Chapter - 4
Chapter-4

4. Structural, transport, magnetic and thermal properties of Ni\textsubscript{2.2}Mn\textsubscript{0.72-x}V\textsubscript{x}Ga\textsubscript{1.08} (x=0, 0.04, 0.08, 0.12) under ambient and high pressure

4.1 Coupled magneto-structural transition in Ni-Mn-V-Ga magnetic shape memory Heusler alloys and its effect on the magnetocaloric and transport properties

4.1.1 Introduction

Heusler alloys are of current interest due to their potential applications in various fields such as magnetic refrigeration, magnetic actuation and spintronics devices [1-13]. The last couple of decades have seen an immense increase of interest in magnetic refrigeration which is based on MCE. The MCE is the temperature change of a magnetic material upon magnetization (or) demagnetization. Its discovery is attributed to Warburg [1] and is employed for achieving ultralow temperatures in research laboratories. This technology has grown significantly due to the large MCE observed near room temperature (RT) in magnetocaloric materials such as Gd-Si-Ge, Mn-Fe-P-Si, La-Fe-Si [2]. Of late, Ni-Mn based Heusler alloys emerged as alternatives for rare earth based magnetocaloric materials because of their large MCE and adiabatic temperature change, comparable to the rare-earth based materials [3-11].

The variations in the composition and/or partial doping at different elemental sites are expected to alter the transport and magnetic properties of these materials [12-14]. Hence, these lead to diverse concerning phenomena such as magnetic SME [15, 16] and MR [17-22]. Especially change in elemental ratio of Ni-Mn alloy series allows a complex multistage transformation in a broad composition range [23-28].

The Heusler and re-entrant metallic alloys may exhibit two different types of magnetic transitions such as a first order structural (martensite) transition, where alloys undergoes from high symmetry lower magnetic austenite phase (low magnetic moment) to a low symmetry martensite phase (high magnetic moment), and a second order transition from PM austenite to FM austenite phase upon cooling [29, 30]. The first
order transitions are generally identified by the presence of latent heat and the hysteresis during heating and cooling cycles.

A huge change in resistivity [31-36] and magnetic entropy change [8, 37-41] can be observed around martensite transition. i.e., the first order phase transition may show higher MCE than the second order phase transition. The tuning of transport and magnetic transition temperatures can be useful to achieve better functional properties. In this respect, the coupled magneto-structural transformations in Ni-Mn-Ga (In) have been studied [8, 42-45].

There are many research groups already reported on doping of different magnetic (Co, Fe and Cr) [46-55] and non-magnetic (B, In and V) [56-60] elements in varies sites of Ni-Mn-Ga Heusler alloys. The substitution of Co at Ni site stabilized austenite (A) phase and suppresses the martensite (M) phase [46-48]. On the other hand, Co at Mn site has a strong effect on A phase FM and weak AFM at M phase due to the influence of Co spin on the nearest Mn–Mn atoms [49, 50]. Co at Ga site of Ni$_{48}$Mn$_{27}$Ga$_{25-x}$Co$_x$ (x=1, 2, 3, 4) alloys enhances M-AFM phase with the existence of an additional first-order transition below their $T_M$ temperatures reported by Chen et al [51]. This effect can be attributed to the variation of intrinsic factors, i.e. decrease in the unit-cell volumes, increase in the electronic concentrations and density. The doping of Fe at Ni site of Ni$_{2.19-x}$Fe$_x$Mn$_{0.81}$Ga exhibits peculiar property such as merged magnetic and structural transitions with well-defined temperature hysteresis which is due to the first-order character in the samples with $x \leq 0.02$ [52]. Further, increase of the Fe content separates these transitions in such a way that $T_m$ is decreased whereas Curie temperature ($T_C$) is increased. The increase of the Fe content at Mn site of Ni$_{48.7}$Mn$_{30.1-x}$Fe$_x$Ga$_{21.2}$ (x=0, 2, 5, 8, 11) alloys results decreasing the degree of ordering so that both M and A transformation temperatures decrease [54]. Substitution of Cr at Ga site of Ni$_{56}$Mn$_{25-x}$Cr$_x$Ga$_{19}$ (x=0, 2, 4, 6) gradually decreases the $T_M$ due to the increase in unit-cell volumes and decrease in the electron concentration [55].

Similarly, doping of non-magnetic elements such as B, In and V in Ni-Mn-Ga are studied [56-60] and discussed as follows: Gauntam et al [56] reported that doping of B at Mn site of Ni$_2$Mn$_{1-y}$Ga$_y$ alloys are found to decrease both martensite phase and
Curie temperatures, whereas doping of B at Ga site of Ni$_2$MnGa$_{1-x}$B$_x$ alloys up to $x=0.1$ increases $T_M$, $T_P$ and slightly decreases the austenite curie ($T_{C^A}$) temperatures [57]. In Indium doped Ni$_{57}$Mn$_{18}$Ga$_{25-x}$In$_x$ ($x=0$–8) alloys, the PM-A phase of Ni-Mn-Ga alloys are significantly stabilized [58]. With the substitution of Vanadium at Mn site of Ni$_{54}$Mn$_{21-x}$V$_x$Ga$_{25}$ ($x=0, 2, 4$) the A-M transition temperature and the Curie temperature are decreased [59]. Substitution of V at Ga site of Ni$_{50.3}$Mn$_{20.8}$Ga$_{27.6}$V$_{1.3}$ shows a partial transformation from A to orthorhombic M through an intermediate phase is reported by Perez-Landazabal et al [60]. They measured the temperature dependent neutron diffraction patterns at 2, 130 and 240 K. The martensite transformations appears around 40 K with orthorhombic modulated structure at 2 K, whereas $L2_1$ pre-martensite with lattice parameter of 5.8 Å and $L2_1$ cubic austenite of cell parameter 5.82 Å are occurred at 130 and 240 K respectively. Thus the V doped sample under goes transformations of austenite, pre-martensite and martensite phases similar to the Ni$_2$MnGa [61, 62]. Thus, doping element irrespective of their magnetic property, alters the transformation temperatures and width of the hysteresis, consequently may affect its relative properties such as magnetoresistance, order of phase transition and magneto caloric effect.

By keeping all these points in mind, we have selected Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ ($x=0.0, 0.04, 0.08, 0.12$) alloys, and investigated various phenomenon such as transformation temperatures, order of phase transitions, magnetocaloric effect and MR through the structural, magnetic, transport, heat capacity and thermal measurements by tuning the temperature and magnetic field.

### 4.1.2 Experimental techniques

Polycrystalline ingots of Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ ($x=0.0, 0.04, 0.08, 0.12$) alloys are prepared by melting the high purity starting elements (99.9 % pure) through employing a vacuum arc melting furnace in partial Ar atmosphere. The samples are re-melted four times to make sure chemical homogeneity. These alloys are sealed in quartz ampoules and further annealed under a high vacuum at 1175 K for 36 hrs followed by quenching in cold water. Elemental compositions of these alloys are determined by using X-ray energy dispersive spectroscope (EDS) setup with SEM (Leo 440i) and found to be close to the nominal composition. For structural characterization powder XRD are performed with Philips 3121 X-ray diffractometer using Cu-K$_\alpha$.
radiation is used at RT. The low temperature XRD measurements are also done for x=0.12. DSC measurements are carried out in the temperature range of 200 K–360 K (DQ-100 system) to get the transformations temperatures. The magnetization measurements are performed by means of a physical property measurement system (PPMS-9T, Quantum Design, USA) using VSM. For magnetization measurements samples are initially cooled in zero magnetic field and the data is collected on warming by applying an external magnetic field (referred as (ZFC)). Followed by ZFC, again the data are collected upon cooling and warming without removing the applied field (referred as (FC) and (FW)). Isothermal M (H) curves are measured at different temperatures near magnetic and structural transitions. The MCE is calculated from M(H) curves by using Maxwell relations. Transport [$\rho (T)$, $MR (T)$] and heat capacity [[$C_p (T)$, $C_p (T^2)/T$]] measurements are carried out using the PPMS-14 T. The adiabatic temperature change ($\Delta T_{ad}$) calculated indirectly by using magnetic entropy change from the heat capacity data.

