Chapter - 3
Chapter-3

3. Pressure effect on magnetic and transport properties of Ni$_{2-x}$Mn$_{1+x}$Ga (x= 0, 0.15) Heusler alloys.

3.1 Investigation of the influence of hydrostatic pressure on the magnetic and magnetocaloric properties of Ni$_{2-x}$Mn$_{1+x}$Ga (x= 0, 0.15) Heusler alloys

3.1.1 Introduction

High-pressure studies have led to the discovery of new phase transformations. The effect of hydrostatic pressure will contribute emphatically to understand the properties of materials near the phase transformation and its mechanism. Among the different phases that exist in magnetic shape memory Heusler alloy systems, the austenite phase exists at high temperature and the martensite phase is at low temperature. Martensite phase transformation induces the spontaneous lattice strain in Heusler alloy materials at low temperature. Recently, Ni-Mn based alloys have attracted much attention for various applications owing to their interesting multi-functional properties such as SME [1,2], MCE [3,4], EB behavior [5] and MR [6-10]. In the above possible applications, the materials with MCE shows promise for use in solid-state cooling technology. Among these different magnetic shape memory alloys, Ni-Mn-Ga has been studied extensively, since it shows large magnetic field induced strain. These alloys undergo a first order structural transition from high temperature austenite phase to low temperature martensite phase and have large magnetocrystalline anisotropy in martensite phase as well as low twinning stress, that gives rise to a magnetic field induced strain. The variation in composition sensitively influences the phase transformations, crystallographic structures and magnetic properties in Ni-Mn-Ga alloys [11-16].

Hydrostatic pressures are known to play a significant role on the magnetic and structural properties of these systems [17-19]. The relative stability of the high temperature cubic phase and the low temperature martensite phase can be influenced by pressure. Magnetism in these alloys mainly arises from RKKY exchange interaction,
within the Mn atoms [20]. The Mn-Mn exchange interaction in Heusler alloys is strongly dependent on the Mn-Mn distance and it can be altered by either chemical substitutions (or) hydrostatic pressure. The experimental results in this regard suggest that the sign of the pressure derivative of $J_{\text{Mn-Mn}}$ is positive [21]. Recently, the effect of pressure on some of the Ni-Mn based systems has been reported [22-26]. Hydrostatic pressure effect on magnetic and martensitic transition shift towards higher temperature with decrease of $\Delta S_M$ in Ni-Mn-In magnetic superelastic alloys [22]. Albertini et al reported the pressure effects on MCE in Mn-rich and Ni-rich Ni$_2$MnGa alloy and found that the MCE decreases (increases) for Ni (Mn) rich alloy [23]. Kamarad et al [27] has studied the effect of hydrostatic pressure on magnetization of Ni rich Ni$_{2-x}$Mn$_{1-x}$Ga ($x=0, 0.15$) compounds and reported that pressure decreases $\Delta S_M^{\text{max}}$ at $T_M$. Further, Esakki Muthu et al [26] has reported the effect of hydrostatic pressure on $M$, and $\Delta S_M$ in Ni$_{50-x}$Mn$_{37+x}$Sn$_{13}$ ($x=2, 3$) alloys. Nayak et al [24] reported on NiCoMnSb alloy that the pressure enhances the stability of the martensite phase and decreases $\Delta S_M^{\text{max}}$ besides an upward shift in $T_M$. Hence, the application of pressure is seen to have a modest effect on the magnetic and MCE behavior of these Heusler alloys. However, till date only few reports are available on the pressure dependence of MCE in Mn rich Ni-Mn-Ga alloys [23]. Here, we report the pressure effect on magnetic and magnetocaloric properties of Ni$_{2-x}$Mn$_{1+x}$Ga ($x=0, 0.15$) alloys for various hydrostatic pressures.

