Chapter - 5
Chapter 5

5. Effect of Co Doping on Structural, Transport, Magnetic, Magnetocaloric Properties and Critical analysis of Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga (x=0, 0.04, 0.12, 0.2) Heusler alloys under ambient pressure

5.1 Introduction

The family of Ni-Mn based Heusler alloys affords an extensive playground of interesting physical properties. The novel properties of Ni-Mn-Ga alloys have attracted a lot of attention in magneto-strain owing to their prospective applications in sensors and actuators [1-2]. The source of phase transformations [3] is displayed in Heusler alloys by indirect exchange interaction between magnetic ions which possesses ferromagnetism, reversibility, thermo elasticity resulting in SME [4-6], MR [7-10] and MCE [11-16].

The transformation temperatures are very significant to determine property selection of operating temperature which is sensitive to the composition and substitution elements [4, 6, 17-19]. In the recent decade, the effect of compositional changes in Ni-Mn-Ga alloys by doping different elements have been studied intensively by experiment and theory [20-25]. Doping of magnetic elements in Heusler alloys exhibits trivial changes in physical properties. Curie and martensitic transitions (T$_C$ and T$_M$) are altered by replacing various elements in X site of Ni-Mn-X (X= Al, Ga, In, Sn and Sb) system [26], T$_C$ can be controlled by substitution of Co at Ni site of Ni$_{53.25-x}$Co$_x$Mn$_{21}$Ga$_{25}$ (x=0.75, 1.5, 2.25) alloys [27].

We discuss about doping of magnetic elements at different sites of Ni-Mn-Ga system as follows. Doping of Co element in Ni site affects the critical temperatures and exchange interactions of martensite and austenite phases in Ni$_{50}$Mn$_{30}$Ga$_{20}$ alloy [28]. Fe doping at Mn site of Ni$_{48.7}$Mn$_{28.1}$Fe$_2$Ga$_{21.2}$ improves the magnetostriction and fracture toughness without modify its magnetic and thermo elastic properties [29, 30]. In Ni-Mn-Ga system, doping of magnetic elements at Ni sites which gives more interesting phenomenon than other sites.
Inter-martensitic transformation is absent by substituting Co at Ni site of Ni_{46.9}Co_{3.3}Mn_{28.8}Ga_{21} system due to local spins inversion of Co [31]. The structural stability and alteration of transformation temperatures (T_M and T_C) causes the change in electron density at the Fermi level by interchanging of Co at Ni site of Ni_{2.16-x}Co_{x}Mn_{0.84}Ga (x=0.03-0.09) system [32]. From the Ni_{50-x}Co_{x}Mn_{50-y}Ga_{y} (7\leq x\leq13, 18\leq y\leq20) system Yu et al [33] reports that partial substitution of Co for Ni atoms tuned the magnetic ordering of the parent phase from AFM to FM which decreases the T_M and increases T_C respectively, Meta magnetic transformations are observed near T_M. The phase diagram of T_M and T_C for the Ni_{2.19-x}Fe_{x}Mn_{0.81}Ga (x=0-0.04) system reveals that T_M decreases gradually whereas T_C increase with Fe concentration Sokolovskiy et al [34]. Soto-parra et al [21] clearly pointed out the e/a variation of T_M and T_C with Co content at Ni site of Ni_{50.8}Mn_{24.4}Ga_{24.4}Co_{x} (x=0-5.2) and Fe doped at Ni site of Ni_{52.7-x}Mn_{21.9}Ga_{25.4}Fe_{x} (x=0-5.3). The doping of both Co and Fe in these system reveals that T_M decreases gently whereas T_C increases with e/a. The magnetic field induced reverse phase transformations from AFM (PM) martensite to FM austenite phase (T_C) is appeared near room temperature in Ni_{45}Co_{5}Mn_{36.7}In_{13.3} single crystal [4]. Either in austenite phase cooling (or) martensitic phase heating, a steep increase (decrease) of thermal expansion is observed in Ni_{41}Co_{9}Mn_{31.5}Ga_{18.5} polycrystalline FSMA alloy due to martensitic (reverse martensitic) transition [35].