4.1.3 Results

4.1.3.1 Structural measurements

Fig. 4.1.1 (a) shows the powder XRD patterns at room temperature (RT) for the Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ (x=0.0, 0.04, 0.08, 0.12) powder samples, which are annealed further at 773 K in vacuum to remove the residual stress generated due to grinding the ingots into powder [63]. All the samples; x=0.0, 0.04, 0.08 and 0.12 exhibit cubic austenite phase at RT with lattice parameters of 3.6, 3.573, 3.536 and 3.525 Å, respectively. The temperature dependent XRD patterns (300, 250, 75 and 15 K) for x=0.12 sample [Fig. 4.1.1 (b)] reveals the coexistence of austenite and martensite phases at low temperatures. It is found that the A phase (ordered) appears at RT and the mixed phase starts appearing from 250 K down to 15 K.
4.1.3.2 Calorimetric measurements

Temperature dependence of heat flow $Q(T)$ during warming and cooling cycles for Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ (x=0.0, 0.04, 0.08, 0.12) Heusler alloys are shown in Fig. 4.1.2. The data collections are made with warming and cooling rate of 20 °C/min. The exothermic and endothermic behaviors are observed in all the samples. These behaviors create transformations due to change in enthalpy and entropy, and also these transformations are shifted by V doping. The transition temperatures related to the martensite transformations are listed in Table 4.1. The enthalpy ($\Delta H$) is measured by integrating the area under the curves in the transformation regions.

Figure 4.1.1 (a) Powder diffraction pattern of Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ (x=0, 0.04, 0.08, 0.12) alloys at room temperature; (b) Powder diffraction pattern of Ni$_{2.2}$Mn$_{0.6}$V$_{0.12}$Ga$_{1.08}$ alloy at different low temperatures.
Figure 4.1.2  Q (T) from DSC measurements of Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ (x=0, 0.04, 0.08, 0.12) alloys.

Table 4.1  The calorimetric, magnetic, transport and heat capacity parameters of Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ (x=0, 0.04, 0.08, 0.12).

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<th>$\Delta H$ (J/g)</th>
<th>Hyst $\Delta T$ (K)</th>
<th>$T_C$ (K)</th>
<th>$\frac{dM}{dH}$ (KT$^{-1}$)</th>
<th>$\Delta S_M$ (Jkg$^{-1}$K$^{-1}$)</th>
<th>$C_p$ (Jkg$^{-1}$K$^{-1}$)</th>
<th>$\Delta T_{ad}$ (K)</th>
<th>RCP (Jkg$^{-1}$)</th>
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Calculation of hysteresis from magnetic measurements

$$\Delta T = \frac{[M_s+M_f]}{2} - \frac{[A_s+A_f]}{2}$$
4.1.3.3 Magnetic measurements

(a) Temperature and Magnetic Field dependence of Magnetization

In order to study the magnetic behaviour of M and A transitions in Ni$_{2.2}$Mn$_{0.72}$V$_x$Ga$_{1.08}$ (x=0.0, 0.04, 0.08, 0.12), temperature dependence magnetization $[M(T)]$ measurements are carried out during ZFC, FC and FW cycles at the magnetic field of 0.01 T in the temperature range 2-320 K [Fig. 4.1.3 (a)-(d)]. The samples x=0.0, 0.04 and 0.08 exhibit a single sharp transition by coupling both $T_M$ and $T_C^A$ during all the cycles (ZFC, FC and FW) of measurements [Fig. 4.1.3 (a)-(c)], whereas two separate transitions ($T_M$ and $T_C^A$) are observed in x=0.12 sample. Transition temperatures ($T_M$ and $T_C^A$) for heating and cooling cycles are estimated from the derivative of corresponding $M(T)$ curves. It is interesting to note that $T_M$ and $T_C^A$ coincide for x=0.0, 0.04 and 0.08 samples are same for all the cycles, which suggests that x=0.0, 0.04 and 0.08 samples have coupled FM (or PM)-A and FM-M transitions. On the other hand, $T_M$ and $T_C^A$ of x=0.12 are different for each cycle, and it shows that decoupling of ferromagnetic austenite (FM-A) and martensite (FM-M) transitions. An enlarged view of FC and FW cycles around FM-A transition for all the samples are shown in an inset of $M(T)$ curves in Fig. 4.1.3 (a-d) and the characteristic transformation temperatures of martensite transition are indicated as $M_s$ (martensite start), $M_f$ (martensite finish), $A_s$ (austenite start) and $A_f$ (austenite finish) for all samples. Further, x=0.0, 0.04 and 0.08, samples show the thermal hysteresis ($\Delta T$) between FC and FW cycles, which suggesting the first order nature of transition [inset of Fig. 4.1.3 (a)-(c)].

It is calculated from the simple equation,

$$\Delta T = \left[ \frac{(M_s + M_f)}{2} - \frac{(A_s + A_f)}{2} \right]$$

(4.1.1)

The $\Delta T$ for all samples are presented in Table 4.1. However, a small hysteresis ($\sim \Delta T=2$ K) between FC and FW is observed at $T_C^A$ for x=0.12 sample [inset of Fig. 4.1.3(d)], which may be due to the existence of local martensite variants in the austenite phase [64]. But, enlarge view of $M(T)$ (inset of Fig.4.1.3d) shows large hysteresis around $T_M$ which indicates a strong first order transition. However, we found that
weakening of first transition and strengthening the second order transition as increasing the temperature in x=0.12.

Figure 4.1.3 Thermomagnetic curves in Ni_{2.2}Mn_{0.72-x}V_xGa_{1.08} (x=0, 0.04, 0.08, 0.12) alloys at constant magnetic field $\mu_0 H=0.01$ T.

The magnetic field dependence of magnetization $M(H)$ have been measured for all the samples across the transitions at 3 K interval by increasing of magnetic field from 0 to 5 T and decreasing from 5 to 0 T. The $M(H)$ curves for x=0.0, 0.04, 0.08 and 0.12 are shown in the Fig. 4.1.4 (a)-(d), respectively. There are two common features are found between Fig. 4.1.4 (a)-(c) as given below: There are three sets of $M(H)$ curves corresponding to below, above and at $T_M$ temperatures. It is observed that $M(H)$ shows PM (below PM-martensite or above PM-austenite) and FM behavior at below, above and $T_M$ respectively for all samples. The hysteresis nature is observed at $T_M$, in $M(H)$ curves at 255, 285 and 306 K for x=0.0, 0.04 and 0.08 respectively which confirms the presence of coupled first order PM-FM structural transition. Further, for x=0.12 sample also three sets of $M(H)$ curves are measured: at $T_M$, below and above
$T_M$ and it is corresponding to FM-A (286 to 250 K), A to M (235 to 226 K) and M (223 to 205 K) transitions respectively and no hysteresis is observed [Fig. 4.1.4 (d)]. Above the austenite transition, all the $M (H)$ curves at different temperatures clearly exhibit pure FM nature in $x=0.12$ sample. This confirms the presence of second order $PM-FM$ transition in the austenite state.

![Graphs showing magnetic properties](image)

**Figure. 4.1.4** Isothermal magnetization of Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ ($x=0$, 0.04, 0.08, 0.12) alloys.

(b) **Calculation of Magentocaloric Effect and Relative cooling power**

The coupled FM martensite-PM austenite transition indicates the possibility of large entropy change [39, 58, 65]. Hence, we study the magnetocaloric effect of V doped Ni-Mn-Ga alloys. From isothermal magnetization curves, the magnetic entropy change ($\Delta S_M$) was calculated for all the samples using Maxwell relation.
\[ \Delta S_M = \frac{H}{0} \left( \frac{\partial M(H,T)}{\partial T} \right) dH \] (4.1.2)