### 3.1.2 Experimental techniques

The magnetization measurements are performed at various pressures by 9 Tesla Physical Property Measurement System (PPMS-9T) -Vibrating Sample Magnetometer (VSM) (Quantum design, USA) module equipped with the Cu-Be clamp type pressure cell with maximum pressure of 10 kbar [28]. The thermomagnetic data are recorded with VSM for both cooling and heating mode in the temperature range 2K-300K under ambient and high pressures upto 7.4 kbar for Ni$_{1.85}$Mn$_{1.13}$Ga ($x=0.15$) and 9.69 kbar for Ni$_2$MnGa ($x=0$) nominal compositions at a constant magnetic field of 0.01T. The isothermal magnetization $M$ ($H$) are recorded upto 5T at ambient and high pressure at different temperatures (180-250 K: $x=0$ & 130-160 K: $x=0.15$) across $T_M$. The materials preparation, characterization and other studies such as isothermal
magnetoresistance, magnetization on Ni$_{2-x}$Mn$_{1+x}$Ga (x=0, 0.15) alloys have been discussed elsewhere [29, 15, 32].

### 3.1.3 Results and Discussion

The temperature dependence of magnetization M(T) are measured for Ni$_{2-x}$Mn$_{1+x}$Ga (x=0, 0.15) alloys at 0.01 and 5 T (Fig. 3.1.1). On cooling from room temperature, in the case of Ni$_2$MnGa, a sudden drop in the magnetization occurs at 209 K in the field of 0.01 T, which indicates the martensitic start temperature (M$_s$=209 K). Further cooling below 188 K, (martensite finish temperature (M$_f$=188 K)) results in constant magnetization upto 5 K. The decrease in magnetization around T$_M$ is due to large magneto crystalline anisotropy in the martensite phase [30, 1]. Here, the T$_M$ is calculated using the relation T$_M$=(M$_s$+M$_f$)/2. The hysteresis is observed between cooling and warming cycles indicates the first order structural transition. Similar behavior is observed in the M(T) curve for Ni$_{1.85}$Mn$_{1.15}$Ga (i.e., x=0.15) at a field of 0.01 T (Fig.3.1.1b), which is in agreement with our earlier M(T) measurement at 0.01 T on Ni$_{1.84}$Mn$_{1.17}$Ga in the limited temperature range [32]. The observed M$_s$ values for x=0 and 0.15 are consistent with reported literature [31, 27, 32]. The various characteristic transition temperatures obtained from our M(T) curves are shown in Table 3.1.1 & 3.1.2 for x=0 and 0.15, respectively. It is found that the characteristic transition temperatures (M$_s$, M$_f$, A$_s$ and A$_f$) and T$_M$ decreases with an increase of Mn content at ambient pressure. The inset of Fig.3.1.1 shows the enlarged view of the M(T) data around T$_M$ measured at 5 T. The magnetic field of 5 T increases the magnitude of magnetization compared to the low field (0.01 T) for both x=0 and 0.15 (Fig.3.1.1). Also, the magnetization of the martensite phase is larger than the austenite phase at 5 T for both specimens. This is due to the orientation of magnetic domains in the field axis, which suppresses the magneto crystalline anisotropy in a high magnetic field of 5 T [33, 34]. Similar increase in magnetization with the application of magnetic field has also been observed in Ni$_{1.84}$Mn$_{1.17}$Ga, Ni$_{50+x}$Mn$_{25-x}$Ga (x= 0, 2, 3, 5) and Ni$_{1.75}$Mn$_{1.25}$Ga [32, 35, 36].
Figure 3.1.1 Temperature dependence of magnetization at \( H = (0.01 \text{ & } 5 \text{ T}) \) for (a) \( \text{Ni}_2\text{MnGa} \) and (b) \( \text{Ni}_{1.85}\text{Mn}_{1.15}\text{Ga} \) alloys.

Table 3.1.1 Transformation temperatures (\( M_s, M_f, A_s, A_f, T_M \)) with various hydrostatic pressures for \( \text{Ni}_2\text{MnGa} \) alloy.

<table>
<thead>
<tr>
<th>Pressure (kbar)</th>
<th>Transformation temperatures (K)</th>
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</thead>
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<tr>
<td></td>
<td>( M_s )</td>
</tr>
<tr>
<td>0</td>
<td>209</td>
</tr>
<tr>
<td>1.37</td>
<td>209</td>
</tr>
<tr>
<td>6.06</td>
<td>210</td>
</tr>
<tr>
<td>9.69</td>
<td>210</td>
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</tbody>
</table>

Table 3.1.2 Transformation temperatures (\( M_s, M_f, A_s, A_f, T_M \)) with various hydrostatic pressures for \( \text{Ni}_{1.85}\text{Mn}_{1.15}\text{Ga} \) alloy.