On the other hand, Co replacing at Mn site of Ni_{47}Mn_{31}X_{1}Ga_{21} (X=Co, Fe) has strong effect on T_C (increases) and T_M (decreases), while for substitution of Fe at Mn site shows opposite effect in the same system [36]. The inter-martensitic transformation is observed in Ni_{49.8}Mn_{27.2}Ga_{21.1}Co_{1.8} system due to spins inversion by Co [31]. The change in transformations temperatures (T_M and T_C) causes the change in electron density at the Fermi level by interchanging of Mn site of Ni_{2.16}Mn_{0.84-y}Co_{y}Ga (y= 0.04-0.14) system [32].

When the Co is doped in Ga site of (Ni_{50.26}Mn_{27.30}Ga_{22.44})_{100-x}Co_{x} (x= 0-6), the phase transformation temperatures and crystal structures of martensitic phase is altered which reveals Curie temperature of the martensitic phase is lower than that of the austenitic phase [37].
From the structural measurements, Satish Kumar et al [31] observed that Co doped in Ni site of Ni$_{46.9}$Mn$_{28.8}$Ga$_{21}$Co$_{3.3}$ system shows cubic austenite structure at RT and martensite at LT (230, 180 K), whereas in the Mn site doped Ni$_{49.8}$Mn$_{27.2}$Ga$_{21.2}$Co$_{1.8}$ system reveals an orthorhombic structure with 7 modulation, non-modulated tetragonal phase and 7M orthorhombic phase at 290 and 200 K respectively. When Fe replaces Ga in Ni$_{50}$Mn$_{27}$Ga$_{23-x}$Fe$_x$ (x=1, 2) a orthogonal structure is observed [36]. Cubic L2$_1$ structure exhibits, When Co doped in Ga and Mn site of Ni$_{48}$Mn$_{27}$Ga$_{25-x}$Co$_x$ (x=1-4) and Ni$_{48}$Mn$_{26-x}$Co$_x$Ga$_{26}$ (x=1-5) respectively Chen et al [38]. XRD patterns for the Ni$_{52.8}$Mn$_{20.1}$Ga$_{25}$Fe$_{2.3}$ [21] sample reveals martensite monoclinic 14 and 10 modulated structure at 145 and 270 K respectively. X-ray patterns depict for Ni$_{52.8}$Mn$_{30.1-x}$Fe$_x$Ga$_{21.2}$ (x=0-11) [39] that cubic parent and tetragonal martensite phase coexist in x=0, 2, whereas only the cubic parent phase exists for remaining x=5, 8, 11 alloys.

The clear visible of martensite transformations are identified from transport measurements Co doped in Ga and Mn site of Ni$_{48}$Mn$_{27}$Ga$_{25-x}$Co$_x$ (x=1-4) and Ni$_{48}$Mn$_{26-x}$Co$_x$Ga$_{26}$ (x=1-5) systems [38].

Some of the compositions variation of ($\Delta$SM) has been reported as follows, The melt spun ribbons of Ni$_{52}$Mn$_{26}$Ga$_{26}$ shows magneto-structural transition around 354 K with the increasing trend of MCE (-15 to -30.3 J kg$^{-1}$K$^{-1}$) for the 2 and 5 Tesla fields Li et al [40]. Rama Rao et al [41] reports that near RT-MCE (~309 K) for Ni$_{55}$Mn$_{20.6}$Ga$_{24.4}$ (-9.5 J kg$^{-1}$K$^{-1}$), Ni$_{55}$Mn$_{19.6}$Ga$_{25.4}$ (-10.4 J kg$^{-1}$K$^{-1}$) ribbons. The Ni$_{2.15}$Mn$_{0.85}$Ga and Ni$_{2.19}$Mn$_{0.81}$Ga alloys shows an increasing trend of MCE (-7.2 to -28 J kg$^{-1}$K$^{-1}$) Pareti et al [42].

