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ARTICLE  in  JOURNAL OF PHYSICS D APPLIED PHYSICS  ·  FEBRUARY 2016
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Coupled magnetostructural transition in Ni-Mn-V-Ga Heusler alloys and its effect on the magnetocaloric and transport properties

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Received 22 July 2015, revised 15 October 2015
Accepted for publication 10 November 2015
Published 23 December 2015

Abstract
In the present work, the magnetocaloric and transport properties of Ni₂₂Mn₇₈₋ₓ₁₋ₓV₁ₓGa¹₈ (x = 0.0, 0.04, 0.08, 0.12) magnetic shape memory alloys are investigated. The alloys show a coupled magnetostructural transition from paramagnetic austenite to ferromagnetic martensite in a composition range of 0 ≤ x ≤ 0.08. For higher V substitution (x = 0.12), the martensite transition is lower than the conventional ferromagnetic transition. Large magnetic entropy change values of about 12.4, 16.2 and 19 J kg⁻¹ K⁻¹ and corresponding refrigeration capacities of 60.6, 82.5, and 103 J kg⁻¹ were observed for x = 0, 0.04 and 0.08 alloys, respectively. The above two parameters linearly increase with increasing magnetic field. The indirect adiabatic temperature change calculated from the heat capacity measurement is found to be at its maximum for x = 0.12 at H = 8 T. The magnetoresistance is observed to increase from 0 % (x = 0.12) to 28 % (x = 0) at the maximum field of 8 T. The Sommerfeld coefficients are almost the same for the parent and a V-doped sample, which reveals a low free electron density, and the Debye coefficients decrease with an increase in V doping, confirming the phenomenon of electron-phonon scattering. The critical exponents at second order magnetic transition for x = 0.12 are calculated as β = 0.482, γ = 1.056, δ = 3.021, which agrees closely with mean field theory.

Keywords: Heusler alloys, magnetocaloric effect, critical exponents, magnetoresistance and heat capacity

(Some figures may appear in colour only in the online journal)

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 in interest in magnetic refrigeration which is based on the magnetocaloric effect (MCE). The MCE is the temperature change of a magnetic material upon magnetization or demagnetization. Its discovery is attributed to Warburg [1] and it is employed to
achieve 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, and La-Fe-Si [2]. Lately, 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, this leads to diverse concerning phenomena such as magnetic shape memory effects (SME) [15,16] and magnetoresistance (MR) [17–22]. In particular, change in the elemental ratio of the 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 change from a high symmetry lower magnetic austenite phase (low magnetic moment) to a low symmetry martensite phase (high magnetic moment), and a second order transition from a paramagnetic (PM) austenite to a ferromagnetic (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 the 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 in achieving better functional properties. In this respect, the coupled magnetostructural transformations in Ni-Mn-Ga (In) have been studied [8, 42–45].

Many research groups have already reported on the doping of different magnetic (Co, Fe and Cr) [46–55] and nonmagnetic (B, In and V) [56–60] elements in various sites of Ni-Mn-Ga Heusler alloys. The substitution of Co at a Ni site stabilizes the austenite (A) phase and suppresses the martensite (M) phase [46–48]. However, Co at a Mn site has a strong effect on the A phase FM and weak AFM at the M phase due to the influence of Co spin on the nearest Mn–Mn atoms [49, 50]. Co at a Ga site of Ni36Mn23.5Ga25.5Co3 (x = 1–4) alloys enhances the M-AFM phase with the presence of an additional first-order transition below their martensitic transformation temperatures, as reported by Chen et al [51]. This effect can be attributed to the variation of intrinsic factors, i.e. a decrease in the unit-cell volumes and an increase in the electronic concentrations and density. The doping of Fe at an Ni site of Ni33.9Fe30.6Mn0.4Ga exhibits peculiar properties 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 ≤ 0.02 [52]. Further, an increase in the Fe content separates these transitions in such a way that martensitic transition (TM) decreases whereas Curie temperature (TC) is increased. The increase in the Fe content at the Mn site of Ni43.65Mn30.15Fe5Ga31.2 (x = 0, 2, 5, 8, 11) alloys results which a decrease in the degree of ordering so that both M and A transformation temperatures decrease [54]. Substitution of Cr at the Ga site of Ni30Mn32.8Cr0.4Ga18 (x = 0, 2, 4, 6) gradually decreases the TM due to the increase in unit-cell volumes and the decrease in the electron concentration [55].

Similarly, doping of nonmagnetic 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 the Mn site of Ni3Mn1.4Ga0.6 alloys are found to decrease both martensite phase and Curie temperatures, whereas doping of B at the Ga site of Ni3MnGa1.4B0.6 alloys up to x = 0.1 increases martensite and premartensite transformations (TM, TC) and slightly decreases the austenite Curie (Tc) temperatures [57]. In indium doped Ni37Mn16Ga25.5Inx (x = 0–8) alloys, the paramagnetic austenite (PM-A) phase of Ni-Mn-Ga alloys are significantly stabilized [58]. With the substitution of vanadium at the Mn site of Ni35Mn21.5VxGa25 (x = 0, 2, 4) the A-M transition temperature and the Curie temperature are decreased [59]. Substitution of V at the Ga site of Ni50Mn20.5Ga27.5V1.5 shows a partial transformation from A to orthorhombic M through an intermediate phase, as reported by Perez-Landazabal et al [60]. They measured the temperature dependent neutron diffraction patterns at 2, 130 and 240 K. The martensite transformation appears at around 40 K with an orthorhombic modulated structure at 2 K, whereas the L21 premartensite with a lattice parameter of 5.8 Å, and the L21 cubic austenite of cell parameter 5.82 Å, occur at 130 and 240 K, respectively. Thus the V doped sample undergoes transformations of austenite, premartensite and martensite phases similar to the Ni3MnGa [61, 62]. Thus the doping element, irrespective of its magnetic property, alters the transformation temperatures and width of the hysteresis, and consequently may affect its relative properties such as magnetoresistance, order of phase transition and magnetocaloric effect.

