noakes equation of state, which should hold in the asymptotic critical region [56]. The representation is often known as Arrott-Noakes-Kouvel plots.

$$(H/M)^{1/\gamma} = (T - T_c)/T_1 + (M/M_1)^{1/\beta} \quad (6.4)$$

where T_1 and M_1 are constants.

The magnetic isotherms are represented as $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ plots at different temperatures for $Nd_{0.6}Sr_{0.4}MnO_3$ manganite using four different models of critical exponents (Fig. 35):

- 1- The 3D-Heisenberg model;
- 2- The tricritical mean-field model;
- 3- The 3D-Ising model;
- 4- The 3D-XY model.

The theoretical values of β , γ , and δ for each model are shown in Table 14. The later model uses usually in case of having superconductor state.

Table 14: Critical exponents (β , γ , and δ) for different universality classes [56]

Model	β	γ	δ
Mean Field Model	0.5	1	3
3D Heisenberg Model	0.365	1.336	4.8
3D Ising Model	0.325	1.24	4.82
Tricritical mean field Model	0.25	1	5
3D XY Model	0.345	1.316	4.81

Based on these curves (Fig.35), all models render quasi-straight lines and nearly parallel through the high-field region. Thus, in some materials; it is not easy to distinguish which model fits the data better and gives the best calculated critical exponents. To help screen these models and compare them to select the one that closely describing the magnetic state at hand; we calculated their relative slopes (RS) as shown in in Figure 36. This figure shows the RS vs. T curve for the four models. The most adequate model should be the one that possesses a RS value that is very close to the unity [58]. This in a way says that the high field isotherms are parallel to each other's; above and below T_c . Therefore, one can infer that the 3D-Heisenberg model is the nearest to the horizontal line at $RS = 1$.

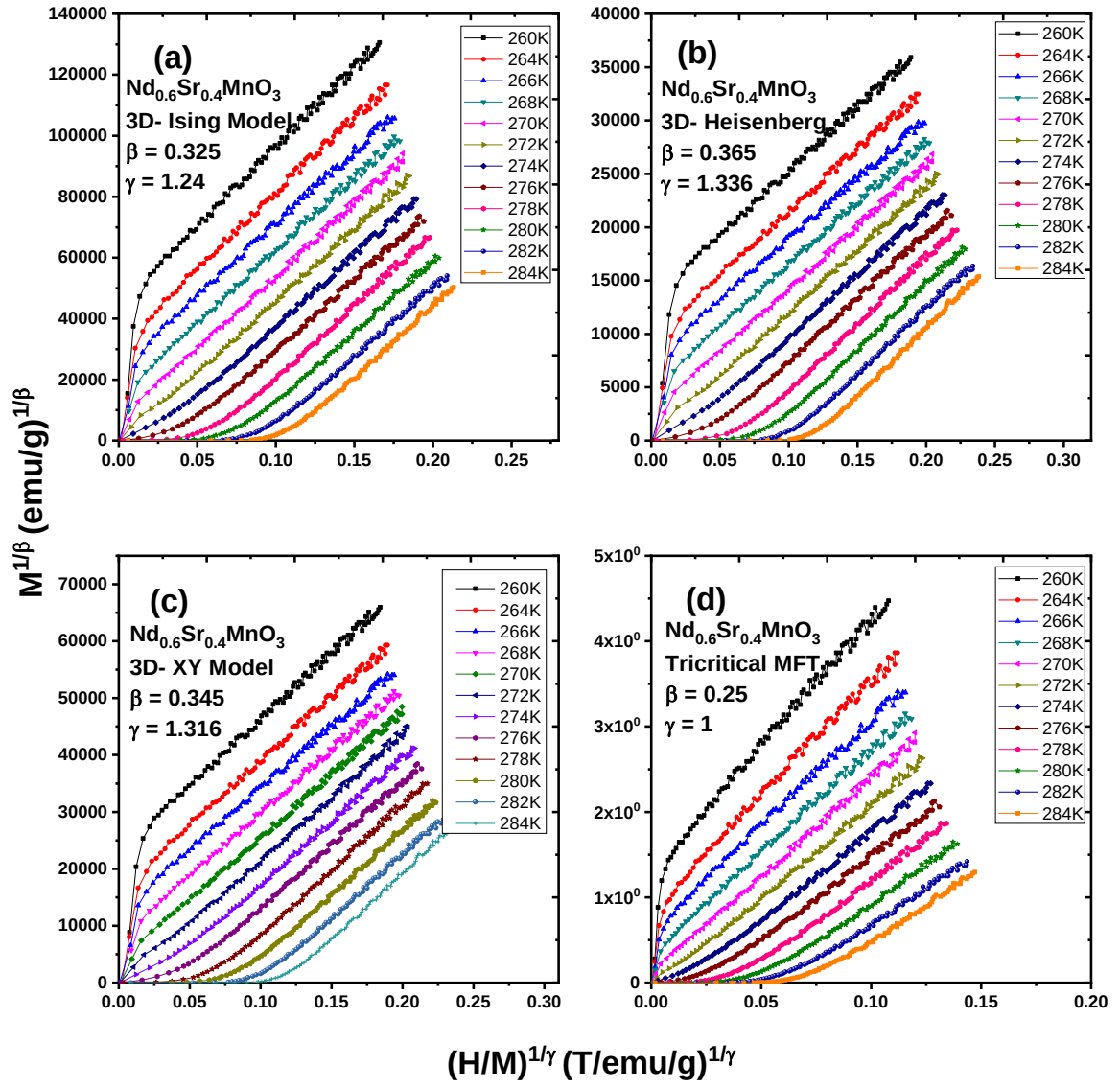


Figure 35: Modified Arrott-plots for $Nd_{0.6}Sr_{0.4}MnO_3$ compound using different models; (a) 3D-Ising model, (b) 3D-Heisenberg model, (c) 3D-XY model, and (d) Tricritical mean field model.

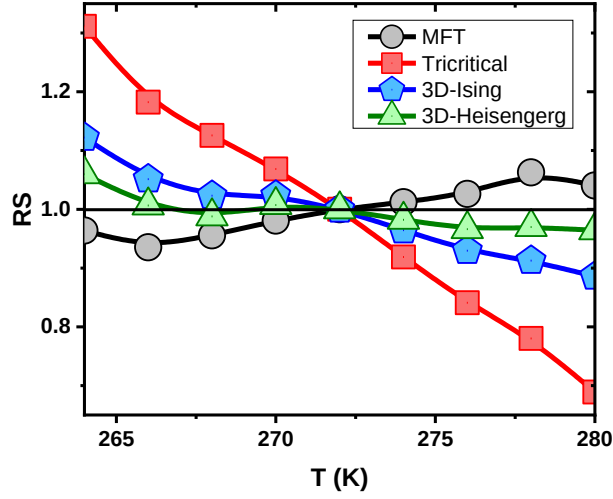


Figure 36: Relative slope (RS) of $Nd_{0.6}Sr_{0.4}MnO_3$ manganite as a function of temperature defined as RS = Slope at any temperature divided by the slope at T_c .

Following the standard procedure, the values of spontaneous magnetization $M_s(T)$, and inverse of initial susceptibility $\chi_0^{-1}(T)$ are obtained from a linear extrapolation of MAP to the intercept with the $M^{\frac{1}{\beta}}$ vs. $(H/M)^{\frac{1}{\gamma}}$ axes, respectively (Fig. 37). the critical exponents of the 3D-Heisenberg model have been chosen to be as initial values. Only the high-field (above 4T) linear region is used for the analysis since MAP deviates from linearity at a low field, due to the nature of the magnetic domains distribution inside the sample. The values of both β , and γ were obtained by fitting the experimental data for each sample with Eqs.6.1, 6.2 respectively (Fig.38). The experimental value of the critical isotherm exponents δ was obtained using the magnetic isotherm at T_c (Eq.6.3) represented as $\ln(M)$ vs $\ln(H)$ graph (known as the critical isotherm) (see Fig.39). Eq.6.1 gives $\beta = 0.314 \pm 0.010$, $T_c = 272.58 \pm 0.54K$ and Eq.6.2 gives $\gamma = 1.34 \pm 0.07$, $T_c = 273.89 \pm 0.23K$. Finally, Eq.6.3 gives $\delta = 4.76 \pm 0.03$.