Heusler alloys exhibit two different magnetic interactions such as PM - FM transition in the austenite, FM transition in martensite phase. Thus, complete FM transition can occur around austenite compared to martensite phase. On the other hand, FM transition may be discontinuous (or) continuous which can be classified by the hysteresis. i.e., the presence of hysteresis suggests the discontinuous (or) first order transition, otherwise continuous (or) second order transition (T$_C$) [43]. Critical exponents are analysed near T$_C$ in manganites [44] re-entrant metallic alloys like
Au$_{0.81}$Fe$_{0.19}$, Ni$_{0.78}$Mn$_{0.22}$, Ni$_{0.79}$Mn$_{0.21}$, amorphous Fe$_{0.98}$Zr$_{0.08}$ [45] and Heusler alloys Ni$_{50}$Mn$_{35}$In$_{14}$Si$_{1}$ [46], Mn$_4$FeGe$_{3-x}$Si$_x$ [47], Ni$_{50}$Mn$_{50-x}$Sn$_x$ (x=13,14) [48]. Hence, the same analysis has been carried out for all samples to find the mechanism of magnetic model theory. Co addition in NiMnGa alloys provides an opportunity to control the Curie temperature of transforming phases (FM-Austenite to PM-Martensite).

The purpose of this work is to reveal how the Co effectively improves structure, electron scattering, curie transition ($T_C$), MCE and critical exponent analysis. To date, to the best of our knowledge, no experimental study of the critical phenomena has been reported for the Co substitution of Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga (x=0-0.2) based system. Hence, we have investigated a critical exponent analysis in the vicinity of the FM-PM region. In our present reports, all samples exhibits second order phase transition which would be selected for critical behaviour analysis. This would be very much potential interest to find type of magnetic ordering which are confirmed the long range FM mean field model by calculating critical analysis. However, effect of Co doping increases the $\Delta S_M$, Curie and martensitic temperatures due to effective magnetic moment (Co) ions at Ni site of Ni-Mn-Ga system. The present samples show conventional MCE with maximum $\Delta S_M$ of -2.8 Jkg$^{-1}$K$^{-1}$ near $T_M$ region in x=0.12 sample. But, we can tailor to the higher MCE to reaching ambient applications by further increasing Co in our systems. Austenite structures are maintained by varying Co (0-0.2) substitution and lowering temperature (320-200 K) for x=0.04 sample. However, for x=0.12 reveals martensite phase Metallic behaviour decrease with increasing of Co in present samples.

5.2 Experimental techniques

Ingots of Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga (x=0, 0.04, 0.12 and 0.2) alloys are prepared by melting the high purity starting elements (99.9% pure) via utilizing vacuum arc melting furnace under partial Argon atmosphere. The samples are re-melted four times to ensure homogeneity. These alloys are sealed and annealed under high vacuum at 1175 K for 24 hrs and then quenched with Ar gas. Elemental compositions of these alloys are determined using SEM (Leo 440i) attached with an X-ray energy dispersive spectroscope (EDS) setup and are found to be close to the nominal composition. The structural analysis at room temperature (RT) is carried out using a Philips 3121 XRD with Cu-K$\alpha$ radiation. The low temperature structural analysis is taken using the RINT
2500 system Rigaku Co. An X-ray beam is generated by a rotating Cu anode. At several temperatures, entire profiles of reflection peaks were measured at a step size of 0.01° and a step-counting time of 6s. For some reflection planes, the X-ray diffraction measurement at a step size of 0.005° and a step-counting time of 60 seconds is performed to accumulate more counts at certain temperatures. The transport studies are carried out from 300-4 K using CCR-VTI. The magnetization measurements are performed by means of PPMS-9T using vibrating sample magnetometer (VSM) module (Quantum Design, USA). The data are collected for all samples during field cooling and warming modes, the isothermal magnetization data are measured at different temperatures around $T_C$ and $T_M$ regions.

5.3 Results and discussions

5.3.1 Structural measurements

5.3.1.1 Powder XRD analysis at room and low temperatures

The powder XRD pattern recorded at RT in Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga ($x=0$, 0.04, 0.12 and 0.2) on well grained powdered are shown in figure.5.1 (a). The Bragg peaks for all samples can be indexed with cubic cell L2$_1$ structure with lattice parameter $a=5.8729$, 5.8691, 5.8637 and 5.8618 Å for $x=0$, 0.04, 0.12 and 0.2 samples respectively. The $x=0.12$ sample has also retained amount of martensite phase, which might be due to the residual strains generated via grinding the ingot into powder [49-50].