By keeping all these points in mind, we have selected Ni12.5Mn40.72–xVxGa1.08 (x = 0.0, 0.04, 0.08, 0.12) alloys, and investigated various phenomena such as transformation temperatures, the order of phase transitions, the magnetocaloric effect and MR through the structural, magnetic, transport, heat capacity and thermal measurements by tuning the temperature and magnetic field.

2. Experimental techniques

Polycrystalline ingots of Ni12.5Mn40.72–xVxGa1.08 (x = 0.0, 0.04, 0.08, 0.12) alloys are prepared by melting the high purity starting elements (99.9% pure), employing a vacuum arc melting furnace in a partial Ar atmosphere. The samples are remelted four times to ensure chemical homogeneity. These alloys are sealed in quartz ampoules and further annealed under a high vacuum at 1175 K for 36 h, followed by quenching in cold water. Elemental compositions of these alloys are determined using an x-ray energy dispersive spectroscope (EDS) setup with a scanning electron microscope (SEM, Leo 440i) and are found to be close to the nominal composition. For structural characterization, powder x-ray diffraction (XRD) is performed with a Philips 3121 x-ray diffractometer using Cu-Kα radiation at RT. The low
Figure 1. (a) Powder diffraction pattern of Ni$_{2}$Mn$_{0.72}$V$_{x}$Ga$_{0.08}$ ($x = 0$, 0.04, 0.08, 0.12) alloys at room temperature. (b) Powder diffraction pattern of Ni$_{2}$Mn$_{0.49}$V$_{0.11}$Ga$_{0.48}$ alloy at different temperatures.

temperature XRD measurements are also taken for $x = 0.12$. Differential scanning calorimetry (DSC) measurements are carried out in the temperature range of 200 K–360 K (DQ-100 system) to get the transformation temperatures. The magnetization measurements are performed by means of a physical property measurement system (PPMS-9T, Quantum Design, USA) using a vibrating sample magnetometer (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 to as zero field cooled (ZFC)). Followed by ZFC, again the data are collected upon cooling and warming without removing the applied field (referred to as field cooled (FC) and field warmed (FW)). Isothermal $M$–$H$ curves are measured at different temperatures near magnetic and structural transitions. The MCE is calculated from the $M$–$H$ curves using Maxwell relations. Transport ($\rho(T)$, $MR(T)$) and heat capacity [$C_p(T)$, $C_p(T)/T$] measurements are carried out using the PPMS-14 T. The adiabatic temperature change ($\Delta T_{ad}$) is calculated indirectly using the magnetic entropy change from the heat capacity data.

3. Results

3.1. Structural studies

Figure 1(a) shows the powder XRD patterns at room temperature (RT) for the Ni$_{2}$Mn$_{0.72}$V$_{x}$Ga$_{0.08}$ ($x = 0$, 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, $x = 0$, 0.04, 0.08 and 0.12, exhibit a 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 the $x = 0.12$ sample (figure 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.

3.2. Calorimetric studies

The temperature dependence of heat flow $Q(T)$ during warming and cooling cycles for Ni$_{2}$Mn$_{0.72}$V$_{x}$Ga$_{0.08}$ ($x = 0$, 0.04, 0.08, 0.12) Heusler alloys are shown in figure 2. The data collections are made with a warming and cooling rate of 20 °C min$^{-1}$. The exothermic and endothermic behaviors are observed in all the samples. These behaviors create transformations due to changes 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 1. The enthalpy ($\Delta H$) is measured by integrating the area under the curves in the transformation regions.

3.3. Magnetic studies

3.3.1. Temperature and magnetic field dependence of magnetization. In order to study the magnetic behaviour of M and A transitions in Ni$_{2}$Mn$_{0.72}$V$_{x}$Ga$_{0.08}$ ($x = 0$, 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 (figures 3(a)–(d)). The samples $x = 0$, 0.04 and 0.08 exhibit a single sharp transition by coupling both $T_M$ and $T_A$ during all the cycles (ZFC, FC and FW) of measurements (figures
Table 1. The calorimetric, magnetic, transport and heat capacity parameters of Ni$_2$ZnMn$_{0.72}$V$_x$Ga$_{1.08}$ ($x = 0, 0.04, 0.08, 0.12$).

| $x$ | $T_M$ (K) | $\Delta H$ (J g$^{-1}$) | Hyst $\Delta T$ (K) | $T_C$ (K) | $\Delta M/dH$ (KT$^{-1}$) | $\Delta \delta_M$ (J kg$^{-1}$ K$^{-1}$) | $C_p$ (J kg$^{-1}$ K$^{-1}$) | $\Delta T_{sd}$ (K) | RCP (J kg$^{-1}$) | $MR$ (%) |
|-----|------|-----------|-------------|------|----------------|----------------|-------------|-------------|-------------|-------------|------|
| 0   | 248  | 4.5       | 4           | 260  | 0.625         | 12.4          | 14.6        | 802         | 812         | 2.9          | 1.6 | 60.6 | 22 | 28 |
| 0.04| 274  | 5.4       | 4           | 285  | —             | 16.2          | —           | —           | —           | 82.5         | —   | —   | —  | —  |
| 0.08| 299  | 7         | 6           | 310  | —             | 19            | —           | —           | —           | 103          | —   | —   | —  | —  |
| 0.12| 219  | 3.6       | 6           | 267  | 0.35          | 10.3          | 27          | 1148        | 1164        | 1.41         | 8   | 35.8 | 0  | 1.5 |