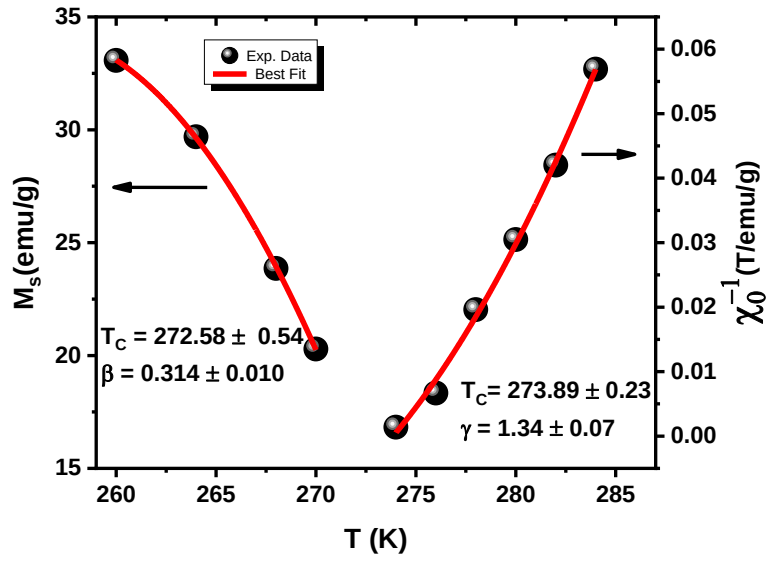


Figure 37: Temperature dependence of the spontaneous magnetization (to the left), and the inverse of the initial susceptibility (to the right) for $Nd_{0.6}Sr_{0.4}MnO_3$ compound.

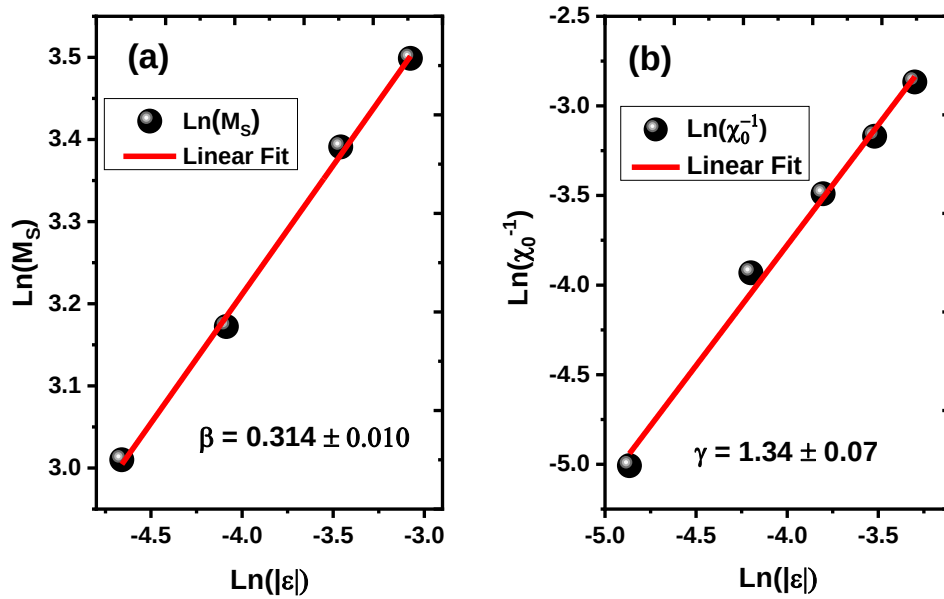


Figure 38: (a) the spontaneous magnetization and, (b) the inverse of the initial susceptibility, both are versus the reduced temperature for the $Nd_{0.6}Sr_{0.4}MnO_3$ compound.

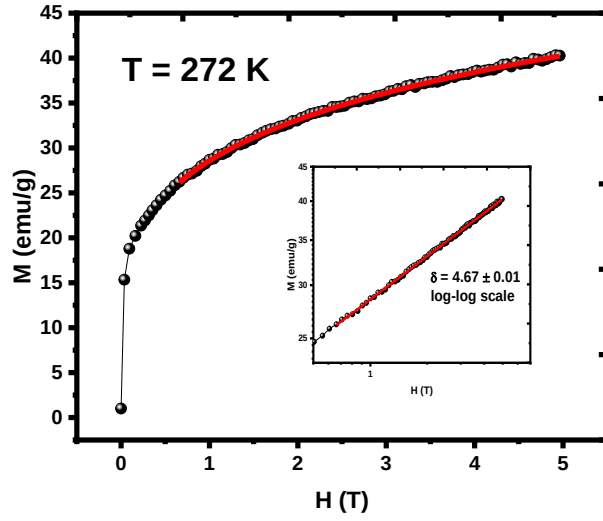


Figure 39: Critical isotherm at $T=T_c$ in the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ compound. The inset shows the log-log scale.

6.2 Kouvel–Fisher Plot

Kouvel–Fisher (KF) suggested a more precise method of determining the critical exponents [24]. The method is based on linearizing the two main order parameters; M_s and χ_0^{-1} near T_c using the following relations [24]:

$$\frac{M_s(T)}{dM_s(T)/dT} = \frac{T-T_c}{\beta} \quad (6.5)$$

$$\frac{\chi_0^{-1}}{d\chi_0^{-1}/dT} = \frac{T-T_c}{\gamma} \quad (6.6)$$

According to this method, Eqs. 6.5 and 6.6, yield straight lines with slopes $1/\beta$ and $1/\gamma$, respectively. The KF plot is illustrated in Fig. 40. for $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. The obtained critical exponent ($\beta = 0.357 \pm 0.025$) slightly increased while $\gamma = 1.334 \pm 0.048$ decreased. The critical exponents obtained from the MAP as well as the KF method along with T_c are shown in Table 15 along with the calculate δ values using the Widom's theory

[25]. Both values of δ obtained from experiment and Widom's theory are very close to each other (Table 15).

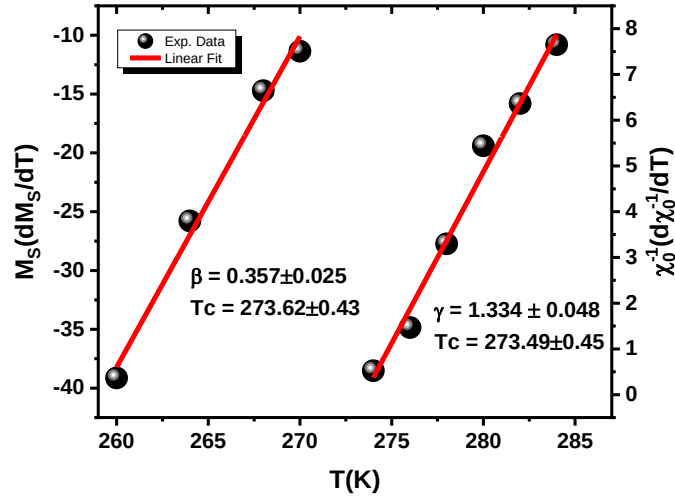


Figure 40: Kouvel-Fisher plots for $M_s(T)$ and $\chi_0^{-1}(T)$ in $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ compound.

Table 15: Critical exponents (β , γ , and δ) for $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ compound, (CI = critical isotherms).

Composition	Technique	$T_c(K)$	β	γ	δ
$\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	MAP	272.65 ± 0.54	0.314 ± 0.010	1.34 ± 0.07	
	K-F analysis	273.62 ± 0.43	0.357 ± 0.025	1.334 ± 0.048	
	CI (Exp)				4.67 ± 0.01
	CI (Cal)				4.74 ± 0.49

To further simplify the analysis, we suggest the following procedure to represent the data:

At $T=T_c$, equation (6.4) can be rearranged to be $M^\delta \propto H$, where $\delta = 1 + \frac{\gamma}{\beta}$. That means,

by plotting M^δ vs H (Fig. 41), the y-intercept ($M_s^\delta(T_c, 0)$) should be zero at T_c , positive

at $T < T_c$ and negative at $T > T_c$. From this figure, the inset shows clearly that we have a straight line passing the origin at T_c .