![XRD pattern](image)

**Figure. 5.1** (a) XRD pattern of Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga ($x=0$, 0.04, 0.12 and 0.2) alloys at room temperature. (b) XRD pattern of Ni$_{2.06}$Co$_{0.04}$Mn$_{0.9}$Ga alloy at different temperatures.
In order to investigate the possible crystal structural variations at different temperatures, we select $x=0.04$ for low temperature X-ray measurements [figure. 5.1(b)]. It is taken at various temperatures such as 320, 300, 280, 260 and 200 K. The corresponding cell parameters are 5.8694, 5.8638, 5.8619, 5.8624 and 5.8607 Å. Therefore, it is found that austenite phase is maintained upto 200 K with small variation of lattice parameter with temperature.

5.3.2 Electrical resistivity measurements

5.3.2.1 Temperature variation of resistivity

Figure 5.2 (a) shows that temperature dependent resistivity $\rho(T)$ curves for $\text{Ni}_{2.1-x}\text{Co}_x\text{Mn}_{0.9}\text{Ga}$ ($x=0-0.2$) alloys. The change in slope of the resistivity curves are due to change in electron scattering on magnetic ion fluctuations which are similar to the $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ ($x=0-0.2$) [6]. The small hump of resistivity which is observed around 147 and 165 K for $x=0.12$ and 0.2 is the clear indication of martensite transitions ($T_m$). Hence, excess Co induces the FM phase transformation in these alloys. The slope of $\rho(T)$ curves increases with Co concentrations.

5.3.2.2 Composition variation on residual resistivity and electron scattering factor

The $\rho_0$ and $A$ are obtained by fitting the simple electrical resistivity equation,

$$\rho = \rho_0 + (AT^2)$$

in the low temperature region of 4-200 K for all samples and the fitted plot is shown in the Figure. 2(b). The $\rho_0$ occurs in the present alloys is due to the impurities (or) defects and (A) is the electron scattering factor. The pressure variant (A) is reported in $\text{Ni}_{2-x}\text{Mn}_{1+x}\text{Ga}$ ($x=0, 0.15$) alloys [51] which indicates that electron-electron scattering occurs at low temperature. The residual resistivity and electron-electron scattering factor are linearly increases with Co atoms due to excess of Co magnetic ion impurity which are indicated in figure.2 (b).
5.4 Magnetic measurements

5.4.1 Temperature and magnetic field dependence of magnetization

The temperature dependent magnetizations $M(T)$ are measured in the range of 320-10 K during (FC) and field warming (FW) modes for Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga ($x=0$, 0.04, 0.12 and 0.2) alloys at a constant magnetic field of $\mu_0H=0.01$ T are shown in the figure 5.3 (a-d). During cooling cycle, an abrupt change in magnetization appears from the paramagnetic (PM) to ferromagnetic (FM) phase, which indicates Curie transitions ($T_C$) at 273, 275, 284 and 309 K for $x=0$, 0.04, 0.12 and 0.2 samples respectively. The exact $T_C$ point is derived from the minima of the $dM/dT$ vs $T$ curves (not shown here). Moreover, addition of Co brings $T_C^A$ to higher values (273-310 K) due to enhanced FM in austenite phase. Below $T_C$, magnetization with temperature is almost constant for $x=0$ and 0.04 samples during cooling. On the other hand, magnetizations are stable upto the first order magneto structural transition (martensite) which appears at 147 and 164 K for $x=0.12$ and 0.2 alloy respectively. The characteristic transformation temperatures of martensite transition ($M_s$, $M_f$, $A_s$ and $A_f$) are indicated around the hysteresis region. We found that $T_C^A$ increases with the effect of Co doping in Ni site. The opposite effect is appeared in some Mn rich Ni-Mn-Ga alloys Fabbrici et al [52] which affects differently the magnetic interactions of the two phases, strengthening the ferromagnetic FM interactions in austenite while weakening the ferromagnetic behaviour of
martensite. Adding Co gives rise to strengthening of magnetic exchange coupling between Mn-Mn atoms which are responsible for modifying structural transition temperatures [33].

**Figure. 5.3** (a-d) Temperature dependent Magnetization Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga ($x=0$, 0.04, 0.12 and 0.2) alloys at 0.01 T field.