Note: Calculation of hysteresis from magnetic measurements
$\Delta T = (M_s + M_l)/2 - (A_s + A_l)/2$. 
3(a)–(c)), whereas two separate transitions (\(T_M\) and \(T_A^C\)) are observed in the \(x = 0.12\) sample. Transition temperatures (\(T_M\) and \(T_A^C\)) for heating and cooling cycles are estimated from the derivative of the corresponding \(M(T)\) curves. It is interesting to note that \(T_M\) and \(T_A^C\) coincide for \(x = 0.0, 0.04\) and \(0.08\) samples and are the same for all the cycles, which suggests that the \(x = 0.0, 0.04\) and \(0.08\) samples have coupled FM (or PM)-A and FM-MM transitions. On the other hand, \(T_M\) and \(T_A^C\) of \(x = 0.12\) are different for each cycle, which shows the 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 the \(M(T)\) curves in figures 3(a)–(d) and the characteristic transformation temperatures of the 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, the \(x = 0.0, 0.04\) and \(0.08\) samples show the thermal hysteresis \(\Delta T\) between FC and FW cycles, suggesting the first order nature of transition (inset of figures 3(a)–(c)). It is calculated from the simple equation,

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

The \(\Delta T\) for all samples are presented in table 1. However, a small hysteresis (\(\sim 2K\)) between FC and FW is observed at \(T_A^C\) for the \(x = 0.12\) sample (inset of figure 3(d)), which may be due to the existence of local martensite variants in the austenite phase [64]. But the enlarged view of \(M(T)\) (insert of figure 3(d)) shows large hysteresis around \(T_M\) which indicates a strong first order transition. However, we found a weakening of the first transition and a strengthening of the second order transition with increasing temperature in \(x = 0.12\).

The magnetic field dependence of magnetization \(M(H)\) has been measured for all the samples across the transitions at 3 K intervals by increasing the magnetic field from 0 to 5 T and decreasing it from 5 to 0 T. The \(M(H)\) curves for \(x = 0.0, 0.04, 0.08\) and 0.12 are shown in figures 4(a)–(d), respectively. There are two common features in figures 4(a)–(c). There are three sets of \(M(H)\) curves, corresponding to below, above and at the \(T_M\) temperature. It is observed that \(M(H)\) shows PM (below PM-martensite or above PM-austenite) and FM behavior at below, above and at \(T_M\) respectively, for all samples. Hysteresis is observed at \(T_A^C\). 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 the \(x = 0.12\) sample, three sets of \(M(H)\) curves are also measured: at \(T_M\), below \(T_M\) and above \(T_M\); they correspond to FM-A (286 to 250 K), A to FM-A (235 to 226 K) and M (223 to 205 K) transitions, respectively, and no hysteresis is observed (figure 4(d)). Above the austenite transition, all the \(M(H)\) curves at different temperatures clearly exhibit a pure ferromagnetic nature in the \(x = 0.12\) sample. This confirms the presence of second order PM-FM transition in the austenite state.

### 3.3.2. Calculation of magnetocaloric effect

The coupled FM martensite-PF 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’s relation.
Figure 4. Isothermal magnetization of Ni$_{1.3}$Mn$_{0.72-}$, V$_x$Ga$_{1.08}$ $(x = 0, 0.04, 0.08, 0.12)$ alloys.

\[
\Delta S_M = \int_0^H \left( \frac{\partial M(H, T)}{\partial T} \right)_H \, dH.
\]  

(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 Ni$_{1.3}$Mn$_{0.72-}$, V$_x$Ga$_{1.08}$ $(x = 0.0, 0.04, 0.08, 0.12)$ alloys are shown in figures 5(a)-(d) respectively. The maximum of $\Delta S_M(\Delta S_M^{\text{max}})$ as a function of field for each sample is shown in an inset of the respective figure. It is observed that all the samples show negative $\Delta S_M$ which is an indication of conventional MCE. It is clear from figures 5(a)-(d) that the $\Delta S_M(T)$ shows a sharp peak with respect to coupled transition temperatures for the $x = 0.0, 0.04, 0.08$ samples. On the other hand, $\Delta S_M(T)$ for the $x = 0.12$ sample shows a sharp peak and a small hump with respect to M and FM-A transitions, respectively. A higher magnetic field (> 1 T) develops a large $\Delta S_M$ at the M phase of $x = 0.12$, the origin of the large $\Delta S_M$ is attributed to the change in magnetization caused by first order structural transition from the martensite to the austenite phase on heating [40]. Whereas, at a lower field (< 1 T) the sample shows inverse MCE, which is related to the large magneto crystalline anisotropy of the martensite phase and a similar effect is also observed for other ferromagnetic shape memory alloys: Ni$_{1.3}$P$_{0.7}$Mn$_{0.08}$Ga [5], Ni$_{1.7}$Mn$_{2.4}$Ga$_{2.8}$ [7] polycrystals and the Ni$_{0.82}$Mn$_{0.23}$Ga$_{1.8}$ single crystal [40]. Generally, the application of field increases the magnitude of $\Delta S_M^{\text{max}}$ and it increases linearly with the application of the field for all the samples, as shown in the corresponding inset figures of all samples. Values of $\Delta S_M^{\text{max}}$ for the magnetic field difference ($\Delta \mu_0 H$) of 5 T are observed to be 12.4, 16.2, and 19 J kg$^{-1}$ K$^{-1}$ for $x = 0.0, 0.04$ and 0.08, respectively, around coupled M and FM-A transitions, whereas it is 10.3 J kg$^{-1}$ K$^{-1}$ for the 0.12 sample. The rate that $\Delta S_M^{\text{max}}$ increases with field (d$\Delta S_M^{\text{max}}$/dH) has also been calculated for each sample from the insets of figures 5(a)-(d), and the values are 2.63, 3, 3.7 and 2.7 J kg$^{-1}$ 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 the increase in V doping up to $x = 0.08$, whereas it is reduced for the $x = 0.12$ sample. $\Delta S_M$ for $x = 0.08$ is 19 J kg$^{-1}$ K$^{-1}$ at 306 K, which is better than the value for Ni$_{57.6}$Mn$_{16}$Ga$_{21.1}$In$_{1.4}$ [58], which is 10 J kg$^{-1}$ K$^{-1}$ at 300 K.