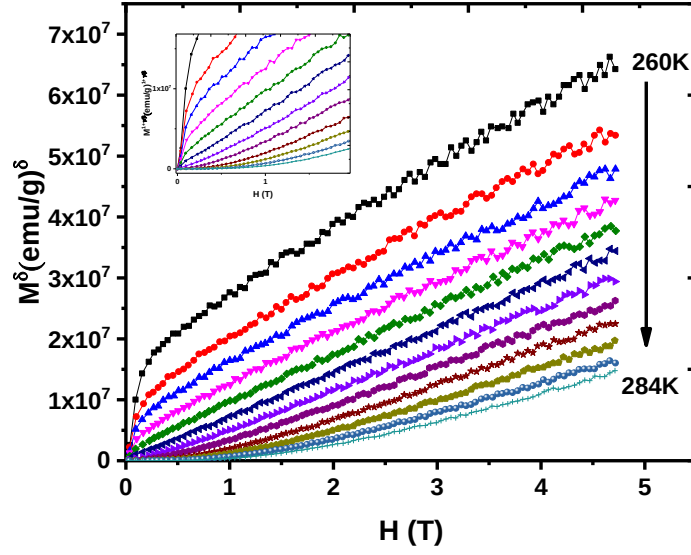


Figure 41: M^δ vs. H for $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ compound. The inset is the “zoom-in” around the origin (0, 0).

Figure 42, shows the $M_S^\delta(T, 0)$ vs. T for both $T < T_c$ and $T > T_c$. The cross-sectional point between $M_S^\delta = 0$ line and the interpolated line, between the last positive y-intercept (M_S^δ) (black), with the first negative one (red), gives a more accurate critical temperature ($T_c = 272.015\text{K}$).

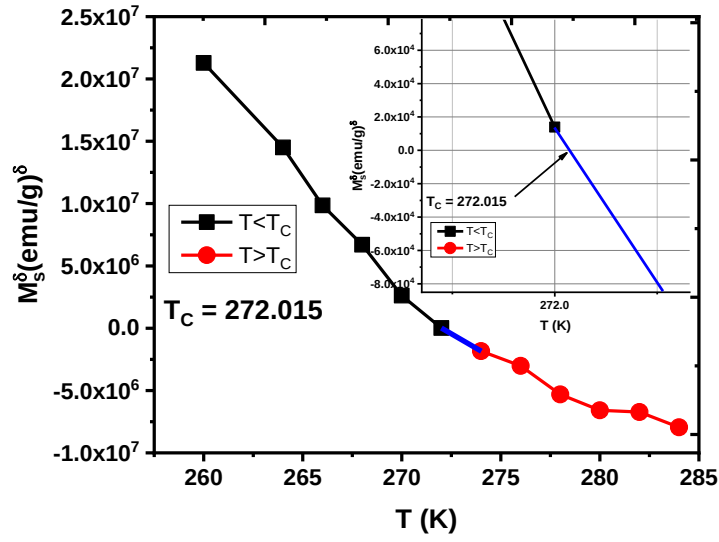


Figure 42: M^δ vs. H for $T > T_c$ and $T < T_c$. The inset shows the intersectional line between $M^\delta = 0$ and the interpolated line (blue).

6.3 Scaling Analysis

Near the critical region, the magnetic equation of state, according to the scaling hypothesis, can be written as:

$$M(H, \varepsilon) = |\varepsilon|^\beta f \pm \left(\frac{H}{|\varepsilon|^{\beta+\gamma}} \right) \quad (6.7)$$

where f_+ is the state function above T_c ($T > T_c$) and f_- is the state function below T_c ($T < T_c$), define ε both are polynomial functions [13]. The renormalized magnetization can be defined as $m \equiv |\varepsilon|^{-\beta} M(H, \varepsilon)$, and renormalized field as $h \equiv H |\varepsilon|^{-(\beta+\gamma)}$. This means, Eq.6.7 can be rewritten as

$$m = f_\pm(h) \quad (6.8)$$

Upon correct calculations of β, γ , and δ Eq. 6.8 points out that $M/|\varepsilon|^\beta$ as a function of $H/|\varepsilon|^{(\beta+\gamma)}$ will give two distinct curves; one for T above T_c and another below T_c [58]. This is an important criterion for critical regime. Thus, we can compare the obtained results with the prediction of the scaling theory with Eq.6.8. The scaled data plotted in Fig.43 fall on two curves, one above T_c and the other below T_c , Both curves merge at $T=T_c$. These findings confirms that the obtained values of the critical exponents and critical temperatures are reliable and consistent with the scaling hypothesis.

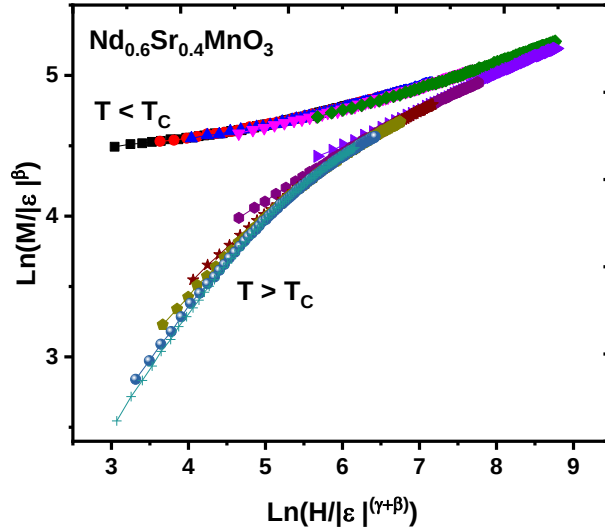


Figure 43: Scaling plots indicating two universal curves below and above T_c .

In the following sections, we investigate the effects of Ni substitution on the magnetic state and the corresponding critical exponents in $Nd_{0.6}Sr_{0.4}MnO_3$, we reported several sample with Ni substitute Mn with $x = 0.05, 0.10, 0.15$, and 0.20 .

6.4 Effect of Ni Substitutions on Critical Behavior of $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$

In Figure 44; we present the MAP $Nd_{0.6}Sr_{0.4}Mn_{0.95}Ni_{0.05}O_3$ sample around T_c for all 4- basic models. Similar to the results obtained, all models in figure 44 give nearly straight and parallel lines at high-field, however, with varying slopes. Accordingly, we calculate their relative slopes as shown in figure 45.