Figure.5.4 (a-d) shows the field dependent magnetization [isothermal - M(H)] curves measured near $T_C$ region at 5 K interval for $x=0$, 0.04, 0.12 and 10 K interval for $x=0.2$ alloys respectively. The magnetization processes are taken at two steps: field up (0-5 T) and field down (5-0 T). All samples show typical ferromagnetic (FM) behaviour below $T_C^A$ whereas paramagnetic (PM) behaviour above $T_C^A$. 
The M (H) is measured near $T_M$ region between 110-170 K and 110-180 K at 10 K interval for $x=0.12$ and 0.2 samples, magnetization decreases with increasing temperatures which are shown in figure.5.5 (a-b). The crossover magnetization observed near 147 and 165 K for these two samples. The magnetization is hard to saturate (martensite phase) below 147 K ($x=0.12$) and 165 K ($x=0.2$) whereas, it is easily saturates above these temperatures (austenite phase). It reveals that near $T_M$ FM-M changes into FM-A phase.
5.4.2 Magneto caloric properties

From isothermal magnetization curves, the $\Delta S_M$ is calculated for $x=0.12$ and 0.2 samples using Maxwell relation

$$\Delta S_M = \int_0^H \left( \frac{\partial M(H,T)}{\partial T} \right) dH$$

(5.2)

The temperature dependence of magneto entropy change [$\Delta S_M(T)$] at different magnetic fields ($\Delta \mu_0 H$) of 1, 3 and 5 T for Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga ($x=0.12$ and 0.2) alloys are shown in figure. 5.6 (a-b). The applied magnetic field increases the magnetic entropy change and the values are negative which corresponds to normal MCE. Around $T_M$ region, which shows maximum $\Delta S_M$ values are -2.8 and -1.75 Jkg$^{-1}$K$^{-1}$ of 5 T for $x=0.12$ and 0.2 alloys respectively. The comparison of MCE with other alloys as follows: -4.1Jkg$^{-1}$K$^{-1}$ for Ni$_{51.5}$Mn$_{22.7}$Ga$_{25.8}$ at 196 K at 0.9 T [11], Ni$_{49.5}$Mn$_{25.4}$Ga$_{25.1}$ has -11 Jkg$^{-1}$K$^{-1}$ around 177 K at H= 2 T [12].
Figure 5.6 Temperature dependent magnetic entropy of near $T_M$ of $\text{Ni}_{2.1-x}\text{Co}_x\text{Mn}_{0.9}\text{Ga}$ ($x=0.12$ and 0.2) alloys.

$T_C$ and $T_M$ variation of magnetic elements (Co, Fe) doped in Ni-Mn-Ga compounds are presented in Figure 5.7 (a-b). In our present series Co doped at Ni site of $\text{Ni}_{2.1-x}\text{Co}_x\text{Mn}_{0.9}\text{Ga}$ ($x=0-0.2$), both $T_M$ (147-165 K) and $T_C$ (273-309 K) are increased due to local atomic disorder of magnetic elements. Whereas, Khovailo et al [27] reports that $T_M$ (318-306 K) decreases and $T_C$ (348-367 K) increases in $\text{Ni}_{2.16-x}\text{Co}_x\text{Mn}_{0.84}\text{Ga}$ ($x=0.03-0.09$) system. From the $\text{Ni}_{2.2-x}\text{Fe}_x\text{Mn}_{0.8}\text{Ga}$ ($x=0.04-0.16$) $T_M$ (317-223 K) decreases and $T_C$ (347-395 K) increases, another system from $\text{Ni}_{2.19-x}\text{Fe}_x\text{Mn}_{0.81}\text{Ga}$ ($x=0-0.04$) reveals that $T_M$ (340-285 K) decreases and $T_C$ slightly (340-345 K) increases [34].