The temperature dependent magnetic entropy change \( [\Delta S_M (T)] \) at different magnetic fields \( (\Delta \mu_0 H) \) of 1, 2, 3, 4 and 5 T for \( \text{Ni}_{2.2}\text{Mn}_{0.72-x}V_x\text{Ga}_{1.08} \) (x=0.0, 0.04, 0.08, 0.12) alloys are shown in Fig. 4.1.5(a)-(d) respectively. Maximum of \( \Delta S_M (\Delta S_M^{\text{max}}) \) as function of field for each sample is shown in an inset of respective figures. It is observed that all the samples show negative \( \Delta S_M \) which is an indication of conventional MCE. It is clear from the Fig. 4.1.5 (a)-(d) that the \( \Delta S_M \) shows a sharp peak with respect to coupled transition temperatures for x=0.0, 0.04, 0.08 samples. On the other hand, \( \Delta S_M \) for x=0.12 sample shows one sharp peak and a small hump with respect to M and FM-A transitions, respectively. Higher magnetic field (>1 T) develops large \( \Delta S_M \) at M phase of x=0.12, the origin the large \( \Delta S_M \) is attributed to the change in magnetization caused by first order structural transition from martensite to austenite phase on heating [40]. Whereas, at lower field (<1T) the sample shows inverse MCE which is related with the large magneto crystalline anisotropy of the martensite phase and similar effect is also observed for other FM shape memory alloys \( \text{Ni}_{1.8}\text{Pt}_{0.2}\text{MnGa} \) [5], \( \text{Ni}_{51.5}\text{Mn}_{22.7}\text{Ga}_{25.8} \) [7] poly crystals and \( \text{Ni}_{52.6}\text{Mn}_{23.1}\text{Ga}_{24.3} \) single crystal [40]. Generally the application of field increases the magnitude of the \( \Delta S_M^{\text{max}} \) and it increases linearly with application of field for all the samples as shown in corresponding inset figures of all samples. \( \Delta S_M^{\text{max}} \) for the magnetic field difference \( (\Delta \mu_0 H) \) of 5 T are observed as 12.4, 16.2, and 19 Jkg\(^{-1}\)K\(^{-1}\) for x=0.0, 0.04 and 0.08 respectively around coupled M and FM-A transitions, whereas 10.3 Jkg\(^{-1}\)K\(^{-1}\) for 0.12 sample. The rate of \( \Delta S_M^{\text{max}} \) increases with field \( [d\Delta S_M^{\text{max}}/dH] \) has been also calculated for each sample from the inset Fig. 4.1.5 (a-d), and the values are 2.63, 3, 3.7 and 2.7 Jkg\(^{-1}\)K\(^{-1}\)T\(^{-1}\) for x=0.0, 0.04, 0.08, and 0.12 alloys respectively. Further, \( d\Delta S_M^{\text{max}}/dH \) increases with increasing of V doping up to x=0.08, whereas it is reduced for x=0.12 sample. The \( \Delta S_M \) for x=0.08 exhibits 19 Jkg\(^{-1}\)K\(^{-1}\) at 306 K which is better than \( \text{Ni}_{57}\text{Mn}_{18}\text{Ga}_{21.6}\text{In}_{3.4} \) [58] having 10 Jkg\(^{-1}\)K\(^{-1}\) at 300 K.
Figure 4.1.5 Magnetic entropy changes of Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ ($x=0$, 0.04, 0.08, 0.12) alloys in the magnetic field change up to 5 T.

The most classical parameter to quantify the MCE properties is Relative Cooling Power ($RCP$). The $RCP$ is a measure of the amount of heat transfer between hot and cold sinks during an ideal refrigeration cycle, and it has been calculated for the samples from $\Delta S_M(T)$ curves using the following equation

$$RCP = \Delta S_M^{\text{max}} \times T_{FWHM}$$  \hspace{1cm} (4.1.3)$$

Field dependence of $RCP$ for all the samples are shown in Fig. 4.1.6 and values of $RCP$ is indicated in Table 4.1. It is found that variation of $RCP$ with increasing V doping at each field is shown in the inset of Fig. 4.1.6. It shows that $RCP$ increases linearly up to $x=0.08$ with the application of field. A large $RCP^{\text{max}}$ of 103 Jkg$^{-1}$ at 5T is observed for $x=0.08$ sample. This value is larger than the reported in literature for similar kind of alloys [9, 38, 39].
Figure 4.1.6 Field dependent Relative cooling power of \( \text{Ni}_{2.2}\text{Mn}_{0.72-x}\text{V}_x\text{Ga}_{1.08} \) (x=0, 0.04, 0.08 and 0.12) alloys.

### 4.1.3.4 Heat capacity measurements

The heat capacity measurements are performed for the evaluation of thermodynamic parameters such as \( C_p \), \( S_T \), and \( \Delta T_{ad} \) from magneto transport properties, which is due to an increasing density of free electrons at low-temperature in any solid materials. The densities of electrons are explained by calculating Sommerfeld coefficient \( (\gamma) \). The temperature dependence of heat capacity \([C_p(T)]\) are performed from 2 to 320 K with an applied field of 0, 5 and 8 T for \( \text{Ni}_{2.2}\text{Mn}_{0.72-x}\text{V}_x\text{Ga}_{1.08} \) (x=0, 0.12) samples which are shown in Fig. 4.1.7 (a, b) respectively. The peak value of \( C_p \) for x=0, 0.12 samples at 5 and 8 T are indicated in Table.4.1. Further, Fig.4.1.7 (c, d) shows \( C_p/T \) vs \( T^2 \) for the same samples. A sigmoid \( C_p-T \) plots shows steady increase of \( C_p \) from 2 to 265 K (\( A_s \)) and sharp peaks are observed around 250 and 270 K for x=0 and 0.12 samples respectively. The upturn points (\( T_u=24 \text{ K} & T_p =117 \text{ K} \)) are same for all the samples. The \( C_p \) over the difference in two points follows the relation

\[
C_p(T) = \gamma T + \beta T^3
\]  

(4.1.4)
Further, Sommerfeld coefficient ($\gamma$) and Debye coefficient ($\beta$) are calculated from the linear fit of $C_p' \text{ vs } T^2$ plot using the above relation, and results are tabulated in Table. 4.2. It is found that Sommerfeld coefficients ($\gamma$) are almost same for both the samples which mean that free electron densities (FED) are evenly distributed. Whereas Debye coefficient ($\beta$) is slightly changes with effect V ion doping, it may be due to domination of electron contribution than phonon. $C_p (T)$ is used to determine both $\Delta S_M$ and $\Delta T_{ad}$ in Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ (x=0, 0.12) alloys.

The change in entropy ($\Delta S_M$) can be calculated using the relation for $C_p-T$ measurements,

\[
S(T)_{B_0} = \int_0^T \frac{C_p(T)_{B_0}}{T}dT + S_{0,B_0} \tag{4.1.5}
\]

\[
S(T)_{B_r} = \int_0^T \frac{C_p(T)_{B_r}}{T}dT + S_{0,B_r} \tag{4.1.6}
\]

\[
\Delta S_m = S(T)_{B_r} - S(T)_{B_0} \tag{4.1.7}
\]

Where, $B_F$ and $B_0$ are final and initial fields.

The change in adiabatic temperature ($\Delta T_{ad}$) can be calculated using the Clausius-Clapeyron relation

\[
\Delta T_{ad} \equiv T \times \Delta S_{M+T} \times C_p^{-1} \tag{4.1.8}
\]

The change of adiabatic temperature [$\Delta T_{ad}$] are shown in Fig.4.1.8 which are calculated from [$C_p (T)$] measurements for x=0 and 0.12 samples. It reveals that $\Delta T_{ad}$ are significantly changes with magnetic field for both the samples. The $\Delta T_{ad}$ around $T_M=-250$ K decreases from 2.9 to 1.6 K for x=0, whereas it increases near $T_c=270$ K from 1.4 to 8 K for x=0.12 sample with increasing field (5-8 T). These $\Delta T_{ad}$ values are shown in Table.4.1. The sharp peaks from $\Delta T_{ad}$ curve near $T_M$ and $T_C$ reveals that intrinsic nature of fast atomic redistribution with damping of spin dynamics due to magnetic field [66].
Figure 4.1.7  \( C_p \) vs \( T \), \( C_p/T \) vs \( T^2 \) of Ni\(_{2.2}\)Mn\(_{0.72-x}\)V\(_x\)Ga\(_{1.08}\) (\( x=0, 0.12 \)) alloys.

Figure 4.1.8  \( \Delta T_{ad} \) vs \( T \) for Ni\(_{2.2}\)Mn\(_{0.72-x}\)V\(_x\)Ga\(_{1.08}\) (\( x=0, 0.12 \)) alloys.
4.1.3.5 Electrical resistivity measurements