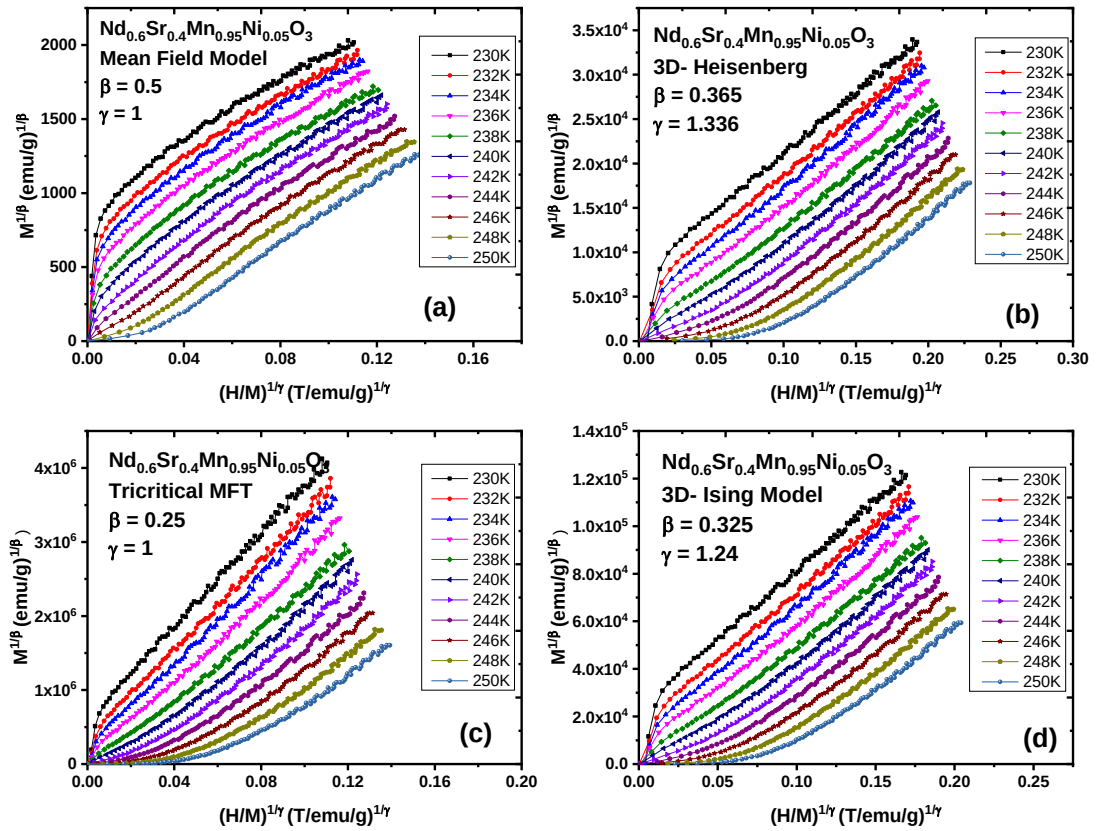


Figure 44: Modified Arrott-plots for $Nd_{0.6}Sr_{0.4}Mn_{0.95}Ni_{0.05}O_3$ compound using different models; (a) Mean Field Theory, (b) 3D-Heisenberg model, (c) Tricritical mean field model, and (d) 3D-Ising model.

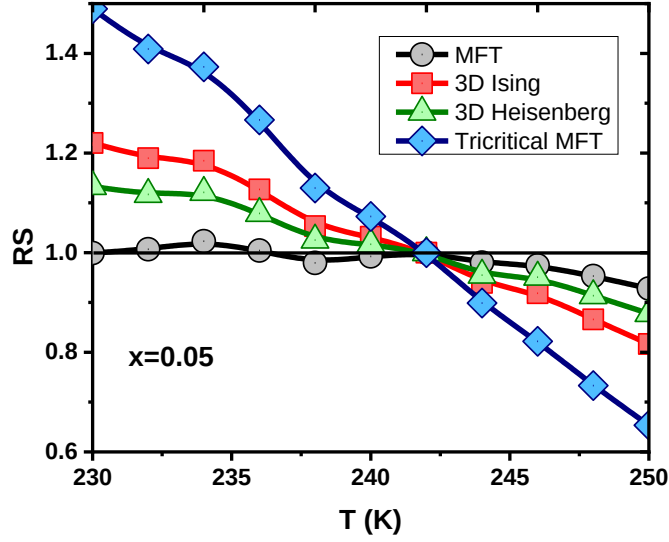


Figure 45: Relative slope of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.95}\text{Ni}_{0.05}\text{O}_3$ manganite as a function of temperature.

The figure shows that the mean field model has the least relative slope deviations from $RS=1$. Hence, the mean field model closely represents the magnetic state of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.95}\text{Ni}_{0.05}\text{O}_3$ (Fig.12). Similar behavior was obtained in other manganites (give the material) by F. Ben Jemaa *et al* [53]. Following similar procedure to evaluate the critical exponents for the rest of the samples ($x = 0.10, 0.15, \text{ and } 0.20$), and to screen which model fits most the corresponding data. We found that all samples follow the mean field model (except $x = 0$ sample which follows 3D Heisenberg). We used the modified Arrott plots to evaluate the critical exponents using $M_s(T)$ and $\chi_0^{-1}(T)$ values as described earlier. The critical exponents of the mean field model have chosen as the initial values in the high field region. The refined values of both β , and γ were obtained by fitting the experimental data with Eqs.6.1, and 6.2 respectively (Fig.46), while the experimental value of the critical isotherm exponents δ was again determined with Eq.6.3 from $\ln(M)$ vs $\ln(H)$ graph at T_c the summery of the results is written in Table 16.

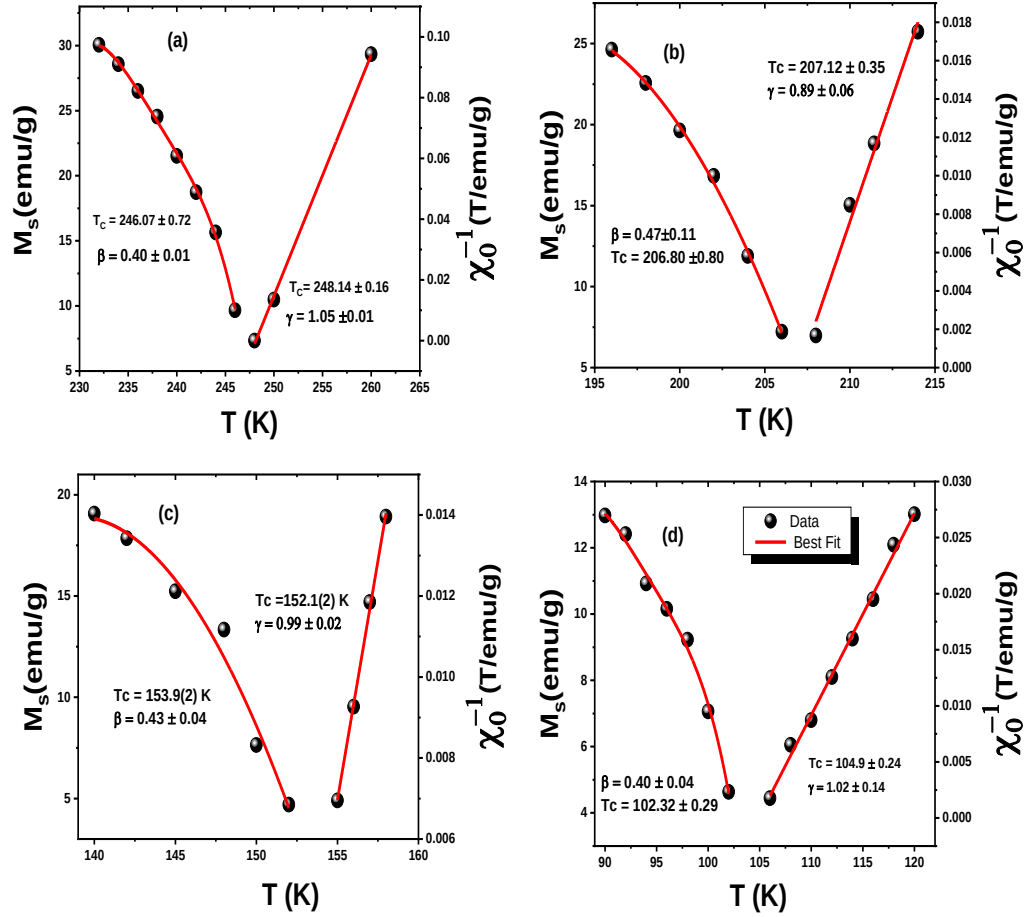


Figure 46: Temperature dependence of the spontaneous magnetization (to the left), and the inverse of the initial susceptibility (to the right) for $Nd_{0.6}Sr_{0.4}Mn_{1-x}Ni_xO_3$ compounds, (a) $x=0.05$, (b) $x=0.10$, (c) $x=0.15$, and (d) $x=0.20$.

The critical exponents are further refined $M_s(T)$ and $\chi_0^{-1}(T)$ data using the Kouvel-Fisher method as shown in figure 47. The experimental data were fitted with Eqs. 6.5, and 6 to obtain β , and γ values respectively, while Eq. 6.7 is used to get δ (see table 16).