<table>
<thead>
<tr>
<th>Pressure (kbar)</th>
<th>Transformation temperatures (K)</th>
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<tbody>
<tr>
<td></td>
<td>( M_s )</td>
</tr>
<tr>
<td>0</td>
<td>137</td>
</tr>
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<td>133</td>
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<tr>
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<td>128</td>
</tr>
<tr>
<td>7.4</td>
<td>122</td>
</tr>
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</table>
Fig. 3.1.2 shows the $M(T)$ (both cooling & warming) at various hydrostatic pressures up to 9.69 kbar for $x=0$ and 7.4 kbar for $x=0.15$ at constant magnetic field of 0.01 T respectively. From Fig. 3.1.2(a) it is observed that $M_s$ increases marginally with pressure, which is due to the hybridization between Ni 3d and Mn/Ga an atom. Table. 3.1.3 Shows the pressure derivative of $M_s$ and $T_M$ compared with reported results. The hysteresis observed between cooling and warming curves seems to be broadened with increase of pressure. This broadening may be due to the change in magneto crystalline anisotropy at low temperature in the martensite phase. Similar pressure dependence has been reported by Kamarad et al in Ni$_2$MnGa [27], where the heating and cooling curve shows opposite trend compared to the present results.

Fig. 3.1.2 (b) shows the $M(T)$ curve at various hydrostatic pressures (0 to 7.4 kbar) for Ni$_{2-x}$Mn$_{1+x}$Ga ($x=0.15$). It is found that $M_s$ and $T_M$ decreases as the pressure increases ($dM_s/dP = -2.027$ K/kbar); $dT_M/dP = -1.081$ (K/kbar). However, Albertini et al [23] found that $T_M$ increases with pressure for Ni$_{1.9}$Mn$_{1.3}$Ga$_{1.8}$. The negative shift of $M_s$ favors the stabilization of the cubic austenite phase indicating that martensite phase is less stable with pressure. Moreover, significant changes occur in electronic structure under pressure may lead to the change in transition temperatures. However, pressure stabilizes the martensite phase in other FM shape memory alloys (FSMA)’s [37]. In addition, a large width of the hysteresis is noticed on increasing the pressure that is attributed to the enhancement of magneto elastic coupling with lattice strain, twin boundary motion and first order transition [38].

**Figure.3.1.2** Thermomagnetic curves (both cool & warm) of Ni$_{2-x}$Mn$_{1+x}$Ga ($x=0$, 0.15) alloys with various applied pressures at $H=0.01$ T.
Pressure derivative values of $T_M$ and $M_S$ for various NiMnGa (Sn) systems.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$dT_M/dP$ (K/kbar)</th>
<th>$dM_S/dP$ (K/kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$MnGa</td>
<td>0.619</td>
<td>0.103</td>
</tr>
<tr>
<td>Ni$<em>{1.85}$Mn$</em>{1.15}$Ga</td>
<td>-1.081</td>
<td>-2.027</td>
</tr>
<tr>
<td>Ni$<em>{2.15}$Mn$</em>{0.85}$Ga</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>Ni$<em>{1.9}$Mn$</em>{1.3}$Ga$_{1.8}$ [23]</td>
<td>1.7</td>
<td>-</td>
</tr>
<tr>
<td>Ni$<em>{2.15}$Mn$</em>{0.77}$Ga [40]</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>Ni$<em>{48}$Mn$</em>{39}$Sn$_{13}$ [26]</td>
<td>-</td>
<td>3.16</td>
</tr>
<tr>
<td>Ni$<em>{47}$Mn$</em>{40}$Sn$_{13}$ [26]</td>
<td>-</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Pressure dependence of $T_M$ for $x=0$ and 0.15 is shown in Fig.3.1.3. It is understood that $T_M$ increases as a function of pressure for Ni$_2$MnGa, whereas $T_M$ decreases for Ni$_{1.85}$Mn$_{1.15}$Ga. This phenomenon could be accounted for as follows. Increase of pressure would reduce the unit cell volume, which influences $T_M$ and other characteristic transition temperatures. Further, the alloys that exhibit lower volume change with pressure results in smaller shift in $M_S$. Kim et al., reported the pressure dependence of $T_M$ in Ni$_2$MnGa and Ni$_{2.14}$Mn$_{0.84}$Ga$_{1.02}$ and found a large volume change [39]. However, the volume change in our present alloys are lower than the reported Ni$_{50-x}$Mn$_{37+x}$Sn$_{13}$ (x=2, 3) [26] and Ni$_{50}$Mn$_{34}$In$_{16}$ [22]. The characteristic transition temperatures under different pressure are given in Table 3.1.1 and 3.1.2 for $x=0$ and 0.15, respectively.