In order to study the characteristics of FM-A and M transitions, the electrical transport property is carried out for parent (x=0) and highest doped (x=0.12) samples. The temperature dependence of resistivity $\rho(T)$ in the temperature range of 2-350 K during cooling and warming cycles are measured under the magnetic fields of 0, 1, 3, 5 and 8 T for Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ (x=0, 0.12) alloys, and they are shown in the Fig. 4.1.9 (a) and (b) respectively. Inset figures show that enlarged view around the $T_M$. It is clear from the main panel of figures that both samples exhibit similar nature of temperature dependent resistivity. By reducing the temperature, initially there is a gradual drop of resistivity, followed by the steep increase and then gradual decrease of resistivity. i.e., both samples exhibit metallic nature below and above $T_M$. For x=0, the $T_M$ is 253 K during cooling cycle at 0 T which is almost equal to the temperature of coupled M and FM-A transition is observed during FCC (254 K) from the magnetization measurements. Similarly for x=0.12, the $T_M$ at 0 T during cooling cycle is 218 K which is nearly equal to the temperature of M transition is observed during FCC (219 K) in M (T). Hence, this sharp transition ($T_M$) is observed from the $\rho(T)$ which are similar to the M transition from magnetic measurements of both samples. This abrupt change of resistivity during M transformation may be a consequence of a change in electron band structure caused by the structural and magnetic phase transition [67]. Moreover, $\rho(T)$ of both samples exhibit the hysteresis between cooling and warming cycles around the M transition, which suggesting that the presence of first order transition. On the other hand, the application of magnetic field on x=0 sample shifts both cooling and warming curves towards the higher temperature region [inset of Fig. 4.1.9 (a)], whereas there is no shift on x=0.12 [inset of Fig. 4.1.9 (b)]. The rate of change of $T_M$ with field $[dT_M/dH]$ are 0.625 and 0.35 KT$^{-1}$ (low value) for x=0 and 0.12 respectively, which are presented in Table.4.1. However, magnetic field does not make any change in the width of hysteresis of both samples. In other words, the application of field stabilizes the first order transition around M transformation for both the samples. This is because of the formation of super zone boundary in the Fermi surface around M transformation of Heusler alloys by the application of external magnetic field [68].
In order to study the effect of magnetic field on resistivity of both the samples the magnetoresistance (\(MR\))

\[ MR(\%) = \Delta \rho = (\rho_H - \rho_0)/\rho_0 \]  

(4.1.9)

has been estimated for different magnetic fields using \(\rho(T)\) plots of both samples. Fig. 4.1.10 (a) and (b) shows that temperature dependence of \(MR\) for \(x=0\) and 0.12 respectively. As the magnetic field increases in \(x=0\) upto 8 T, the \(MR\) sharply increases around \(T_M\), and the plots are shifted towards higher temperature region. We found that \(MR_{\text{max}}\) of 28\% is observed at \(T_M\) for \(x=0\) sample, whereas no appreciable change of \(MR\) around \(T_M\) in \(x=0.12\). The MR values at various fields of samples are shown in Table.4.1. The parent (\(x=0\)) compound well responds to magnetic field due to the presence of pure FM Ni ions, whereas increase of V ions dilutes the magnetic subsystem around the transition. Hence, \(x=0.12\) poorly responses to magnetic field [59].
Figure 4.1.10 MR vs T at different magnetic field of Ni_{2.2}Mn_{0.72-x}V_xGa_{1.08} (x=0, 0.12) Heusler alloys.

4.1.3.6 Calculation of Critical Exponents

In order to verify the presence of second order transition, Arrott plot ($M^2$ vs $H/M$) is used for $x=0.12$ sample around FM-A state, as shown in Fig. 4.1.11(a). It is clear from Arrott plot that slopes of $M^2$ vs $H/M$ are positive over the entire range, as per the generalized approach of first to second order phase transition from Banerjee criterion [69] results to authenticate the presence of second order transition for $x=0.12$ sample. In the same plot, the curve for $T=T_C$ passes through the origin. The $T_{C^A}$ is found to be 268 K from this method, which closely agrees with $T_{C^A}$ derived from $M(T)$ plots.

Generally, the system which is having second order FM transition should obey one of the common universality classes such as mean field, three dimensional Heisenberg, three dimensional Ising [70] and tricritical mean field [71]. These models have unique set of critical exponents. Hence, determining the values of critical exponents close to second order FM-A transition, and assigning one of these models to second order systems have been extremely useful for better understanding of nature of phase transition. The set of critical exponents $\beta$ (spontaneous magnetization), $\gamma$ (initial susceptibility) and $\delta$ (critical magnetization isotherm), are defined by the following equations is
\[ M_S(0,T) = M_0(-\epsilon)^\beta \quad \epsilon < 0, T < T_c \quad (4.1.10) \]
\[ \chi_0^{-1}(0,T) = \left(\frac{h_0}{M_0}\right)(\epsilon)^\gamma \quad \epsilon > 0, T > T_c \quad (4.1.11) \]
\[ M(H,T_c) = D(H)^{1/\delta} \quad \epsilon = 0, T = T_c \quad (4.1.12) \]

Where, \( M_0, h_0/M_0 \) and \( D \) are the critical amplitudes. \( M_S, \chi_0^{-1} \) and \( \epsilon = (T-T_{CA})/T_{CA} \) are spontaneous magnetization, initial inverse susceptibility and reduced temperature respectively and these can be calculated as follows: the temperature at which the curve passes through the origin is \( T_{CA} \). The polynomial fitting of each curve and linear extrapolation above \( T_{CA} \) yields \( M_S \) whereas below \( T_{CA} \) yields \( \chi_0^{-1} \). The temperature dependence of \( M_S \) and \( \chi_0^{-1} \) of the alloy is shown in Fig. 4.1.11(b). Kouvel–Fisher method is used for the efficient and accurate determination of \( T_{CA} \) and the critical exponent \( \beta, \gamma \) and \( \delta \). [72]. The equations (4.1.10), (4.1.11) and (4.1.12) are modified as per Kouvel-Fisher method.

\[ \frac{M_S(T)}{dM_S(T)/dT} = \frac{T-T_c}{\beta} \quad (4.1.13) \]
\[ \frac{\chi_0^{-1}(T)}{d\chi_0^{-1}(T)/dT} = \frac{T-T_c}{\gamma} \quad (4.1.14) \]
\[ \log M(H,T_c) = \frac{\log H}{\delta} \quad (4.1.15) \]

According to equations (4.1.13) and (4.1.14), \( M_S \left( \frac{dM_S/dT}{dT} \right)^{-1} \) vs \( T \) and \( \chi_0^{-1} \left( \frac{d\chi_0^{-1}/dT}{dT} \right)^{-1} \) vs \( T \) should be a straight line with slopes of \( 1/\beta \) and \( 1/\gamma \) According to equation (15), the critical exponent \( \delta \) which is associated with the critical magnetization isotherm at \( T_{CA} \) can be determined using \( \log (M) \) vs \( \log (H) \) plot at \( T_{CA} \). Fig. 4.1.11(c) shows the Kouvel-Fisher plots \([M_S \left( \frac{dM_S/dT}{dT} \right)^{-1} \) vs \( T \) and \( \chi_0^{-1} \left( \frac{d\chi_0^{-1}/dT}{dT} \right)^{-1} \) vs \( T \)], and both straight lines meet at temperature axis corresponds to \( T_{CA} \) of 268 K. The values of \( \beta \) and \( \gamma \) of the sample are calculated from the reciprocal of slopes of \( M_S \left( \frac{dM_S/dT}{dT} \right)^{-1} \) vs \( T \) and \( \chi_0^{-1} \left( \frac{d\chi_0^{-1}/dT}{dT} \right)^{-1} \) vs \( T \) plots respectively, and the values of \( \beta \) and \( \gamma \) are 0.482 and 1.056 respectively. In order to calculate the value of \( \delta \), we have chosen \( M \left( H \right) \) at 268 K. The Fig. 4.1.11(d) shows the \( \log (M) \) vs \( \log (H) \) plot at \( T_{CA} \), and linear fit of this plot yields \( \delta \) as 3.021. The reliability of the calculated value is obtained using Widom scaling.
relation $\gamma - \beta (\delta - 1) = 0$, and the value is -0.09. The value of critical exponents ($\beta = 0.482$, $\gamma = 1.056$, $\delta = 3.021$) are determined from the magnetic measurements very well match with the values of mean field theory ($\beta = 0.5$, $\gamma = 1.0$, $\delta = 3.0$). This indicates that $x=0.12$ exhibits long range ferromagnetic interactions around FM-A state.

Figure. 4.1.11 (a) $M^2$ vs H/M (Arrott plot) of isotherms for Ni$_{2.2}$Mn$_{0.6}$V$_{0.12}$Ga$_{1.08}$ (b) spontaneous magnetization ($M_s$) and inverse initial susceptibility ($\chi_0^{-1}$) vs T of Ni$_{2.2}$Mn$_{0.6}$V$_{0.12}$Ga$_{1.08}$, (c) Kouvel- Fisher plots of $M_s(dM_s/dT)^{-1}$ and $\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}$ vs T. (d) Scaling plot on $\ln M$–$\ln H$.

4.1.4 Discussion

The structural investigations are carried out to identify and understand the nature of phase transitions by the variation of both doping concentration [Fig. 4.1.1 (a)] and temperatures [Fig. 4.1.1(b)] across the transformation region. All the samples exhibit cubic A phase at RT and by increasing V, the lattice parameters decreases from 3.6 Å ($x=0$) to 3.52 Å ($x=0.12$). The temperature dependent structure investigation of
$x=0.12$ shows the coexistence of A and M phase below $T_M$ upto 15 K. Thus, it is clear that crystal structure is not varied by the effect of V doping in the present compounds. However, variation of temperature changes the crystal structures in $x=0.12$.