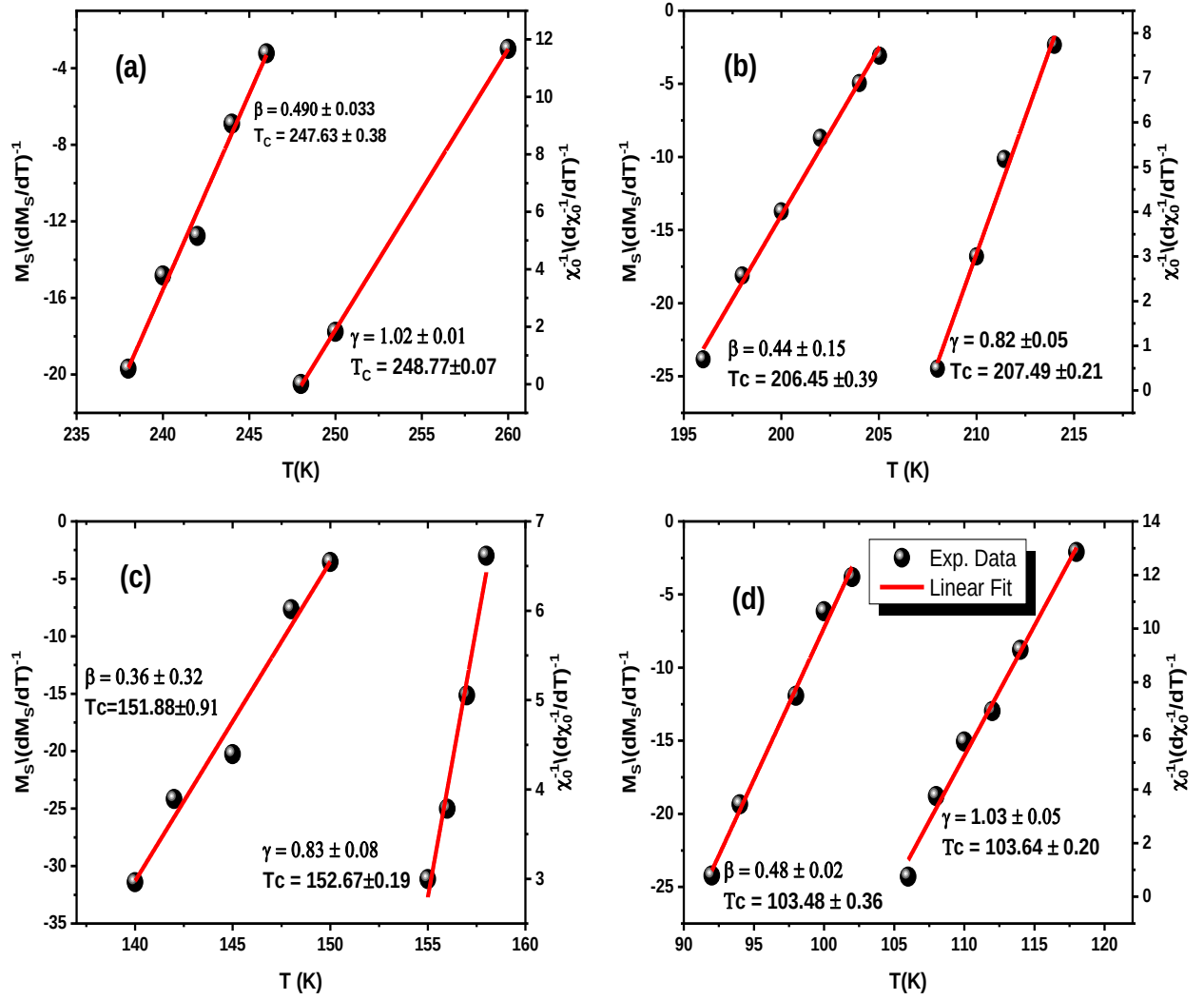


Figure 47: Kouvel-Fisher plots for $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ compounds, (a) $x=0.05$, (b) $x=0.10$, (c) $x=0.15$, and (d)

$x=0.20$.

Table 16: Critical exponents β , γ , and δ for $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ compound, (CI = critical isotherms).

x	$Technique$	$T_c(K)$	β	γ	δ
0.00	MAP	272.65 ± 0.54	0.314 ± 0.010	1.34 ± 0.07	
	K-F analysis	273.62 ± 0.43	0.357 ± 0.025	1.334 ± 0.048	
	CI				
0.05	MAP	246.07 ± 0.72	0.40 ± 0.01	1.05 ± 0.01	
	K-F analysis	247.63 ± 0.38	0.49 ± 0.03	1.02 ± 0.01	
	CI				
0.10	MAP	207.12 ± 0.35	0.47 ± 0.11	0.89 ± 0.05	
	K-F analysis	206.45 ± 0.39	0.44 ± 0.15	0.82 ± 0.05	
	CI				
0.15	MAP	152.12 ± 0.02	0.43 ± 0.04	0.99 ± 0.02	
	K-F analysis	152.67 ± 0.19	0.36 ± 0.32	0.83 ± 0.06	
	CI				
0.20	MAP	104.9 ± 0.24	0.40 ± 0.04	1.02 ± 0.14	
	K-F analysis	103.64 ± 0.20	0.48 ± 0.02	1.03 ± 0.05	
	CI				

CHAPTER 7

CRITICAL BEHAVIOR OF QUASI-TWO DIMENSIONAL FERROMAGNETIC $CrTe_{1-x}Sb_x$

Discovery of single-layer graphene has revived the interest in two-dimensional (2D) materials from basic science and possible new application [59]. Reduced dimensional magnetic materials have an immense potential in spintronic applications. Their electrical properties can be tuned using charge and spin degree of freedom [60]. However, little attention was devoted to use 2D materials in spintronics devices due to the lack of long-range ferromagnetic order that is crucial for spintronic applications [61]. Recently, Cr-based ternary chalcogenides ($CrMX_3$) where M is a non-transition metal (Sb, Ge) and X = S, Se, Te have attracted renewed interest for their possible applications in spintronics technologies. These materials are exfoliatable magnetic layers with van der Waals forces weakly bond the magnetic layers. For example, CrTe is ferromagnetic conductors [46], while CrSb is predominately antiferromagnetic [47]. According to the de Gennes theory, substituting Sb on the Te site will change the magnetic state of the solid solution $CrTe_{1-x}Sb_x$ due to double exchange interaction [48].

In an effort to understand the ferromagnetic magnetic state in these materials and their possible applications as magnetocaloric material, we study, in this chapter, the effect of Sb

substitution in the $\text{CrTe}_{1-x}\text{Sb}_x$ ($x=0.2, 0.3, 0.4$, and 0.5). In particular, we investigate the critical behavior and the magnetocaloric effect near FM-PM phase transition.

7.1 The Critical Behavior In $\text{CrTe}_{1-x}\text{Sb}_x$

The ac-susceptibility measurements performed on $\text{CrTe}_{1-x}\text{Sb}_x$ series revealed that the FM-transition temperature for the CrTe and $\text{CrTe}_{0.9}\text{Sb}_{0.1}$ are 360K and 312K respectively, which are higher than maximum available temperature that can be reached in our magnetometer. We were not able to perform detailed magnetocaloric and critical exponent analyses for these two samples ($x=0.0, 0.1$). For this reason, we use various techniques such as Arrott plot, Kouvel-Fisher plot, and critical isotherms analysis. Firstly, there will be problems in estimating the critical temperature T_c . For example, the obtained critical temperature from the Curie-Weiss law ($1/\chi$) would be overestimated. To avoid such problem, we need to stick as close as possible to the transition temperature. Similar problem was reported in CrSbSe_3 [56]. In this compound, the obtained $T_c \sim 145\text{K}$ from Curie-Weiss temperature; while T_c obtained from the inflection point of the susceptibility is $\sim 70\text{K}$. The estimated T_c from both Arrott plot and Kouvel-Fisher was near 71K. Secondly, the antiferromagnetic exchange interaction could affect the values of spontaneous magnetization M_s and the behavior of the magnetization at low temperatures ($\ll T_c$) leading to irregular behavior in several order parameters (M_s and χ_0^{-1}) around T_c .

7.1.1 The Critical exponent analysis of the $\text{CrTe}_{1-x}\text{Sb}_x$ system with $x \geq 0.2$:

To obtain the Curie temperature (T_c) we specify the inflection point of the total ac-susceptibility for each sample (see Chapter 4). For example, Figure 48 shows that $T_c \sim 278\text{K}$ for $\text{CrTe}_{0.8}\text{Sb}_{0.2}$ sample.