Generally, $e/a$ values are decreased while doping magnetic elements at Ni site of the NiMnGa systems. The $e/a$ variation of doped (Co, Fe) magnetic elements at Ni site of Ni-Mn-Ga and our system are shown in Figure 5.8 (a-c). Soto–parra et al [21] reported that doping of Co in Ni site of $\text{Ni}_{2.03}\text{Co}_x\text{Mn}_{0.9}\text{Ga}_{0.97}$ ($x=0-0.2$) and Fe in $\text{Ni}_{2.108-x}\text{Fe}_x\text{Mn}_{0.87}\text{Ga}$ ($x=0-0.21$) reveals that $T_M$ increases and $T_C$ decreases with $e/a$. whereas in our selected compounds, $e/a$ decreases with increasing Co ions. Both, $T_M$ and $T_C$ are decreases with $e/a$ value due to local spin inversion of Co atoms [31]. Hence, doping of magnetic elements and changing $e/a$ value are constructing gradual changes near magneto-structural transitions in Heusler alloys.
5.5 Critical exponent behavior of Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga (x=0-0.2) alloys

The order of FM transition was first proposed in 1964 by Banerjee et al [53]. It can be identified from the slopes of the Arrott plot [$M^2$ vs $H/M$] Arrott et al [54]. The negative and positive slope corresponds to first and second order transition respectively. Figure 5.9 (a-d) shows the Arrott plots around austenite phase (T$_C$) for x=0, 0.04, 0.12 and 0.2 alloys respectively and the positive slopes are observed in all the curves at T$_C$ and confirm that all samples exhibit second order FM transition at...
austenite phase. Further, it is found that all the curves are perfectly linear with respect to magnetic field and suggesting the mean-field theory for this second order transition Fan et al [55]. Hence, we focus the detailed critical analysis for the second order transition to understand the type of interaction present in these materials.

![Arrott plots](image_url)

**Figure 5.9** (a-d) Arrott plots of Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga ($x=0, 0.04, 0.12, 0.2$) alloys.

The second order FM transition near the Curie points are characterized by a set of critical exponents’ $\beta$ (associated with the spontaneous magnetization $M_s$), $\gamma$ (associated with the initial susceptibility $\chi_0$), and $\delta$ (associated with the critical magnetization isotherm at $T_C$). The mathematical definitions of the critical exponents from magnetization measurements are given as following relation:
\[ M_s(0,T = M_0(\varepsilon)^\beta \quad \varepsilon < 0, T < T_C \quad (5.3) \]

\[ \chi_0^{-1}(0,T) = (h_0 / M_0)(\varepsilon)^\gamma \quad \varepsilon > 0, T > T_C \quad (5.4) \]

\[ M(H,T_c) = D(H)^{1/\delta} \quad \varepsilon = 0, T = T_C \quad (5.5) \]

Where, \( M_0, h_0/M_0 \) and \( D \) are the critical amplitudes. \( M_s, \chi_0^{-1} \) and \( \varepsilon = (T - T_C^A)/T_C^A \) are the spontaneous magnetization, initial inverse susceptibility and reduced temperature respectively, these can be calculated from figure. 5.10 (a-d) and 5.11 (a-d) as follows: the temperature at which the curve passes through the origin is \( T_C^A \). The polynomial fitting of each curve and linear extrapolation above \( T_C^A \) yields \( M_s \) whereas below \( T_C^A \) yields \( \chi_0^{-1} \). The temperature dependence of \( M_s \) and \( \chi_0^{-1} \) of x=0, 0.04, 0.12 and 0.2 alloys are shown in figure 5.10 (a-d).

**Figure. 5.10** (a-d) Temperature dependence of spontaneous magnetization (\( M_s \)) and inverse initial susceptibility (\( \chi_0^{-1} \)) of \( \text{Ni}_{2.1-x}\text{Co}_x\text{Mn}_{0.9}\text{Ga} \) (x= 0, 0.04, 0.12, 0.2) alloys.
Kouvel–Fisher method is used for the efficient and accurate determination of $T_C$ and the critical exponents $\beta$, $\gamma$ and $\delta$ Kouvel et al [56]. The equations (5.3), (5.4) and (5.5) are modified as per Kouvel–Fisher method as

$$\frac{M_S(T)}{dM_S(T)/dT} = \frac{T - T_C}{\beta}$$

(5.6)

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

(5.7)

$$\log M(H,T_C) = \frac{\log H}{\delta}$$

(5.8)