The most classical parameter for quantifying 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

\[
\text{RCP} = \Delta S_M^{\text{max}} \times T_{\text{FWHM}}
\]  

(3)

The field dependence of RCP are shown for all the samples in figure 6 and the values of RCP are indicated in table 1. The variation of RCP with increased V doping at each field is shown in the inset of figure 6. It shows that RCP increases linearly up to $x = 0.08$ with the application of field. A large RCP$^{\text{max}}$ of 103 J kg$^{-1}$ at 5 T is observed for the $x = 0.08$ sample. This value is larger than that reported in the literature for similar kinds of alloys [9, 38, 39].

3.4. Heat capacity studies

Heat capacity measurements are performed for the evaluation of thermodynamic parameters such as $C_p$, $S_T$, and $\Delta T_{id}$ from
magneto transport properties, which is due to an increasing density of free electrons at low temperature in any solid material. The densities of electrons are explained by calculating the Sommerfeld coefficient ($\gamma$). Measurements of the temperature dependence of heat capacity ($C_p(T)$) are performed from 2 to 320 K with applied fields of 0, 5 and 8 T for $\text{Ni}_{2.2} \text{Mn}_{0.72-x} \text{V}_x \text{Ga}_{1.08}$ ($x = 0, 0.04, 0.08, 0.12$) samples, which are shown in figures 7(a) and (b) respectively. The peak value of $C_p$ for $x = 0, 0.12$ samples at 5 and 8 T are indicated in table 1. Further, figures 7(c) and (d) show $C_p/T$ versus $T^3$ for the same samples. A sigmoid $C_p-T$ plot shows a steady increase of $C_p$ from 2 to 265 K ($A_s$) and sharp peaks are observed around 250 and 270 K for the $x = 0$ and 0.12 samples, respectively. The upturn points ($T_s = 24$ K and $T_p = 117$ K) are the same for all the samples. The $C_p$ over the difference in the two points follows the relation

$$C_p(T) = \gamma T + \beta T^3.$$  
(4)

Further, the Sommerfeld coefficient ($\gamma$) and the Debye coefficient ($\beta$) are calculated from the linear fit of the $C_p$ versus $T^3$ plot using the above relation, and results are tabulated in table 2. We found that the Sommerfeld coefficients ($\gamma$) are almost the same for both the samples which means that free electron densities (FED) are evenly distributed. The Debye coefficient ($\beta$) changes slightly with the effect of V ion doping; this may be due to the domination of electron contribution over phonon contribution. $C_p(T)$ is used to determine both $\Delta S_m$ and $\Delta T_{ad}$ in $\text{Ni}_{2.2} \text{Mn}_{0.72-x} \text{V}_x \text{Ga}_{1.08}$ ($x = 0, 0.12$) alloys.

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

$$S(T)_{B_0} = \int_0^T \frac{C_p(T)B_0}{T} \, dT + S_0, B_0$$  
(5)

and

$$S(T)_{B_0} = \int_0^T \frac{C_p(T)B_0}{T} \, dT + S_0, B_0$$  
(6)

$$\Delta S_m = S(T)_{B_0} - S(T)_{B_0}$$  
(7)

where, $B_0$ and $B_0$ are final and initial fields.

The change in adiabatic temperature ($\Delta T_{ad}$) can be calculated using the Clausius–Clapeyron relation
Table 2. The Sommerfeld coefficient (γ) and Debye coefficient (β) of Ni_{x}Mn_{0.72−x}V_{x}Ga_{0.18} (x = 0, 0.12).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sommerfeld coefficient (γ) (J kg⁻¹ K⁻²)</th>
<th>Debye coefficient (β) (10⁻⁶ J kg⁻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>

\[ \Delta T_{ad} \equiv T \times \Delta S_{HF \rightarrow A} \times C_{p}^{-1}. \] (8)

The changes in adiabatic temperature (\(\Delta T_{ad}\)) are shown in figure 8 and are calculated from \(C_{p}(T)\) measurements for \(x = 0\) and 0.12 samples. It reveals that \(\Delta T_{ad}\) significantly changes with magnetic field for both the samples. The \(\Delta T_{ad}\) around \(T_M = \sim 250\) K decreases from 2.9 to 1.6 K for \(x = 0\), whereas it increases near \(T_C = \sim 270\) K from 1.4 to 8 K for the \(x = 0.12\) sample, with increasing field (5–8 T). These \(\Delta T_{ad}\) values are shown in table 1. The sharp peaks on the \(\Delta T_{ad}\) curve near \(T_M\) and \(T_C\) reveal the intrinsic nature of fast atomic redistribution with a damping of spin dynamics due to magnetic field [66].