The unequivocal signals are observed from the DSC (heating and cooling) curves which indicate appearance of first order transitions during cooling (or) heating due to the changes from M to A phase [Fig. 4.1.2]. The observations of average $T_M$ ($255 \text{ K} \rightarrow x=0, 279 \text{ K} \rightarrow x=0.04, 304 \text{ K} \rightarrow x=0.08$ and $222 \text{ K} \rightarrow x=0.12$) from DSC are nearly correlated with our magnetic measurements. Also, the latent heat (enthalpy) of Ni$_{2.18}$Mn$_{0.82}$Ga is 9.6 J/g [44] and it is comparatively less ($x=0$: 4.5 J/g, $x=0.12$: 3.6 J/g) with our present samples. Some of the doped systems like Co and Fe substitutions are not substantially modified with thermal entropy change ($\Delta S$) near $T_M$ in Mn site of Ni$_{50.6}$Mn$_{25-x}$Ga$_{24.4}$Co$_x$ and Ni$_{52.5}$Mn$_{22.3-x}$Ga$_{25.2}$Fe$_x$ systems respectively [53]. However, non-magnetic (V) ion [Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ (x=0, 0.12)] increases the thermal entropy change ($\Delta S$) from 13.6 to 15.8 Jkg$^{-1}$K$^{-1}$. Cr doped in Mn site of Ni$_{56}$Mn$_{25-x}$Cr$_x$Ga$_{19}$ (x=0, 2, 4, 6) decreases the thermal entropy which are in Yun-qing et al [55]. Therefore, thermal entropy ($\Delta S$) and enthalpy ($\Delta H$) is comparatively higher for V doped samples than other (Co, Fe) doped compounds.

Similarly, substituting and doping effect of different elements are drastically changed by some important factors like transformations temperatures and e/a in Ni-Mn-Ga system. While, Fe doping level increases in Mn site of Ni-Mn-Ga (Ni$_{48.7}$Mn$_{30.1}$Ga$_{21.2}$ and Ni$_{48.7}$Mn$_{28.1}$Fe$_2$Ga$_{21.2}$) exhibits narrow thermal hysteresis which is involved by phase transformations due to small driving force of chemical energy. Further, transition temperatures are decreased by increasing e/a ratio and it is due to induced martensitic transformations by chemical pressure [54]. The suppression of phase transformations temperatures are observed by Yun-qing et al [55] in Ni$_{56}$Mn$_{25-x}$Cr$_x$Ga$_{19}$ (x=0, 2, 4, 6). Chen et al [51] reported effect of Co doping in both site at Ga and Mn of Ni$_{48}$Mn$_{27}$Ga$_{25-x}$Co$_x$ (x=1, 2, 3, 4), Ni$_{48}$Mn$_{26-x}$Co$_x$Ga$_{26}$ (x=1, 2, 3, 5) samples and it is found that transformation temperatures (martensitic) and e/a ratio are increased, when Co doped in Ga site. On the other hand, during Co doping at Mn site the transformation temperatures are not much changed and small variation of e/a. Shao Meng et al [73] reported that phase transformation temperatures (martensitic) and
$e/a$ increase with Co in $(\text{Ni}_{52.5}\text{Mn}_{23.5}\text{Ga}_{24})_{100-x}\text{Co}_x$ ($x=0, 2, 4, 6, 8$) alloys. Also, the unit cell volume are gradually reduced with increasing Co content, which may be related to lower scattering factor of Co than Ni and Ga. Substitution of Co at Mn site of $\text{Ni}_{50}\text{Mn}_{29-x}\text{Co}_x\text{Ga}_{21}$ ($x=0, 0.8, 2.4, 3.3, 4.0, 4.7, \text{and } 6.8$) [50] system resulted that the of non-modulated tetragonal phase is stabilized by the higher Co content. AC susceptibility results of $\text{Ni}_{47}\text{Mn}_{31-x}\text{Ga}_{21}$ ($x=\text{Fe, Co}$) [49] reveals that Fe increases the $T_M$ and decreases $T_C$, while doping of Co is shown the inverse effect. The $M_s$ and $T_C$ are almost linear with doping of Mn site by Fe in $\text{Ni}_{52.5}\text{Mn}_{22.3-x}\text{Ga}_{25.2}\text{Fe}_x$ ($0 \leq x \leq 5.2$) [53] which exhibits increase of $e/a$, when replacing Mn by either Fe (or) Co. On the other hand, both pre-martensitic ($T_I$) and inter-martensitic ($T_{IM}$) transition temperatures decrease with increasing Co, whereas $T_C$ slightly increases which are observed in $\text{Ni}_{50.6}\text{Mn}_{25-x}\text{Ga}_{24.4}\text{Co}_x$ ($0 \leq x \leq 5.1$) [53].

The effect of B substitution in Mn site of $\text{Ni}_2\text{Mn}_{1-x}\text{B}_x\text{Ga}$ system has been studied by Gautam et al [56], it leads to decrease of $e/a$ (7.5 to 7.2) and transformations temperatures ($T_C$, $T_{PM}$, $T_M$) due to the change in concentration of magnetic ions. However, the $T_M$ temperature remains constant at $7.5 \geq (e/a) \geq 7.42$ interval and then it decreases with increasing B content. Another report from Gautam et al [57] reveals that substitution of B in Ga site of $\text{Ni}_2\text{Mn}\text{Ga}_{1-x}\text{B}_x$ system increases $T_M$ and $T_P$ due to the structure distortion and reduction of cell volume, whereas $T_C$ decrease slowly with increasing B concentration at $0 \leq x \leq 0.1$ interval and it is attributed by the weakening of the exchange interaction. Aydogdu et al [74] found that substituting B in Ga site of $\text{Ni}_{51}\text{Mn}_{28.5}\text{Ga}_{20.5-x}\text{B}_x$ alloys decrease the transformation temperatures, increase saturation magnetization and form the $(\text{Ni, Mn, Ga})_{23}\text{B}_6$ phase. Hence, it is clear that investigation of Fe, Co, B, and V doping in different series Ni-Mn-Ga systems are essential to understand the phase transformations, constructing of new phase diagrams and confirm the characteristic temperatures for the magneto-structural behaviors.

It is well known that very large $MCE$ has been observed in materials which having first order magneto-structural phase transition ($MSPT$) [75] and both $T_M$, $T_C$ are coupling together at the same temperature. The nature of first order $MT$ implies that exchange of latent heat and presence of hysteresis. Simultaneous occurrence of both temperature and magnetic field hysteresis during $MSPT$ requires more complex
description of the thermodynamics of a system. MT is leading to giant MCE at 240 K has been first observed in Gd$_3$Si$_{1.8}$Ge$_{2.2}$ [76]. The compound Gd$_3$Si$_2$Ge$_2$ displays FM first order transition at 276 K and showing better MCE (~19 Jkg$^{-1}$K$^{-1}$) twice that of pure Gd [77]. Correspondingly, replacement of Co by Indium in MnCo$_{1-x}$In$_x$Ge compounds exhibit coupled MSPT and MCE [65]. Further, coupling of both $T_M$ and $T_C$ have been reported in Ni$_{49.5}$Mn$_{25.4}$Ga$_{25.1}$, Ni$_{2.19}$Mn$_{0.81}$Ga and Ni$_{2.18}$Mn$_{0.82}$Ga systems [8, 39, 42, 44, 45]. The MSPT is observed in Ni$_{1.72}$Co$_{0.28}$Mn$_{1.25}$Ga$_{0.75}$ (2 K) and Ni$_{1.65}$Co$_{0.34}$Mn$_{1.31}$Ga$_{0.62}$In$_{0.07}$ (1.2 K) with high magnetic field of 60 T [78]. Also, polycrystalline Ni$_{2.19}$Mn$_{0.81}$Ga (Aliev et al [42]) and Ni$_{2.18}$Mn$_{0.82}$Ga (Khovailo et al [44]) alloys exhibit MSPT during continuous heating and cooling in various magnetic fields (2.6 T, 0.01 T) between 330 to 340 K. Weak coupling of MSPT is also observed in Ni$_{49.5}$Mn$_{25.4}$Ga$_{25.1}$ alloy system at 4 T due to weak spin-phonon dispersion which results in a transition entropy change and independent of the magnetic field [8]. Zhang et al [58] reports that partial substitution of Indium at Ga site of NiMnGa reveals PM-A phase is well stabilized and MSPT can be tailored around RT. However, only few of them reported MSPT and MCE doping of Co, Fe, Cr, B in Mn site of Ni-Mn-Ga system. Min et al [59] reports $T_A$-$T_M$, $T_C$ (325-265 K) and $[\Delta S_M/T_C]$ (2.49-1.81 Jkg$^{-1}$K$^{-1}$) decreased with increasing V concentration, by the substitution of V in Mn site of Ni$_{54}$Mn$_{21-x}$V$_x$Ga$_{25}$ (x=0,2,4) alloys.