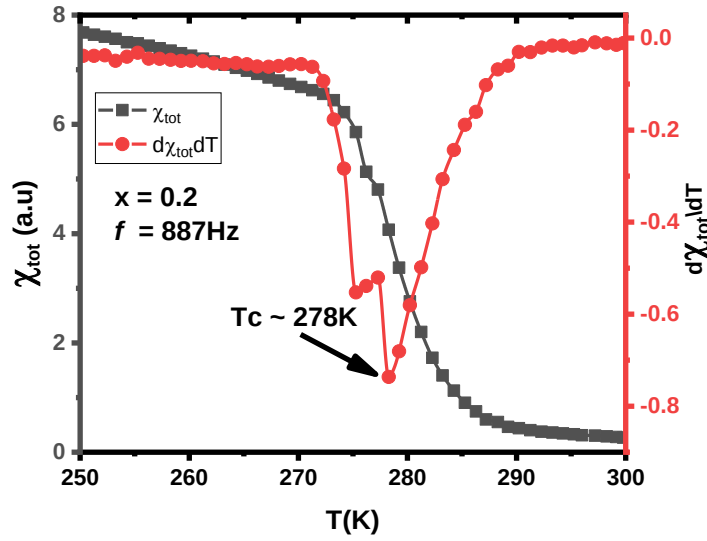


Figure 48: Temperature dependence of ac-susceptibility (black squares) and its derivative (red circles) of the $\text{CrTe}_{0.8}\text{Sb}_{0.2}$ sample.

The MAP for $\text{CrTe}_{1-x}\text{Sb}_x$ (with $x=0.2$) is illustrated in figure 49. The figure reveals that all models yield quasi-straight lines in the high field region, however, the lines in tri-critical mean field model (Figure 49 (d) are not parallel. This indicates that this model is not convenient for the analysis. To identify which model is the best, the relative slopes (RS) are plotted in Fig. 50 where T_c is obtained from Fig. 48. For more details about the relative slope method, see chapter 6.

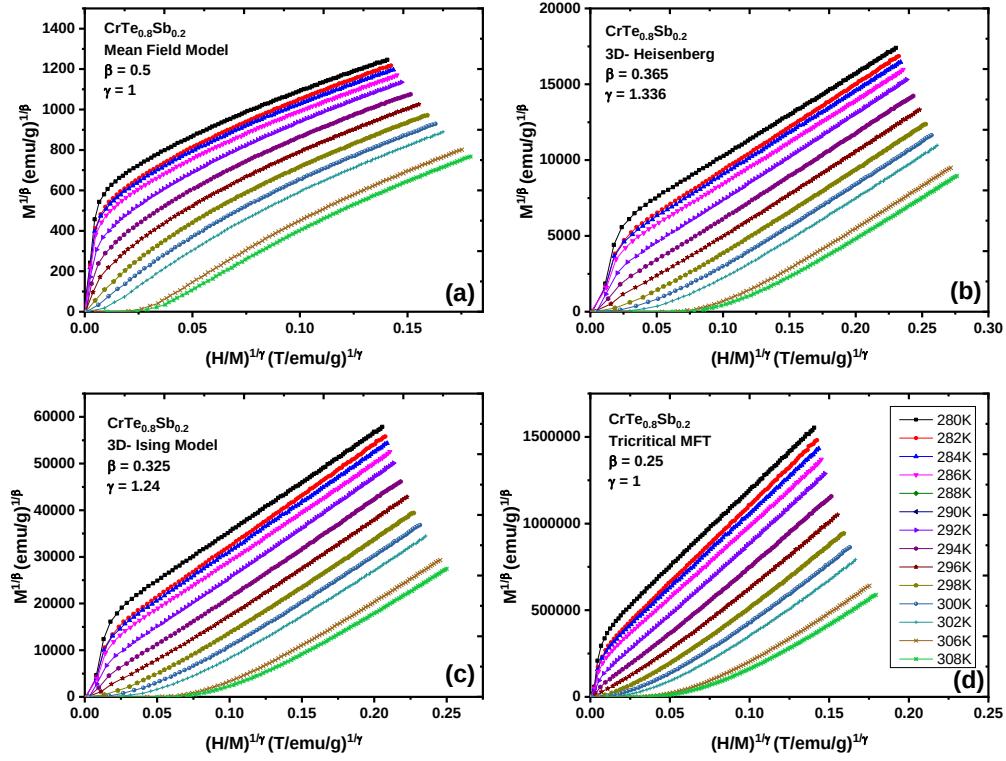


Figure 49: The MAP of the $\text{CrTe}_{0.8}\text{Sb}_{0.2}$ sample; (a) Mean field model, (b) 3D-Heisenberg model, (c) 3D-Ising model, and (d) Tricritical mean field model.

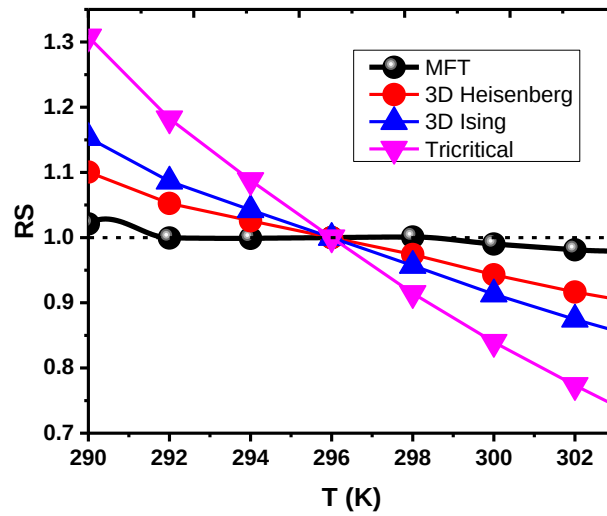


Figure 50: Temperature dependence of the relative slope of $\text{CrTe}_{0.8}\text{Sb}_{0.2}$ sample.

For this sample ($\text{CrTe}_{0.8}\text{Sb}_{0.2}$), Fig. 50 shows that the RS of the mean field model is the nearest to $\text{RS} = 1$ in both regions, above and below T_c . Indicating that the mean field theory describes well the ferromagnetic phase of the sample despite the fact that the magnetization isotherms in MAP (Fig. 49 a) are concave downwards to relatively high fields. The temperature dependence of both, spontaneous magnetization and the inverse of the initial susceptibility of $\text{CrTe}_{0.8}\text{Sb}_{0.2}$ are shown in Fig. 51. The obtained critical temperature from the spontaneous magnetization ($T_c \sim 300.85\text{K}$) is consistent with the critical temperature that is obtained from the inverse of the initial susceptibility ($T_c \sim 300.58\text{K}$) for the $\text{CrTe}_{0.8}\text{Sb}_{0.2}$. This temperature is higher than what we get from the ac-susceptibility ($T_c \sim 286$). This clearly reflects the findings that transition temperature (T_c) obtained from Curie law behavior is commonly higher than T_c obtained from the inflection point of the susceptibility. Moreover, the value of $\gamma = 1.01$ is in a good agreement with mean field theory, while the value of $\beta = 0.79$ is a little higher than the corresponding values expected from mean field theory. The value of the third critical exponent $\delta = 2.28$ is also obtained from Widom's theory (see Eq.1.10).

To obtain better values of both β and γ , we have re-analyzed the $M_s(T)$ and $\chi_0^{-1}(T)$ data using Kouvel–Fisher (KF) plot (see Chapter 6). Figure 52 portrays the KF plots for both $M_s(T)$ and $\chi_0^{-1}(T)$ as functions of temperature. This method (KF) confirms the value of critical temperature ($T_c \sim 300\text{K}$) that obtained from the MAP. However, the value of $\beta = 0.52 \pm 0.03$ is very close to the mean field model while $\gamma = 0.83 \pm 0.03$ deviate slightly from the mean field model. As a result, the value of $\delta = 2.6$ pushed toward the mean field model (see Table 1 in Chapter 1).

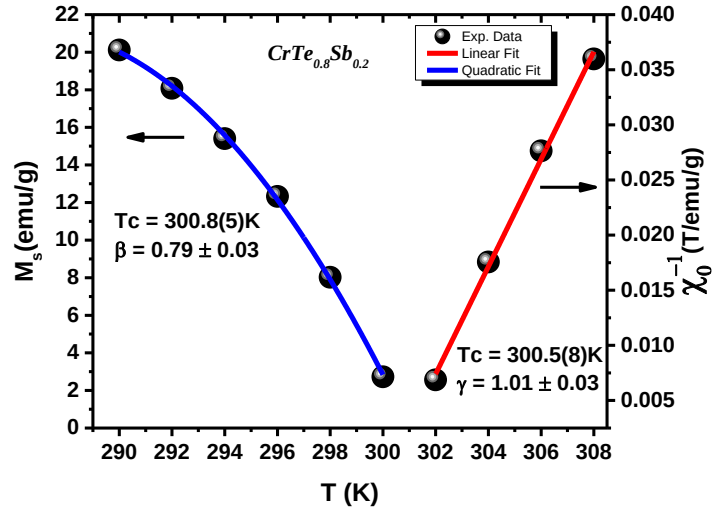


Figure 51: Temperature dependence of the spontaneous magnetization (to the left), and the inverse of the initial susceptibility (to the right) for $\text{CrTe}_{0.8}\text{Sb}_{0.2}$ polycrystalline.