**Figure 5.11** (a-d) Kouvel-Fisher plots of $M_S(dM_S/dT)^{-1}$ and $\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}$ vs $T$ of Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga ($x=0, 0.04, 0.12, 0.2$) alloys.
According to equations (5.6) and (5.7), $M_S (dM_S/dT)^{-1}$ vs $T$ and $\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}$ vs $T$ should be a straight line with slopes $1/\beta$ and $1/\gamma$, and should meet $T$ axis corresponds to the $T_C^A$. Figure 5.12 shows the Kouvel-Fisher plots [$M_S (dM_S/dT)^{-1}$ vs $T$ and $\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}$ vs $T$] for $x=0$, 0.04, 0.12 and 0.2 samples respectively. The $T_C^A$ for $x=0$, 0.04, 0.12 and 0.2 samples obtained from these methods are 273, 275, 284 and 309 K respectively, which agrees with $T_C^A$ derived from $M(T)$ plots. The values of $\beta$ and $\gamma$ for $x=0$, 0.04, 0.12 and 0.2 samples are calculated from the reciprocal of slopes from $M_S (dM_S/dT)^{-1}$ vs $T$ and $\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}$ vs $T$ plots respectively. The $\beta$ values are 0.66725, 0.5772, 0.67522 and 0.66925 for $x=0$, 0.04, 0.12 and 0.2 samples respectively. The $\gamma$ values are 1.5029, 1.3172, 0.97403 and 1.38375 for $x=0$, 0.04, 0.12 and 0.2 samples, these values are tabulated in Table 5.1.

![Figure 5.12](image_url) (a-d) $\ln(M)$ vs $\ln(H)$ plot of Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga ($x=0$, 0.04, 0.12, 0.2) alloys.
The critical exponent $\delta$ which is associated with the critical magnetization isotherm at $T_c^A$ is determined using equation (5.8). The figure 12 (a-d) shows the $\ln M$ vs $\ln H$ plots at $T_c^A$ of $x=0$, 0.04, 0.12 and 0.2 samples. Based on the equation (5.8), the linear fit of each plot yields the value of $1/\delta$. The $\delta$ values are 3.02745, 3.25870, 2.558 and 2.859185 for $x=0$, 0.04, 0.12 and 0.2 samples respectively. The reliability of the calculated values with Widom scaling relation $\gamma - \beta(\delta - 1) = 0$, the obtained values are 0.1, 0.01, -0.07 and 0.13 for $x=0$, 0.04, 0.12 and 0.2 samples respectively. Our critical exponents values are nearly match the values of mean field theory ($\beta=0.5$, $\gamma=1.0$, $\delta=3.0$). This confirms that all the samples exhibit long range FM ordering.

**Table 5.1** Critical exponents values of Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga ($x=0$, 0.04, 0.12, 0.2) alloys.

<table>
<thead>
<tr>
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<th>$T_c$ (K)</th>
<th>Critical exponents</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$\beta$</td>
</tr>
<tr>
<td>0</td>
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<td>273</td>
<td>0.66725</td>
</tr>
<tr>
<td>0.04</td>
<td>-</td>
<td>275</td>
<td>0.5772</td>
</tr>
<tr>
<td>0.12</td>
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<td>284</td>
<td>0.67522</td>
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<tr>
<td>0.2</td>
<td>164</td>
<td>309</td>
<td>0.66925</td>
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**5.6 Conclusion**

In summary, the partial substitution of Co in Ni site of Ni$_{2.1-x}$Co$_x$Mn$_{0.9}$Ga ($x=0$, 0.04, 0.12 and 0.2) alloys has been investigated through structural, transport, magnetic, magnetocaloric properties and critical exponents behaviour. The L2$_1$ cubic structure is confirmed by powder XRD at room temperature. Transport measurement reveals decreasing of metallic behaviour with Co ion and increasing of $\rho_0$ and (A). The
magnetization results exhibit that second order-(T_C) increases towards RT which are appeared in all samples and first order martensite-transitions (T_M) are observed around at 147, 164 K for x=0.12, 0.2 samples respectively. Around T_M FM-M changes into FM-A phase whereas near T_C FM-M to PM-A phase. The ΔS_M are calculated using Maxwell’s relation for x=0.12 and 0.2 samples. The ΔS_M^{\text{max}} is obtained -2.8 Jkg^{-1}K^{-1} for x=0.12 sample. The clear views of exact T_C are identified from the Arrott plots. The critical exponents are calculated using Kouvel–Fisher method and confirmed that all the samples obey long range FM mean field theory.
References


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