The $M$ ($H$) curves have been measured for Ni$_2$MnGa near $T_M$ (180 K $\leq T \leq$ 250 K) at ambient and highest pressures. (Fig.3.1.4 (a, b)). The magnetization process is taken up into two steps: magnetic field is increased from 0 to 5 T and decreased from 5 to 0 T during the measurements. It is found that a field induced first order metamagnetic-like transition occurs at 220 K at ambient pressure for Ni$_2$MnGa (Fig.3.1.4 (a)). The insert of Fig.3.1.4 (a) shows this transition clearly. However, the metamagnetic transition vanishes at 9.69 kbar. Similar behavior has been observed by Mandal et al in Ni$_{2.208}$Mn$_{0.737}$Ga alloy [40]. From Fig.3.1.4 (b), the crossover in magnetization is observed in the $M$ ($H$) curve around 190-235 K. The magnetization is hard to saturate.
for temperatures 190 and 196 K indicating a martensite phase, whereas for
temperatures 223 K and 235 K the magnetization is easy to saturate, representing the
austenite phase. This may be due to the strong magnetocrystalline anisotropy around
$T_M$ in Ni$_2$MnGa at high pressure. Fig. 3.1.4 (c, d) shows the M (H) curve for $x=0.15$ at
ambient and highest pressure of 7.4 kbar. M (H) is measured in the range of 130
$K \leq T \leq 160$ K in steps of 2 K; however selected temperatures are plotted in
Fig. 3.1.4 (c, d) for the sake of clarity. At ambient pressure, the field induced
metamagnetic-like transition is observed in low field (0.68 T) at 146 K insert
(Fig 3.1.4(c)). However, this transition is suppressed at 7.4 kbar (Fig. 3.1.4(d)). Similar
to Ni$_2$MnGa, the crossover in magnetization has been observed between martensite and
austenite temperature for Ni$_{1.85}$Mn$_{1.15}$Ga at higher pressure of 7.4 kbar, as shown in
(Fig. 3.1.4(d)). Hence, the application of pressure induces the large magnetocrystalline
anisotropy in both the alloys.

![Graph](image)

**Figure 3.1.3** Pressure dependence of $T_M$ for Ni$_{2-x}$Mn$_{1+x}$Ga ($x=0, 0.15$) measured at
0.01 T under various hydrostatic pressures.
Figure 3.1.4 M (H) of Ni$_2$MnGa at different temperatures for (a) ambient and (b) 9.69 kbar pressure. M (H) of Ni$_{1.85}$Mn$_{1.15}$Ga at different temperatures for (c) ambient and (d) 7.4 kbar pressure.

The magnetic entropy change ($\Delta S_M$) for different pressures are measured using the Maxwell’s equation

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

(3.1)