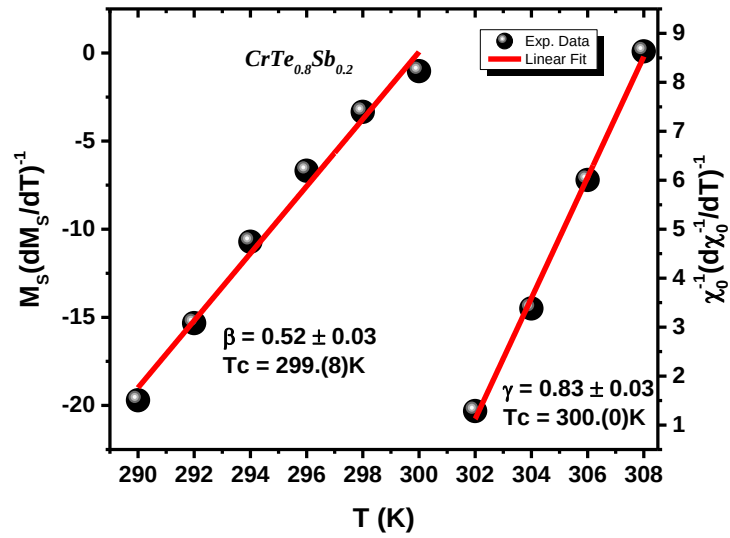


Figure 52: Kouvel-Fisher plot for $\text{CrTe}_{0.8}\text{Sb}_{0.2}$ polycrystalline.

We further tested the obtained critical exponents according to the prediction of the scaling hypothesis. In the critical asymptotic region, the magnetic equation can be written according to Eq. 6.8. Following this equation, the m vs. h has been plotted in a log-log scale in figure 53. All data collapsed into two separated curves; one above T_c and another below T_c , confirming that the obtained values of the critical exponents and critical temperatures are reliable and consistent with the scaling hypothesis.

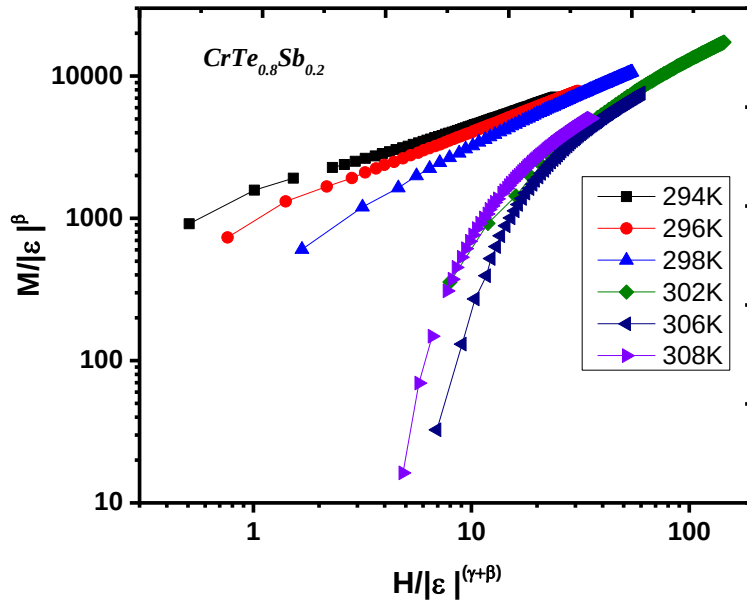


Figure 53: Scaling plots indicating two universal curves below and above T_c for $\text{CrTe}_{0.8}\text{Sb}_{0.2}$ polycrystalline.

To evaluate the experimental value of the critical exponent δ , we analyze the critical isotherm $M(H)$ at the transition temperature $T_c=300\text{K}$, and by using Eq. 6.3. The inverse of the slope in log-log scale gives this experimental value of δ (see Fig. 54). The experimental value of $\delta = 3.22$ is obtained. Clearly, the determined values of δ from MAP

($\delta = 2.28$) and KF plot ($\delta = 2.60$) are deviated from the critical isotherm analysis. This deviation indicates that the critical behavior of $\text{CrTe}_{0.8}\text{Sb}_{0.2}$ does not belong to a single universality class because of possible complex competition of different magnetic interactions [57]. Similar behavior has been found in CrSbSe_3 and CrXTe_3 single crystals [62]. Moreover, the log-log plot of the critical isotherm shows deviation from straight line. This may indicate that at $T \sim 300\text{K}$, there may be still some magnetic ordering, and the sample may not be completely in the paramagnetic state. In linear fit to the critical isotherm does not pass zero at $H=0$, indicating there is small remnant value of spontaneous magnetization.

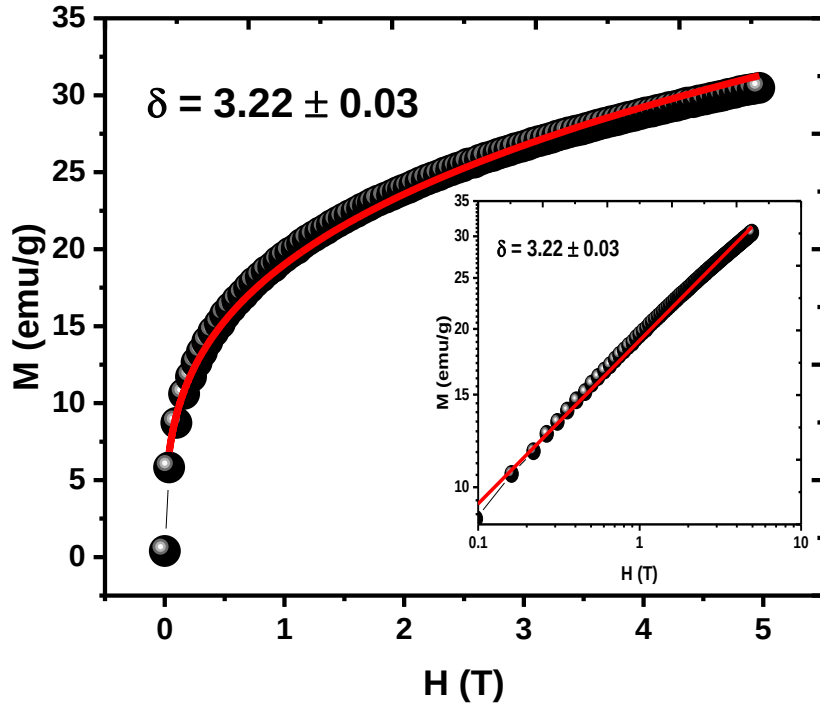


Figure 54: Isotherm M vs H plot collected at $T_c = 300\text{ K}$ for $\text{CrTe}_{0.8}\text{Sb}_{0.2}$ polycrystalline. Inset: the same plot in log-log scale with a solid fitting curve.

For further investigation; we study the critical behavior near FM-PM phase transition for higher Sb concentrations. Here we report only the Kouvel-Fisher analysis, as it provides the most reliable critical exponents and critical temperature amongst other methods, as discussed earlier. Figure 55 through 57 show the Kouvel-Fisher plots for $\text{CrTe}_{1-x}\text{Sb}_x$ ($x=0.3, 0.4$, and 0.5) respectively. In Figure 55, and upon increasing the Sb concentration from 0.2 to 0.3 , the value of $\beta = 0.54$ remains in the long-range order indicating that the mean field model best describes the ferromagnetic state. The $\gamma = 1.24$ value expected from the mean field model. The value is close to that of the short-range Ising like behavior. When the fraction of the Sb increased to $x=0.4$, both $\beta=0.38$, and $\gamma=1.36$, the magnetic state exhibits a Heisenberg-like behavior. Finally, when the Sb concentration reaches $x=0.5$, the sample behave like a long-range two dimensional material in the region below the critical temperature where $\beta = 0.28$, but it behaves like mean field theory above the critical temperature with $\gamma =0.91$ (Figure 57). The summary of these figures is depicted in Table 17. It is worth mentioning that the obtained critical temperature T_c from to the spontaneous magnetization is underestimated while it is overestimated when it calculated from the inverse of the initial susceptibility.