3.5. Transport studies

In order to study the characteristics of FM-A and M transitions, the electrical transport property is carried out for the parent (\(x = 0\)) and the 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_{x}Mn_{0.72−x}V_{x}Ga_{0.18} (x = 0, 0.12) alloys, and they are shown in figures 9(a) and (b), respectively. The inset figures show an enlarged view around \(T_M\). It is clear from the main panel of the figures that both samples exhibit similar temperature dependent resistivity. By reducing the temperature, initially there is a gradual drop in resistivity, followed by the steep increase and then a gradual decrease in resistivity i.e. both samples exhibit a metallic nature below and above \(T_M\). For \(x = 0\), the \(T_M\) is 253 K during the cooling cycle at 0 T, which is almost equal to the temperature at which 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 the cooling cycle is 218 K, which is nearly equal to the temperature at which 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 in 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 hysteresis between the cooling and warming cycles around the M transition, suggesting the presence of first order transition. On the other hand, the application of magnetic field on the \(x = 0\) sample shifts both the cooling and warming curves towards the higher temperature region (inset of figure 9(a)), whereas there is no shift on \(x = 0.12\) (inset of figure 9(b)). The rate of change of \(T_M\) with field (\(d T_M/d H\)) is 0.625 and 0.35 K T⁻¹ (low value) for \(x = 0\) and 0.12, respectively, as presented in table 1. However, the magnetic field does not cause any change in the width of the hysteresis in either sample. In other words, the application of field stabilizes the first order transition around the M transformation for both the samples. This is because of the formation of a super zone boundary in the Fermi surface around the
M transformation of Heusler alloys, by the application of an external magnetic field [68]. In order to study the effect of magnetic field on resistivity in both the samples, the magnetoresistance (MR)

$$MR(\%) = \frac{\Delta \rho}{\rho_0} = \frac{\rho_{H} - \rho_0}{\rho_0}$$

has been estimated for different magnetic fields using $\rho(T)$ plots of both samples. Figures 10(a) and (b) show the temperature dependence of MR for $x = 0$ and 0.12, respectively. As the magnetic field increases in $x = 0$ up to 8 T, the MR sharply increases around $T_M$ and the plots are shifted towards the higher temperature region. We found that a $MR_{\text{max}}$ of 28% is observed at $T_M$ for the $x = 0$ sample, whereas there is no appreciable change in MR around $T_M$ in the $x = 0.12$ sample. The MR values at various fields for the samples are shown in table 1. The parent ($x = 0$) compound responds well to magnetic field due to the presence of pure ferromagnetic Ni ions, whereas an increase in V ions dilutes the magnetic subsystem around the transition. Hence, the $x = 0.12$ sample responds poorly to magnetic field [59].

3.6. Calculation of critical exponents

In order to verify the presence of second order transition, an Arrrott plot ($M^2$ versus $H/M$) is used for the $x = 0.12$ sample around the FM-A state, as shown in figure 11(a). It is clear from the Arrrott plot that the slopes of $M^2$ versus $H/M$ are positive over the entire range, as per the generalized approach of the first to second order phase transition from Banerjee criteria [69] results to authenticate the presence of second order transition for the $x = 0.12$ 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 the value for $T^A_C$ derived from $M(T)$ plots.

Generally, a system which is undergoing second order ferromagnetic transition should obey one of the common universality classes such as mean field, 3D Heisenberg, 3D Ising [70] and tricritical mean field [71]. These models have a 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 has been extremely useful for better understanding the nature of phase transition. The set of critical exponents $\beta$ (spontaneous magnetization), $\gamma$ (initial susceptibility) and $\delta$ (magnetization isotherm) are defined by the following equations:

$$M_s(0, T) = M_0(-\varepsilon) = 0, T < T_C$$ (10)

$$\chi_0^{-1}(0, T) = (h_0/M_0)(\varepsilon)^{\gamma} = 0, T > T_C$$ (11)

$$M(H, T_C) = D(H)^{1/\delta} = 0, T = T_C$$ (12)

where $M_0$, $h_0/M_0$ and $D$ are the critical amplitudes. $M_0$, $\chi_0^{-1}$ and $\varepsilon = (T - T^A_C)/T^A_C$ 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 $T^A_C$. The polynomial fitting of each curve and linear extrapolation above $T^A_C$ yields $M_0$ whereas below $T^A_C$ they yield $\chi_0^{-1}$. The temperature dependence of $M_0$ and $\chi_0^{-1}$ of the alloy is shown in figure 11(b). The Kouvel–Fisher method is used for the efficient and accurate determination of $T^A_C$ and the critical exponents $\beta$, $\gamma$ and $\delta$ [72]. The equations (10)–(12) are modified as per the Kouvel–Fisher method.

$$\frac{M_s(T)}{dM_s(T)/dT} = \frac{T - T_C}{\beta}$$ (13)

$$\frac{\chi_0^{-1}(T)}{d\chi_0^{-1}(T)/dT} = \frac{T - T_C}{\gamma}$$ (14)

$$\log M(H, T_C) = \frac{\log H}{\delta}$$ (15)

According to equations (13) and (14), $M_s(dM_s/dT)^{-1}$ versus $T$ and $\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}$ versus $T$ 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 $T^A_C$, can be determined using a $\log(M)$ versus $\log(H)$ plot at $T^A_C$.