$\Delta S_M$ is calculated from the above equation by numerical integration of the M (H) curves. $\Delta S_M$ as a function of temperature for various pressures is plotted in Fig.3.1.5. The application of pressure decreases the $\Delta S_M$ value from 19.21 Jkg$^{-1}$K$^{-1}$ (P=0 kbar) to 6.04 Jkg$^{-1}$K$^{-1}$ (P=9.69 kbar) for Ni$_2$MnGa. However, the peak temperature of $\Delta S_M$ (i.e. the temperature at which $\Delta S_M$ is maximum) increases towards higher temperature with pressure. Hence, it is possible to increase the peak temperature of $\Delta S_M$ towards room temperature with the application of higher pressure. The magnitude of $\Delta S_M$ decreases from 8.9 Jkg$^{-1}$K$^{-1}$ at P=0 to 1.27 Jkg$^{-1}$K$^{-1}$ at P=7.4 kbar for
Ni$_{1.85}$Mn$_{1.15}$Ga and the peak temperature of $\Delta S_M$ shifts towards low temperature. Similarly, for Ni rich Ni$_{2.208}$Mn$_{0.737}$Ga, $\Delta S_M$ decreases from 96 Jkg$^{-1}$K$^{-1}$ at P=0 to 86 Jkg$^{-1}$K$^{-1}$ at 8 kbar [40]. Further, for Ni$_{2.13}$Mn$_{0.85}$Ga composition, $\Delta S_M$ decreases from 24 Jkg$^{-1}$K$^{-1}$ at P=0 to 20 Jkg$^{-1}$K$^{-1}$ at 11.7 kbar whereas in Mn rich Ni$_{1.5}$Mn$_{1.3}$Ga$_{0.8}$, $\Delta S_M$ increases from 4.5 Jkg$^{-1}$K$^{-1}$ at P=0 to 6 Jkg$^{-1}$K$^{-1}$ at 12.2 kbar [23]. From the above results, it is understood that the pressure induces more MCE in large Mn excess Ni$_{2-x}$Mn$_{1+x}$Ga compositions compared to the x=0.15 composition studied here and the Ni excess Ni$_{2-x}$Mn$_{1+x}$Ga.

![Graph](image)

**Figure 3.1.5** Temperature dependence of magnetic entropy change for Ni$_{2-x}$Mn$_{1+x}$Ga (x=0, 0.15) alloys at various hydrostatic pressures.

### 3.1.4 Conclusion

The application of external magnetic field increases the magnetization for both Ni$_2$MnGa (x=0) and Ni$_{1.85}$Mn$_{1.15}$Ga (x=0.15). The hydrostatic pressure influences $M_s$ and broadens the hysteresis width in both the specimens. The observed metamagnetic transition at ambient pressure gets suppressed at higher pressure. Higher pressure also induces larger magnetocrystalline anisotropy. The effect of pressure on MCE is decreased in $\Delta S_M$ for both Ni$_2$MnGa and Ni$_{1.85}$Mn$_{1.15}$Ga.
References


3.2 Investigation on the electronic transport and Piezoresistivity properties of Ni$_{2-X}$Mn$_{1+x}$Ga (x=0, 0.15) Heusler alloys under hydrostatic pressure