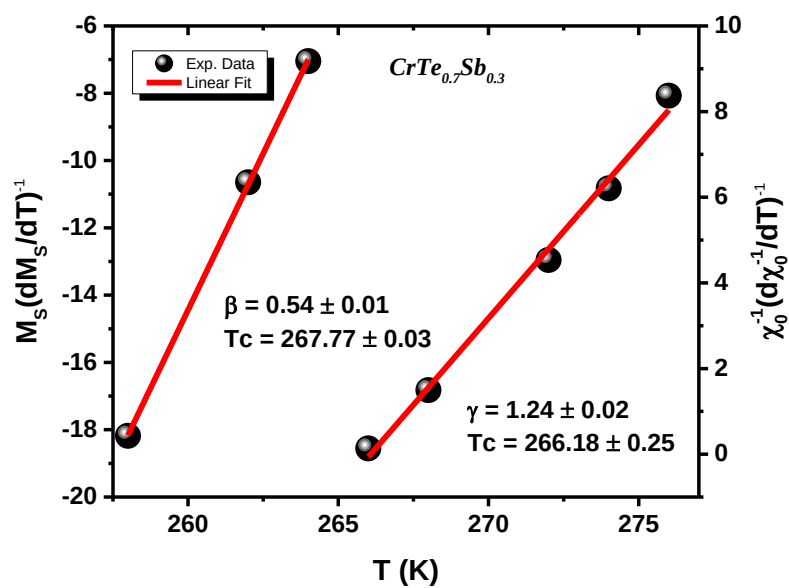


Figure 55: Kouvel-Fisher plot for CrTe_{0.7}Sb_{0.3} polycrystalline.

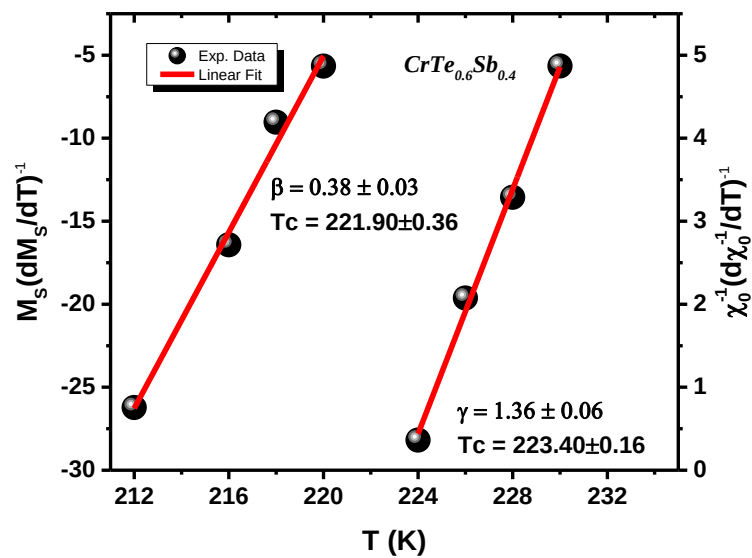


Figure 56: Kouvel-Fisher plot for CrTe_{0.6}Sb_{0.4} polycrystalline.

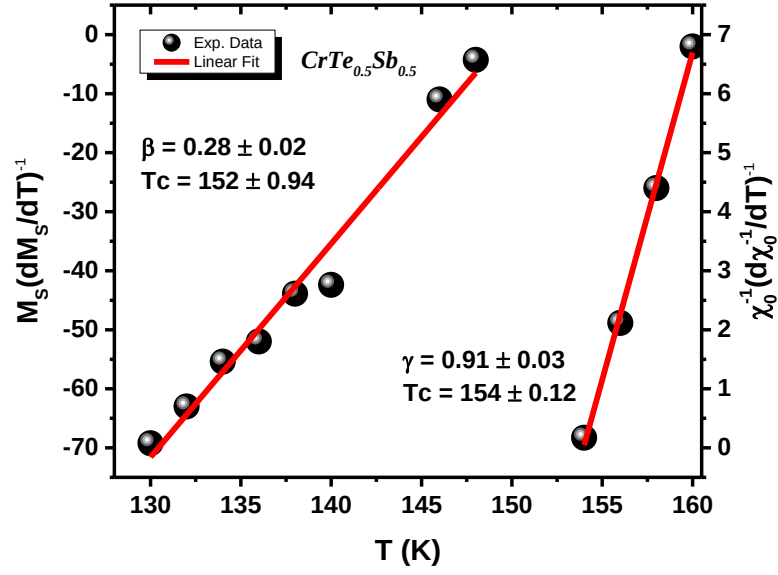


Figure 57: Kouvel-Fisher plot for $\text{CrTe}_{0.5}\text{Sb}_{0.5}$ polycrystalline.

Table 17: Critical exponents of $\text{CrTe}_{1-x}\text{Sb}_x$ samples from Kouvel-Fisher.

<i>Sb concentration (x)</i>	<i>T_c from $\chi_{ac}(K)$</i>	<i>T_c from KF(K)</i>	β	γ	δ
0.2	~278	~300	0.52±0.03	0.83±0.03	2.6
0.3	~258	~267	0.54±0.01	1.24±0.02	3.3
0.4	~221	~ 222	0.38±0.03	1.36±0.06	4.6
0.5	~150	~ 153	0.28±0.02	0.91±0.03	4.25

CONCLUSION

In this thesis, we investigated the critical magnetic behavior, magnetocaloric and structural properties of two set of samples: $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ perovskite ceramics, and quasi one/two dimensional transition metal based chalcogenide $\text{CrTe}_{1-x}\text{Sb}_x$. These materials are important for their potential usage in magnetic cooling systems. The MCE of the ceramics show that maximum cooling power occurs close to the curie temperatures consistent with T_c measurements obtained from the ac-susceptibility. The highest relative cooling power RCP is about 900J/kg that extends over a wide temperature range ($\Delta T \sim 200\text{K}$) which occur for $x=0.10$ sample at $T_c \sim 195\text{K}$, comparing to the prototype material for magnetic refrigeration, the “expensive” elemental gadolinium, which has RCP $\sim 410\text{J/kg}$ at $T_c \sim 300\text{K}$. These results indicate that this set of samples can be promising candidate in near room temperature refrigeration applications. Moreover, cooling range ($\Delta T \sim 200\text{K}$) can be extended by using composite ceramic materials with different Ni-concentrations.

The MCE of the $\text{CrTe}_{1-x}\text{Sb}_x$ alloys, on the other hand, did not show any enhancement of the cooling power near Curie temperature. The elemental substitutions in all samples lead to decrease in the Curie temperature, indicating that the ferromagnetic coupling is weakened by Sb substitutions, while the super exchange antiferromagnetic interaction was reinforced.

Critical exponents analyses based on modified Arrott plots, relative slope and Kouvel–Fisher methods have been used to investigate the FM-PM phase transition near the Curie temperature. The results revealed that the Nd-based ceramic samples with ($x = 0.00$) is

consistent with a 3D-Heisenberg-like ferromagnetic. Upon Ni substitutions, the ceramic samples follow the mean field model.

The critical behavior for all $\text{CrTe}_{1-x}\text{Sb}_x$ samples was also investigated. Modified Arrott plots and Kouvel–Fisher methods were used to refine the critical exponents β , γ , and δ values, and the Curie temperature. The reliability of the obtained critical exponent (β , γ , and δ) values was confirmed by the universal scaling hypothesis. In $\text{CrTe}_{1-x}\text{Sb}_x$ polycrystalline, the critical behavior analysis showed that the material does not belong to a single universality class behavior and possibly indicating a complex competition of different magnetic interactions, indicating that this quasi one/two dimensional system needs more investigation in the full-range of temperature.

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