Figure 11(c) shows the Kouvel–Fisher plots of $M_s(dM_s/dT)^{-1}$ versus $T$ and $\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}$ versus $T$. Both straight lines meet at the temperature axis, corresponding to a $T^A_C$ of 268 K. The values of $\beta$ and $\gamma$ for the sample are calculated from the reciprocal of the slopes of the $M_s(dM_s/dT)^{-1}$ versus $T$ and $\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}$ versus $T$ 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 $M(H)$ at 268 K. Figure 11(d) shows the $\log(M)$ versus $\log(H)$ plot at $T^A_C$ and the linear fit of this plot yields $\delta$ as 3.021. The reliability of the calculated value is obtained using the Widom scaling relation $\gamma = \beta(\delta - 1) = 0$, and the value is 0.09. The value of the critical exponents ($\beta = 0.482$, $\gamma = 1.056$, $\delta = 3.021$) are determined from the magnetic measurements, which match very well with the values from the mean field theory ($\beta = 0.5$, $\gamma = 1.0$, $\delta = 3.0$). This indicates that the $x = 0.12$ sample exhibits long-range ferromagnetic interactions around the FM-A state.
4. Discussion

Structural investigations are carried out to identify and understand the nature of phase transitions by varying both doping concentration (figure 1(a)) and temperatures (figure 1(b)) across the transformation region. All the samples exhibit cubic A phase at RT and, by increasing V, the lattice parameter 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 phases below T_M up to 15 K. Thus it is clear that the crystal structure is not varied by the effect of V doping in the present compounds. However, variation of temperature changes the crystal structure in the x = 0.12 sample.

Unequivocal signals are observed in the DSC (heating and cooling) curves which indicate the appearance of first order transitions during cooling or heating due to the changes between the M and A phases (figure 2). The observations of average T_M (255 K → x = 0, 279 K → x = 0.04, 304 K → x = 0.08 and 222 K → x = 0.12) from DSC almost correlate with our magnetic measurements. Also, the latent heat (enthalpy) of Ni_{0.2}Mn_{0.8}Ga is 9.6 J g⁻¹ [44] and it is comparatively less (x = 0: 4.5 J g⁻¹, x = 0.12: 3.6 J g⁻¹) with our present samples. Some of the doped systems like Co and Fe substitutions are not substantially modified, with a thermal entropy change (∆S) of close to the value of T_M in the Mn sites of Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6} and Ni_{0.2}Mn_{0.8}Ga_{0.2}Fe, systems, respectively [53]. However, a non-magnetic (V) ion (Ni_{1.2}Mn_{0.8}Ga_{0.4}Ca_{0.6}) increases the thermal entropy change (∆S) from 13.6 to 15.8 J K⁻¹ Kg⁻¹. Cr doped in the Mn site of Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6} (x = 0, 2, 4, 6) decreases the thermal entropy, as shown by Yun-qing et al. [55]. Therefore, thermal entropy (∆S) and enthalpy (∆H) are comparatively higher for V doped samples than other Co, Fe) doped compounds.

Similarly, the substitution and doping effects of different elements are drastically changed by some important factors like temperature transformations and e/a in the Ni-Mn-Ga system. The Fe doping level increases in the Mn site of Ni-Mn-Ga (Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6}), and Ni_{0.2}Mn_{0.8}Ga_{0.2}Fe exhibits narrow thermal hysteresis, which is involved in phase transformations due to the small driving force of chemical energy. Further, transition temperatures are decreased by increasing the e/a ratio, which is due to induced martensitic transformations by chemical pressure [54]. The suppression of phase transition temperature transformations are observed by Yun-qing et al. [55] in Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6} (x = 1, 2, 4, 6). Chen et al. [51] reported the effect of Co doping in both the Ga and Mn sites of Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6} (x = 1, 2, 4, 6). Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6} (x = 1, 2, 4, 6) samples and it is found that transformation temperatures (martensitic) and the e/a ratio are increased when the sample is Co doped in the Ga site. On the other hand, during Co doping at the Mn site the transformation temperatures are not much changed and there is a small variation in e/a. Shao Meng et al. [73] reported that phase transformation temperatures (martensitic) and e/a increase with Co in Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6} (x = 0, 2, 4, 6, 8) alloys. Also, the unit cell volume gradually reduces with increasing Co content, which may be related to the scattering factor of Co being lower than that of Ni and Ga. Addition of Co at the Mn site of the Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6} (x = 0, 2, 4, 6, 8) [50] system resulted that the of non-modulated tetragonal phase is stabilized by the higher Co content. AC susceptibility results of Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6} (x = Fe, Co) [49] reveal that Fe increases the martensitic transformation temperature (T_M) and decreases T_C, while Co doping shows the inverse effect. The M_S and T_C are almost linear with the doping of the Mn site by Fe in Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6} (x = Fe) [49] which exhibits an increase in e/a, when replacing Mn by either Fe or Co. On the other hand, both premartensitic (T_I) and intermartensitic (T_M) transition temperatures decrease with increasing Co, whereas T_C slightly increases, which are observed in Ni_{0.5}Mn_{0.5}Ga_{0.4}Ca_{0.6}Co (x = 0, 2, 4, 6) [53].