The coupled ($A$ and $M$) and decoupled ($T_M$ and $T_C$) MSPT are represented in $M$ ($T$) measurements [Fig.4.1.3 (a-d)] of our selected samples. The present x=0, 0.04 and 0.08 samples show that the coupled MSPT at 255, 280 and 306 K respectively, which means that increase V doping upto x=0.08 in Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga system the first order-MSPT moves nearer to RT. Hence, the selective compound in this work effectively improves the MCE ($\Delta S_M$= 12.4, 16.2 and 19 Jkg$^{-1}$K$^{-1}$) under ambient condition. Whereas x=0.12 sample exhibits decoupling of MSPT due to the dilution of Mn by higher percentage of V which gives lower MCE ($\Delta S_M$=10.3 Jkg$^{-1}$K$^{-1}$) than the parent (x=0) sample. The performances of a given material for solid-state refrigeration are typically analyzed by calculating the RCP and it is higher in the present system than previous reports.
Generally, the resistivity of Heusler alloys has a metallic character during continuous heating. It increases at high temperature due to the increase of any one of the parameter like electron-electron, electron-phonon, electron-magnon scatterings and spin disorder which are depends on composition of Heusler alloys. The phonon contribution increases while increasing temperatures. Many researchers reported transport and MR in Heusler alloys, since it is one of the potential candidates for spintronic applications. They are as follows: The Ni-Mn-Sn and Ni-Mn-In system \[21, 22\] show negative MR of 50% at 160 K \[21\] and 64% at 230 K \[22\] respectively. Both positive and negative MR of \( \sim 25\% \) has been observed in Ni\(_{50}\)Mn\(_{29}\)Ga\(_{21}\) \[33\] single crystal which depends on the twin variation and applied magnetic field of \( I.2\ T \) at 298 K. Wide range negative MR has been observed in the Ni\(_{50}\)Mn\(_8\)Fe\(_{17}\)Ga\(_{25}\) ribbon at \( T_M \) due to the redistribution of electrons and increase of phase boundary scattering \[35\]. A spin valve-like MR has been reported in Mn\(_2\)NiGa at RT \[18\]. The negative MR of 8% and MCE have been observed in nickel-rich Ni\(_{2+x}\)Mn\(_{1-x}\)Ga Heusler alloys \[79\] where the structural and magnetic transitions are almost coincide with each other. Till date none of the reports are found in MR effect of V (non magnetic element) doped NiMnGa alloy and it is reported first time in this work. From our results we infer that increase of V doping leads to drastic suppression of MR in our selected compounds. The parent sample \( (x=0) \) exhibits 28% MR near \( T_M \), whereas MR is completely diminished in \( x=0.12 \) sample at \( 1\ T \). Further increase of field upto \( 8\ T \), MR does not make any changes at \( x=0.12 \) sample and it may be due to diluting of magnetic phases by the non-magnetic V ion. The observed MR values of V free (Ni\(_{2.2}\)Mn\(_{0.72}\)Ga\(_{1.08}\)) and V doped (Ni\(_{2.2}\)Mn\(_{0.62}\)V\(_{0.12}\)Ga\(_{1.08}\)) alloys are shown in Table 4.1.

Heat capacity measurements are executed in order to calculate magnetocaloric potential of the samples. The results show that less expensive Heusler alloys [Ni-Mn-Ga (Sn)] could be produced as a magnetic refrigerant at ambient temperature \[60, 66\]. The Sommerfeld coefficient \((3.002, 3.035\ mJ/K^2\ mol)\) and Debye coefficient \((8.377\times 10^{-5}, 9.43\times 10^{-5}\ J/K^4\ mol)\) at 0 and 5 T are reported in Ni\(_{50.3}\)Mn\(_{20.8}\)Ga\(_{27.6}\)V\(_{1.3}\) alloy \[60\]. On the other hand, Prasanna et al \[66\] reported that partial substitution of Ni by Sn \([\text{Ni}_{41-x}\text{Mn}_{50}\text{Sn}_x\ (0\leqslant x\leqslant 1.5)]\) alloys exhibits inverse MCE \((11.6\ \text{to}\ 10.8\ \text{Jkg}^{-1}\text{K}^{-1})\), \(\Delta T_{ad} \) \((-26\ \text{to}\ -15.7\ \text{K})\) and then Sommerfeld coefficient \(\gamma =0.10\ \text{J/kgK}^2\), Debye coefficient \(\beta = 8.9 \times 10^{-4}\ \text{J/kgK}^4\) are estimated for the alloys. We calculated all the
above important parameters from heat capacity measurements for our present samples. The values are presented in Table 4.1 and 4.2. However, \( \Delta T_{ad} \) are decreased (x=0) and increased (x=0.12) with magnetic field. As per the thermodynamic concerns, \( \Delta T_{ad} \) is always inversely changes with \( \Delta S_M \). Hence, from the heat transport measurements it confirm that x=0, 0.04, 0.08 are more convenient with magnetic refrigeration than x=0.12 sample.

**Table: 4.2** The Sommerfeld Coefficient (\( \gamma \)) and Debye Coefficient (\( \beta \)) of Ni\(_{2.2}\)Mn\(_{0.72-x}\)V\(_x\)Ga\(_{1.08}\) (x=0, 0.12).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Sommerfeld Coefficient (( \gamma )) (Jkg(^{-1})K(^{-2}))</th>
<th>Debye Coefficient (( -\beta )) (10(^{-6})) (Jkg(^{-1})K(^{-4}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0</td>
<td>2.7866</td>
<td>6.37316</td>
</tr>
<tr>
<td>x=0.12</td>
<td>2.7694</td>
<td>5.9420</td>
</tr>
</tbody>
</table>

In order to understand FM nature of the second order transition, the critical behavior is also analyzed in Heusler alloys [29] and re-entrant metallic alloys [30]. The reported value of critical exponents for Ni\(_{50}\)Mn\(_{35}\)In\(_{14}\)Si\(_1\) [80] and Mn\(_4\)FeGe\(_3\).\(_x\)Si\(_x\) (x=0,0.2) [81] are consistent with mean-field and 3 dimensional Heisenberg models, and hence suggesting the presence of long range and short range magnetic orderings respectively. Similarly, Au\(_{0.81}\)Fe\(_{0.19}\), Ni\(_{0.78}\)Mn\(_{0.22}\), Ni\(_{0.79}\)Mn\(_{0.21}\) and amorphous \( a\)-Fe\(_{0.98}\)Zr\(_{0.08}\) alloys are corresponding to 3 dimensional Heisenberg model [30]. Long Phan et al [82] reports transformation of FM ordering from short to long range by the increasing doping concentration from 14 to 13 in Ni\(_{50}\)Mn\(_{50-x}\)Sn\(_x\) (x=13,14) samples. In the present study, Banerjee criteria and Kouvel-Fisher method are used for calculating critical exponents analysis for x=0.12 sample at \( T_C^A \). Even \( T_C^A \) has small hysteresis which is a mixture of first and second order transition. The second order is more dominant than the first order. Hence, we choose Arrott plots [M\(^2\) vs H/M] near \( T_C^A \) region to find exact second order transition (\( T_C^A \)), and then critical exponents are calculated by using Kouvel- Fisher plots. From that values it can be identified, x=0.12 exhibits both first (minority) and second order (majority) phase transition which obeys mean field theory with long range FM order. The comparative values of critical exponents with other samples are tabulated (Table 4.3).
Table: 4.3 Comparison of critical exponent values of various Heusler alloys.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Sample system</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>$T_C$</th>
<th>Order of $T_C$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni$<em>2$Mn$</em>{0.72-x}$V$<em>x$Ga$</em>{1.08}$</td>
<td>0.482</td>
<td>1.056</td>
<td>3.021</td>
<td>268K</td>
<td>Long range FM with mean field</td>
<td>present work</td>
</tr>
<tr>
<td>2</td>
<td>Ni$<em>{50}$Mn$</em>{35-x}$In$_x$Si$_x$</td>
<td>0.510</td>
<td>$\rightarrow$T$_{CA}$</td>
<td>0.987</td>
<td>$\rightarrow$T$_{CA}$</td>
<td>2.935</td>
<td>$\rightarrow$T$_{CA}$</td>
</tr>
<tr>
<td>3</td>
<td>Ni$<em>{50}$Mn$</em>{50-x}$Sn$_x$ (x=13, 14)</td>
<td>0.385 $\rightarrow$x=13, 0.496 $\rightarrow$x=14</td>
<td>1.083 $\rightarrow$x=13, 1.024 $\rightarrow$x=14</td>
<td>3.82 $\rightarrow$x=13, 3.01 $\rightarrow$x=14</td>
<td>302K $\rightarrow$x=13, 310K $\rightarrow$x=14</td>
<td>Short range FM with 3D Heisenberg model $\rightarrow$x=13, short to long range $\rightarrow$x=14</td>
<td>Phan et al [82]</td>
</tr>
<tr>
<td>4</td>
<td>Mn$<em>{1-x}$Fe$<em>x$Ge$</em>{0.5}$Si$</em>{0.5}$ (x=0,0.2,0.6,1)</td>
<td>0.459 $\rightarrow$x=0, 0.445 $\rightarrow$x=0.2, 0.645 $\rightarrow$x=0.6, 0.748 $\rightarrow$x=1</td>
<td>1.47 $\rightarrow$x=0, 1.457 $\rightarrow$x=0.2, 1.127 $\rightarrow$x=0.6, 1.054 $\rightarrow$x=1</td>
<td>4.204 $\rightarrow$x=0, 4.237 $\rightarrow$x=0.2, 2.75 $\rightarrow$x=0.6, 2.416 $\rightarrow$x=1</td>
<td>320K $\rightarrow$x=0, 320K $\rightarrow$x=0.2, 319K $\rightarrow$x=0.6, 318 K $\rightarrow$x=1</td>
<td>x=0, 0.2 $\rightarrow$ mean field theory with long FM $@&lt;T_C$, 3-D Heisenberg model with short FM $@&gt;T_C$, x=0.6, 1 $\rightarrow$Mean field theory.</td>
<td>Halder et al [81]</td>
</tr>
</tbody>
</table>