3.2.1 Introduction

Band ferromagnetism is a significant phenomenon developed in several transition-metal compounds. High pressure studies can provide valuable information in electronic structure and electron-electron interactions in intermetallics. Among many of these studies, hydrostatic pressure [1] has been recognized as an effective tool to change physical and chemical properties in solids. Nevertheless, resistivity, piezoresistance (PR) [2] and pressure induced phase transition [3, 4] are renowned as an important phenomena that occur in Heusler alloys. PR is the change in resistance provoked by pressure effect was first discovered by Smith [5] in semiconductors (Si, Ge) possessing anisotropic energy with wide band structures. Further, they are being broadly used as stress and strain sensors [6]. Numerous kinds of Heusler alloy systems such as Ni-Mn-X (X = Sn, Ga, Si, Sb) have been extensively studied [7-26]. Among them Ni$_2$MnGa, a potentially well known magnetic shape memory alloy (MSMA) [7-9] has been considerably investigated material for both scientific and technological purposes and is known to exhibit various phenomena such as MCE, EB [10] MR and magnetic field induced strain (MFIS) [11-14]. It undergoes structural transformation from cubic austenite (high temperature, high symmetry phase) to low temperature martensite phase at T$_M$=202 K [15] and second-order paramagnetic to FM phase transition at T$_C$=376 K [4]. Further, with pressure the T$_M$ of this material is enhanced at the rate of 0.55 K/kbar. On the contrary, for Ni$_{1.85}$Mn$_{1.15}$Ga (T$_M$=138 K), T$_M$ is reduced at the rate of -1.08 K/kbar under constant hydrostatic pressure and magnetic field [16, 17]. Temperature dependent electrical resistivity $\rho(T)$, which is often used to distinguish metals from insulators and also band-gap insulators from the Anderson localized insulators, has been investigated for some of the Ni-Mn-Ga based Heusler alloys such as, Ni$_{2}$MnGa$_{1-x}$B$_x$ (x=0.03,0.05) [18], Ni$_2$MnGa$_{1-x}$In$_x$ (x=0.05-0.15) [4], Ni$_{2.16}$Mn$_{0.84}$Ga alloy [19],Ni$_{2+y}$Mn$_{1-x}$Ga (x=0-0.2) [20,21] and Ni$_{49.5}$Mn$_{25.4}$Ga$_{25.1}$, Ni$_{51.1}$Mn$_{24.9}$Ga$_{24}$ alloys [22]. Furthermore, the time dependent and field induced hump in the resistivity were also observed in Ga doped Ni-Mn-Sn alloy [23]. Clear view of
magneto structural transition has been investigated in Ni$_{2.18}$Mn$_{0.82}$Ga [24]. Temperature dependence of electrical resistivity under various hydrostatic pressures has been studied for Ni$_{2.14}$Mn$_{0.84}$Ga$_{1.02}$, Ni$_{2.14}$Mn$_{0.92}$Ga$_{0.94}$ and Ni$_2$MnGa single crystals [25,26]. Large value of piezoresistance and magnetoresistance under uniaxial stress has been observed in Ni$_{45}$Co$_5$Mn$_{37.5}$In$_{12.5}$ [27]. In this work, we investigate the effect of hydrostatic pressure on the resistivity and piezoresistivity (PR) of Ni$_{2-x}$Mn$_{1+x}$Ga (x=0, 0.15) magnetic shape memory alloys. We have also determined the $\rho_0$ and $(A)$ for the alloys.

### 3.2.2 Experimental techniques

The samples have been prepared by standard arc melting technique [28, 29, 30]. The compositions are determined using energy dispersive analysis of X-rays, which give the actual composition as Ni$_{1.99}$Mn$_{1.01}$Ga$_{1.00}$ and Ni$_{1.9}$Mn$_{1.15}$Ga$_{0.95}$ for x=0 (Ni$_2$MnGa) and 0.15 (Ni$_{1.85}$Mn$_{1.15}$Ga), respectively. High pressure resistivity measurements are performed by four probe resistivity technique. During measurements, the samples with four-probe contacts are dipped in a Teflon capsule filled with Daphane (#7074) and placed inside the Be-Cu clamp type hybrid pressure cell (30 kbar). Typical constant DC current of 80 mA is supplied by programmable constant current source (224, Keithely, USA), voltage is measured with nanovoltmeter (34420A, Agilent, USA), and temperature is controlled through temperature controller (Lakeshore, USA) and is automated with LABVIEW software in a personal computer. The pressure is applied externally to the pressure cell with 20 Ton hydraulic press and clamped with required pressure. The clamped pressure cell is loaded into the closed cycle refrigerator (CCR-VTI) setup (Cryo Industries, USA). The pressure is calibrated using Bi-resistive transitions of Bi I–II (25.5 kbar) and II–III (27 kbar) at room temperature and low temperature was attained (300-4 K) using CCR-VTI. Using a turbo molecular pump, the chambers of CCR-VTI has been evacuated up to $10^{-6}$ mbar. A small amount of helium gas is passed into the sample chamber of CCR-VTI while the sample is cooling, and the temperature of the sample is reduced by continuous running of the compressor. An external mechanical refrigerator extracts the warmer helium exhaust vapor, which is cooled and recycled.
3.2.3 Results and discussion