The effect of B substitution in the Mn site of the Ni_{0.5}Mn_{0.5}Ga_{0.4}Ga_{0.6} system has been studied by Gautam et al. [56]. It leads to a decrease in e/a (7.5 to 7.2) and transformation temperatures (T_C, T_M, T_M) due to the change in concentration of magnetic ions. However, the martensitic transition (T_M) temperature remains constant in the 7.5 ≥ (e/a) ≥ 7.4 interval and then it decreases with increasing B content. Another report from Gautam et al. [57] reveals that substitution of B in the Ga site of the Ni_{0.5}Mn_{0.5}Ga_{0.4}Ga_{0.6} system increases T_M and T_P due to the structure distortion and reduction of cell volume, whereas T_C decreases slowly with increasing B concentration in the 0 ≤ x ≤ 0.1 interval and it is attributed to the weakening of the exchange interaction. Aydogdu et al. [74] found that substituting B in the Ga site of Ni_{0.5}Mn_{0.5}Ga_{0.4}Ga_{0.6} alloys decreases the transformation temperatures, increases saturation magnetization and forms the (Ni, Mn, Ga)B phase. Hence, it is clear that investigations into Fe, Co, B, and V doping in different series of NiMnGa systems are essential in order to understand the phase transformations, construct new phase diagrams and to confirm the characteristic temperatures for the magnetostuctural behaviors.

It is well known that very large MCE has been observed in materials which have first order magnetostuctural phase transition (MSPT) [75] and both T_M and T_C couple together at the same temperature. The nature of first order MPT implies the exchange of latent heat and the presence of hysteresis. The simultaneous occurrence of both temperature and magnetic field hysteresis during MSPT requires a more complex description of the thermodynamics of a system. MPT leading to giant MCE at 240 K was first observed in Gd_{0.1}Si_{1.4}Ge_{2.2} [76]. The compound Gd_{0.1}Si_{1.4}Ge_{2.2} displays FM first order transition at 276 K and shows a better MCE (~24 J Kg⁻¹ K⁻¹), twice that of pure Gd [77]. Correspondingly, the replacement of Co by indium in Mn-Co-In-Ga compounds exhibits coupled MSPT and MCE [65]. Further, the coupling of both T_M and T_C have been reported in Ni_{0.5}Mn_{0.5}Ga_{0.4}Ga_{0.6} and Ni_{0.5}Mn_{0.5}Ga_{0.4}Ga_{0.6} systems [8, 39, 42, 44, 45]. The MSPT is observed in Ni_{0.5}Co_{0.5}Ga_{0.4}Ca_{0.6} (2 K) and Ni_{0.5}Co_{0.5}Ga_{0.4}Ga_{0.6} (1.2 K) with a high magnetic field of 60 T [78]. Also, polycrystalline Ni_{0.5}Mn_{0.5}Ga_{0.4}Ga (Aliev et al. [42]) and Ni_{0.5}Mn_{0.5}Ga_{0.4}Ga (Khvostov 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 the Ni_{0.5}Mn_{0.5}Ga_{0.4}Ga_{0.6} system.
alloy system at 4 T due to weak spin-phonon dispersion which results in a transition entropy change and is independent of the magnetic field [8]. Zhang et al. [58] report that partial substitution of indium at the Ga site of NiMnGa reveals that the PM-A phase is well stabilized and that MSPT can be tailored around RT. However, there are few reports on the MSPT and MCE of Co, Fe, Cr, B in the Mn site of the NiMnGa system. Min et al. [59] report that $T_a - T_m$, TC (325 - 265 K) and [$\Delta S_M$]TC (2.49 - 1.81 J kg$^{-1}$ K$^{-1}$) decreased with increasing V concentration, by the substitution of V in the 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 $T_C^A$) MSPT are represented in the $M(T)$ measurements (figures 3(a)-(d)) of our selected samples. The samples $x = 0, 0.04$ and 0.08 samples show that the coupled MSPT at 255, 280 and 306 K, respectively, which means that increases V doping up to $x = 0.08$ in Ni$_{52}$Mn$_{38-2x}$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 J kg$^{-1}$ K$^{-1}$) under ambient conditions. Whereas the $x = 0.12$ sample exhibits decoupling of MSPT due to the dilution of Mn by a higher percentage of V, which gives a lower MCE ($\Delta S_M = -10.3$ J kg$^{-1}$ K$^{-1}$) than the parent ($x = 0$) sample. The performances of a given material for solid-state refrigeration are typically analyzed by calculating the relative cooling power (RCP). The RCP is higher in the present system than those reported previously.

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 parameters, such as electron-electron scattering, electron-phonon scattering, electron-magnon scattering and spin disorder, which depend on the composition of the Heusler alloys. The phonon contribution increases as temperature increases. Many researchers have reported on transport and MR in Heusler alloys, since it is one of the potential candidates for spintronic applications. They are as follows: the NiMnSn and NiMnIn systems [21, 22] show a negative MR of 50% at 160 K [21] and 64% at 230 K [22], respectively. Both positive and negative MR values of $\sim 25$% have been observed in Ni$_{50}$Mn$_{25}$Ga$_{25}$ [33] single crystal, which depends on the twin variation and applied magnetic field of 1.2 T at 298 K. A wide range of negative MR values have been observed in the Ni$_{50}$Mn$_{40}$Fe$_{10}$Ga$_{25}$ ribbon at $T_M$ due to the redistribution of electrons and the increase in phase boundary scattering [35]. A spin-valve-like MR has been reported in Mn$_3$NiGa at RT [18]. A negative MR of 8% and MCE have been observed in nickel-rich Ni$_{52}$Mn$_{38}$Ga$_{25}$ Heusler alloys [79] where the structural and magnetic transitions almost coincide with each other. To date, we have found no reports on the MR effect of V (nonmagnetic element) doped NiMnGa alloy and it is reported for the first time in this work. From our results we infer that increasing V doping leads to the 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 the $x = 0.12$ sample at 1 T. With a further increase in field of up to 8 T, MR does not change in the $x = 0.12$ sample and this may be due to the dilution of magnetic phases by the nonmagnetic V ion. The observed MR values of V-free (Ni$_{52}$Mn$_{38}$Ga$_{25}$) and V-doped (Ni$_{52}$Mn$_{38}$V$_{0.12}$Ga$_{25}$) alloys are shown in table 1.