4.1.5 Conclusion

In summary, we investigated the magnetocaloric and transport properties of Ni$_{2.2}$Mn$_{0.72-x}$V$_x$Ga$_{1.08}$ (x=0, 0.04, 0.08, 0.12) Heusler alloys. The alloys show coupled magneto-structural transition near room temperature for compositions below x<0.12. The $\Delta S_M^{\text{max}}$ and $RCP$ are linearly increases with increase of V concentration for composition range 0<x<0.08, where the coupled magneto-structural transition is realized and after that decreased for higher substitution of V (x=0.12), which does not show coupled magneto-structural transition. The $\Delta S_M^{\text{max}}$ and RCP are increases linearly with magnetic field strength for all the alloys. The x=0.08 is highly suitable for the magnetic refrigeration application, since it has high $\Delta S_M^{\text{max}}$ of 19 Jkg$^{-1}$K$^{-1}$ and RCP of 103 Jkg$^{-1}$ at room temperature. Transport studies reveal that all samples exhibits metallic nature. Parent compound (x=0) is more suitable magnetic recording applications due to high MR (28%). The even distribution of free electron density and domination of electron contribution than phonon are confirmed by calculating Sommerfeld and Debye coefficients from the heat capacity measurements. The critical analysis for x=0.12 confirms mean field theory. As in Ni-Mn-Ga shape memory alloys the martensite-austenite transition is reversible compared to the Ga free Ni-Mn-X based shape memory alloys, hence the present alloys have potential for application in magnetic refrigeration near room temperatures.
References


[46]. A. Satish Kumar, M. Ramudu and V. Seshubai, phase transitions. **85** 1045 (2012).


4.2 Investigation of the pressure induced martensitic transition and piezo-resistivity of Ni$_{2.2}$Mn$_{0.6}$V$_{0.12}$Ga$_{1.08}$ Heusler alloy using cubic anvil press

4.2.1 Introduction

There have been a lot of investigations of the Quantum Phase Transition (QPT) in intermetallic compounds, which is usually induced by changing some controlled parameters such as composition, magnetic field and pressure. High-pressure have controlled the QPT to finding novel properties in new engineering materials. The effect of hydrostatic and quasi-hydrostatic techniques provides more pressure emphatically to understand the properties of materials near the phase transformation and its mechanism [1-4]. Pressure is one of the thermodynamic variables which render a change in inter atomic distances in solid materials with a controlled manner [5-6]. The pressure and temperature can result in structural phase transitions [7-8] as well as affecting band structure and magnetic interaction in transition metals and its compounds [9-10]. Pressure effect changes the magnetic and its martensitic transition are previously reported [11-16]. Hydrostatic pressure can evaluate volume change of TM using Clausius-Clapeyron equation. Pressure induced structural transformations with symmetric systems such as iso-symmetric, group-subgroup, intersection group and order-disorder transitions are reported by Gupta et al [17].

Transport measurements which can be used to distinguish metals, semi-metal, insulators and also band-gap semiconductors. The temperature dependence of the resistivity [ρ (T)] of a metal contains a wealth of information about its electronic, magnetic and lattice states. It is commonly adopted that in all metals and its compounds, electron-phonon scattering (ρ$_{e-p}$) and electron-electron scattering (ρ$_{e-e}$) are the most contribution dominant factors at sufficiently high and low temperatures respectively [18]. High pressure resistivity measurements are challenging task to put point electrical contact on the sample and have to survive at an extreme stress conditions. These methods of measurements are carried out in some single element and binary semiconductors materials such as Si, Ge [19] InP, GaP, GaSb and PbTe [10].
Cubic press techniques are now well established and powerful methods for measuring physical properties of materials to achieve very high pressure.

Heusler alloys have attracted considerable research attention in recent years due to the discovery of the interesting PR [20-21], ferromagnetic FSME [22-23], MCE [24-25], EB [26] and MR [27-31] in the ternary Heusler alloy Ni-Mn-Ga system. Magnetic and structural properties of Ni$_2$MnGa are strongly dependent on internal parameters such as interatomic distances, stoichiometry, density of 3d electron states, concentration of conduction electrons and d-d exchange interaction [32]. The application of hydrostatic pressure on Ni$_2$MnGa results in a decrease of the Mn-Mn distance, and thus causes a decrease of $T_M$ [33]. Martensitic phase transition with complex tetragonal structure occurs on cooling below 202 K which is correlated with transport and magnetic measurements [7]. Also in some single crystal Ni$_{2.14}$Mn$_{0.84}$Ga$_{1.02}$ and Ni$_{2.14}$Mn$_{0.92}$Ga$_{0.94}$ alloys reveals that volume changes of martensitic transformations with hydrostatic pressures are calculated by Clausius–Clapeyron equation and change in Curie temperature with pressures by Ehrenfest equation [34]. Intermediate phase appears between parent austenite and martensite phases in Ni$_2$MnGa under hydrostatic pressures, whereas new (X) phase is formed by uniaxial stress measurements [35]. However, as far as the authors are aware that there are few works on the effect of hydrostatic pressure on $T_M$ in Ni-Mn-Ga alloys [21, 36-37]. In transport measurements of Ni$_{2-x}$Mn$_{1+x}$Ga (x=0-0.20) [38] alloys one can observe the magnetic phase transition ($T_M$) and structural phase transition ($T_C$) temperatures which gets converged, ($T_M$ and $T_C$ are essentially identical) for x=0.18-0.20. Magnetic field influence of martensitic transformations on resistivity measurements of Ni-Mn-Ga alloys reveals that low hysteresis at pre-martensitic transition [30, Barandiaran et al].

We reports from our earlier work [21] that Ni$_{2-x}$Mn$_{1+x}$Ga (x=0, 0.15) alloy exhibits positive PR (x=0) and negative PR (x=0.15) with respect to pressures, static disorder and spin fluctuations are observed in x=0.15 alloy. Both large PR (122%) and MR (60%) are exhibited in Ni$_{45}$Co$_3$Mn$_{37.5}$In$_{12.5}$ Heusler single crystal by uniaxial measurements [39]. 5% of MR at room temperature is observed in Ni$_{2-x}$Mn$_{1-x}$Ga (x=0-0.2) [40, 41] which is interesting in magnetic and spintronic applications.
The calculation of activation energy \( (E_a) \) is an important way to determine the electronic band structure in Heusler alloys. This leads to identify the electronic properties of materials. However, only few reports change in \( (E_a) \) by pressure in manganites [42. R. Thiyagarajan et al]. Pressure effects on \( E_a \) are not reported in Ni-Mn-Ga Heusler alloys. Hence, we have opted these studies by Arrhenius plot.