Heat capacity measurements are executed in order to calculate the 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$^{-1}$) and the Debye coefficient (8.377 $\times$ 10$^{-5}$, 9.43 $\times$ 10$^{-5}$ J K$^{-4}$ mol$^{-1}$) at 0 and 5 T for the Ni$_{50}$Mn$_{20}$Ga$_{27.6}$V$_{1.4}$ alloy [60]. On the other hand, Prasanna et al. [66] reported that partial substitution of Ni by Sn in Ni$_{51-2x}$Mn$_{30}$Sn$_{2x}$ (0 $\leq$ x $\leq$ 1.5) alloys exhibit inverse MCE (11.6 to 10.8 J kg$^{-1}$ K$^{-1}$), $\Delta T_{ad}$ ($\sim 26$ to $\sim 15.7$ K) and then the Sommerfeld coefficient, $\gamma$ = 0.10 J K$^{-2}$ G$^{-2}$, and the Debye coefficient, $\beta$ = 8.9 $\times$ 10$^{-4}$ J kg$^{-4}$, 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 tables 1 and 2. However, $\Delta T_d$ values are decreased ($x = 0$) and increased ($x = 0.12$) with magnetic field. As per the thermodynamic concerns, $\Delta T_d$ always inversely changes with $\Delta S_M$. Hence, from the heat transport measurements it is confirmed that $x = 0$, 0.04, 0.08 samples are more convenient with magnetic refrigeration than the $x = 0.12$ sample.

In order to understand the 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 values of the critical exponents for Ni$_{50}$Mn$_{30}$In$_{25}$Sb$_{15}$ [80] and Mn$_2$FeGe$_{15}$Si$_5$ (x = 0, 0.2) [81] are consistent with mean-field and 3D Heisenberg models, hence suggesting the presence of long range and short range magnetic orderings, respectively. Similarly, Au$_{63.8}$Fe$_{40.19}$, Ni$_{50.7}$Mn$_{29}$, Ni$_{50.7}$Mn$_{29}$ and amorphous a-Fe$_{50}$Zr$_{50}$ alloys correspond to the 3D Heisenberg model [30]. Long Phan et al. [82] report transformation of FM ordering from short to long range by increasing the doping concentration from 13 to 14 in Ni$_{50}$Mn$_{30}$-Sn$_{5}$, (x = 13, 14) samples. In the present study, the Banerjee criteria and the Kouvel–Fisher method are used for calculating the critical exponents analysis for the $x = 0.12$ 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 ($M^2$ versus $H/M$) near the $T_C^A$ region to find the exact second order transition ($T_C^A$), and then the critical exponents are calculated using Kouvel–Fisher plots. From these values it can be identified that $x = 0.12$ exhibits both first (minority) and second order (majority) phase transitions, which obeys mean field theory with long range FM order. The values of the critical exponents are compared with those of other samples in table 3.

5. Conclusions

In summary, we investigated the magnetocaloric and transport properties of Ni$_{52}$Mn$_{38}$V$_{0.12}$Ga$_{25}$ (x = 0, 0.04, 0.08, 0.12) Heusler alloys. The alloys show coupled magnetic-structural transition near room temperature for compositions below $x < 0.12$. The $\Delta S_M$ and $RCP$ linearly increase.
with increasing V concentration for the composition range 0 < χ < 0.08, where the coupled magnetostructural transition is realized, and after that decrease for higher substitutions of V (χ = 0.12), which does not show coupled magnetostructural transition. The ΔSM and RCP increase linearly with magnetic field strength for all the alloys. The χ = 0.08 sample is highly suitable for the magnetic refrigeration application, since it has a high ΔSM of 19 J kg⁻¹ K⁻¹ and an RCP of 103 J kg⁻¹ at room temperature. Transport studies reveal that all samples exhibit a metallic nature. The parent compound (χ = 0) is more suitable for magnetic recording applications due to its high MR (28%). The even distribution of free electron density and the domination of electron contribution over phonon contribution are confirmed by calculating the Sommerfeld and Debye coefficients from the heat capacity measurements. The critical analysis for χ = 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 temperature.

Acknowledgments

The authors acknowledge the DST (SERB, SERC, TSDP), BRNS, DRDO, CEFIPRA and UGC-RFMS for their financial support. The authors would also like to acknowledge the Defense Metallurgical Research Laboratory (DMRL), Hyderabad, for their support in carrying out sample preparation. The authors wish to thank S R Barman, UGC-DAE CSR Indore for fruitful discussions regarding the preparation of the manuscript. SS thanks the Alexander von Humboldt Foundation, Germany, for a research fellowship. The author R T thanks the NSRF (Grant no U1530402) Republic of China for the research fellowship.

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