As per our literature review, pressure effect on martensitic transition, piezoresistivity, electron scattering factor are not reported previously in the particular Ni\(_{2.2}\)Mn\(_{0.68}\)V\(_{0.12}\)Ga alloy. Hence, we carried out the above objective work.

### 4.2.2 Experimental techniques

Bulk polycrystalline ingots of nominal compositions Ni\(_{2.2}\)Mn\(_{0.6}\)V\(_{0.12}\)Ga\(_{1.08}\) is prepared by an arc melting technique using appropriate quantities of Ni, Mn and In in an argon atmosphere. After ensuring the homogeneity, these are annealed at 750°C for 48 h in an evacuated sealed quartz tube and subsequently quenched in ice-cold water. High pressure transport measurements are carried out using Cubic press is an most important instruments which is used to produce super high pressure and for processing and production of super hard materials like synthetic diamond, cubic boron nitride single crystals. The electrical resistivity is measured by standard four-probe technique in a cryogen free closed cycle refrigerator (Cryogenics Limited) down to 1.5 K at ambient pressure but the measurements under external pressure are done in a closed cycle refrigerator in the temperature range 100-300 K. A cubic anvil device is used for measurements upto a pressure of 80 kbar. The sample is immersed in a pressure medium of Daphne#7373 oil to maintain the hydrostatic pressure and encapsulated in a Teflon cell, surrounded by a pyrophyllite block. This block is evenly compressed from six directions using six tungsten carbide (WC) anvils. The six WC anvils crush the pyrophyllite gasket and compress the Teflon cell from six directions equally and the hydrostatic nature of the pressure is maintained beyond the solidification of the pressure medium. Furthermore, since the load from outside is controlled during cooling, pressure is kept constant in the course of the pressure cycle. The pressure is calibrated using Bi-resistive transitions of Bi I–II (25.5 kbar), Bi II–III (27 kbar) and III–IV (77 kbar) at room temperature [43].
4.2.3 Results and discussions

Temperature dependence of resistivity [\(\rho (T)\)] at different pressures range (0-80 kbar) of \(\text{Ni}_{2.2}\text{Mn}_{0.6}\text{V}_{0.12}\text{Ga}_{1.08}\) is represented in figure 4.2.1. The \(\rho\) is measured from 150-300 K. Particularly, it is taken from heating cycle for the convenience of experimental results. The \(\rho\) increases with increasing pressure, which indicates that metallic nature depressed with pressure. Similar kind of behaviour has been observed in \(\text{Ni}_{1.85}\text{Mn}_{1.15}\text{Ga}\) alloy by Devarajan et al [21]. A sharp \(T_M\) is appeared for ambient pressure from 230 to 245 K. The midpoint of the transition is taken as \(T_M\). The derivative of \(T_M\) and \(\rho\) with pressure (\(dT_M/dP\), \(d\rho/dP\)) are 0.4 K/kbar and 0.1\(\mu\Omega\).cm/kbar respectively. The \(T_M\) is shifted towards room temperature by the application of pressure. It is clearly viewed from the figure 4.2.1. The effect of pressure stabilizes the martensite phase.

![Figure 4.2.1](image)

**Figure 4.2.1** Temperature dependence of resistivity for \(\text{Ni}_{2.2}\text{Mn}_{0.6}\text{V}_{0.12}\text{Ga}_{1.08}\) alloy at various pressures.

The pressure dependence of (0-20, 20-40, 20-60 and 60-80 kbar) of \(\rho\) are measured at room temperature, for variation of is shown in the figure 4.2.2. Initially \(\rho\) increases sharply from 0-20 kbar. Further, increase in pressure shown a smooth change in the \(\rho\) is increased upto the region of 20-80 kbar region. The \(\rho\) is almost constant at higher pressures (\(\geq 60\) kbar). From this figure 4.2.2, it is clear that \(\rho\) increases with the
application of pressure at 300 K. The sample changes from metallic to insulating nature due to change in indirect exchange between the magnetic and non-magnetic atoms by the application of pressure.

Figure 4.2.2  Hydrostatic pressure dependence of resistivity at room temperature for Ni$_{2.2}$Mn$_{0.6}$V$_{0.12}$Ga$_{1.08}$ alloy.

The temperature dependence of piezoresistivity (PR) at difference pressures are given in the Figure.4.2.3. It is calculated using the relation

$$PR(T) = \left[ \frac{\rho_P(T) - \rho_A(T)}{\rho_A(T)} \right]$$  \hspace{1cm} (4.2.1)

Where, $\rho_P$ is resistivity at pressure P and $\rho_A$ is the resistivity at ambient pressure. It exhibits positive PR. The PR increases with increasing pressure around the $T_M$ region. The change in PR of $\sim 48\%$ is obtained at 80 kbar pressure. This similar behavior is observed in some other Heusler alloys in Ni$_{45}$Co$_5$Mn$_{37.5}$In$_{12.5}$ [39] and Ni$_{2-x}$Mn$_{1+x}$Ga (x=0, 0.15) [21].
Figure 4.2.3  Temperature dependence of piezoresistivity at different pressures for Ni$_{2.2}$Mn$_{0.6}$V$_{0.12}$Ga$_{1.08}$ alloy.

The hydrostatic pressure variation of PR and $T_M$ is presented in Figure 4.2.4. The $T_M$ is taken as the peak point of PR at each individual pressure. From these, we observed that the PR increases with pressure as increasing the $T_M$.

Figure 4.2.4  Pressure variation of both piezoresistivity and martensitic transition for Ni$_{2.2}$Mn$_{0.6}$V$_{0.12}$Ga$_{1.08}$ alloy.
Figure 4.2.5 shows variation of both $\rho_0$ and (A) with pressure for this sample. $\rho$ (T) at low temperature was fit to the following equation, $\rho(T) = \rho_0 + AT^n$ (n=2 at ambient pressure). The equation is modified as

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

(4.2.2)

The equation is fitted in low temperature region of 150-230 K. Where, $\rho_0$ is the residual resistivity at low temperature and (A) is electron-electron scattering factor. The $\rho_0$ occurs in the present alloys is due to the impurities or defects. The value of both $\rho_0$ and (A) increases with the application of pressure.

![Graph showing pressure variation of both residual resistivity ($\rho_0$) and electron scattering factor (A) for Ni$_{2.2}$Mn$_{0.6}$V$_{0.12}$Ga$_{1.08}$ alloy.](image)

**Figure 4.2.5** Pressure variation of both residual resistivity ($\rho_0$) and electron scattering factor (A) for Ni$_{2.2}$Mn$_{0.6}$V$_{0.12}$Ga$_{1.08}$ alloy.

At very low temperatures, the electron-electron scattering, impurity scattering and size effects become important contributions to electrical resistivity, in addition to the electron-phonon scattering.

There is an energy gap between valence and conduction band. If the thermal energy is sufficient to overcome the band gap, the electron becomes free to conduct. The expression of the resistivity can be written as follows,

$$\rho = \rho_0 \exp\left(\frac{E_a}{2kT}\right)$$

(4.2.3)
Where,

- \( T \) is absolute temperature,
- \( \rho_0 \) is absolute resistivity
- \( E_a \) is activation energy
- \( K \) is Boltzmann constant.

Figure shows Arrhenius plot \([\ln (\rho) \text{ vs } (1/T)]\) of \( \text{Ni}_{2.2}\text{Mn}_{0.6}\text{V}_{0.12}\text{Ga}_{1.08} \) alloy. Insert represents pressure dependent activation energy of this sample. It is observed that \( E_a \) is decreased with increasing pressures. This kind behaviour reveals that resistivity increases with scattering of electron by the application of pressure due to suppression of metallic nature.

![Arrhenius plot](image_url)

**Figure 4.2.6 Arrhenius plot:** Pressure variation of \( \ln (\rho) \) vs \((1/T)\), [insert: Pressure variant activation energy] for \( \text{Ni}_{2.2}\text{Mn}_{0.6}\text{V}_{0.12}\text{Ga}_{1.08} \) alloy.

### 4.2.4 Conclusion

We have examined the effect of hydrostatic pressure on \( T_M \) temperatures, PR and \((A)\) in the polycrystalline \( \text{Ni}_{2.2}\text{Mn}_{0.6}\text{V}_{0.12}\text{Ga}_{1.08} \) alloy. It permits depression of metal properties with increasing pressures. Also it exhibits positive PR (48%) near \( T_M \) region. The \( \rho_0 \) and \((A)\) values are increases with pressures. The Arrhenius plot reveals that \( E_a \) decreases with increasing hydrostatic pressures.
References