Temperature dependence of resistivity $\rho$ (T) is measured for polycrystalline Ni$_{2-x}$Mn$_{1+x}$Ga (x=0, 0.15) alloys at various hydrostatic pressures (0-30 kbar) in cooling and warming cycles. To show the features clearly, the warming curve has been given for all pressure (Figure 3.2.1) and the cooling-warming curves are given as an inset of Figure 3.2.1 for ambient and final pressure. At ambient pressure, $\rho$ decreases with decrease of temperature for x=0 (Figure 3.2.1(a)) and shows a small thermal hysteresis loop around martensite transition. This signifies the first order structural transition and the characteristic transition temperatures such as martensite start (M$_s$), martensite finish (M$_f$), austenite start (A$_s$) and austenite finish (A$_f$) are indicated in the inset of Figure 3.2.1(a). Similar $\rho$ (T) is reported for Ni$_2$MnGa by Maeda et al [26]. These authors observed a hysteresis loop at ambient and final pressure of 7 kbar. Our interesting observation is that at 25 kbar pressure, the hysteresis loop gets suppressed in x=0, and at 30 kbar, the hysteresis completely vanishes and it can be clearly seen in the inset of Figure 3.2.1(a). The increase of pressure decreases $\rho$ throughout the whole temperature range (4-300 K) and enhances the metallic nature in the alloy due to enhanced hybridization of valence band states by the application of pressure [18, 31, 32]. A signature of the pre-martensite transition (T$_{PM}$) observed at 260 K at ambient pressure for x=0. The signature of the T$_{PM}$ is not clearly observed at higher pressure, for example at 30 kbar (Figure 3.2.1(a)). The effect of magnetic field and hydrostatic pressure on T$_M$ and T$_{PM}$ of Ni$_2$MnGa system has been already reported [17, 33].

Similar $\rho$ (T) has been observed for x=0.15 (Figure 3.2.1(b)), where the application of pressure increases the $\rho$ due to the pressure induced phase transformation which indicates the phase changes from pre-martensite to martensite [25, 26]. However, overall $\rho$ for x=0.15 is lower than x=0. Moreover, in contrast to x=0, substantial thermal hysteresis is observed for all the pressure. The thermal hysteresis may be related to electronic structure compared to magnetic behavior [32, 34, 35]. The application of pressure shifts the transformation temperature to higher values, the clear view of transformations for x=0.15 are illustrated in the inset Figure 3.2.1(b).
Figure 3.2.1 Temperature dependence of resistivity for (a) Ni$_2$MnGa, (b) Ni$_{1.85}$Mn$_{1.15}$Ga alloys at various pressures. Inset: shows $\rho$ vs $T$ in the temperature region of 180–300 K for the pressure of 0 kbar and 30 kbar.

The Figure 3.2.2 shows the pressure dependence of $T_{av}$ [$T_{av} = (A_s+A_f)/2$, martensite to austenite transition] for $x=0$ and 0.15, which increases with the increase of pressure. The pressure derivative of $T_{av}$ for $x=0$ and 0.15 are 0.15 K/kbar and 0.82 K/kbar respectively. This indicates that the volume change with pressure is higher for Ni$_{1.85}$Mn$_{1.15}$Ga compared to Ni$_2$MnGa. The excess Mn atoms will occupy the Ga and Ni sites resulting in hybridization between Ni and Mn/Ga states in NiMnGa alloy [32]. The application of pressure increases the exchange interactions between Mn-Mn ions which enhance the hybridization between Ni and Mn/Ga. This needs more thermal energy to drive martensite transition which in turn increases the characteristic transformation temperature [36, 37]. An important aspects is that width of the hysteresis (given by the difference of $(A_s+A_f)/2$ and $(M_s+M_f)/2$) [38] decreases. This implies larger mobility of the twin boundaries with the application of hydrostatic pressure.
The temperature dependence of piezoresistivity (PR) of $\text{Ni}_{2-x}\text{Mn}_{1+x}\text{Ga}$ ($x=0$, 0.15) alloys at different hydrostatic pressures are calculated using the relation

$$PR(T) = \left(\frac{\rho_p(T)}{\rho(T)} - 1\right) \frac{\rho(T)_0}{\rho(T)}$$

where, $\rho_p$ is resistivity at pressure $P$ and $\rho$ is the resistivity at ambient pressure. Interestingly, PR has opposite sign for $x=0$ and 0.15, it is negative for the former and positive for the later composition (Figure 3.2.3). The maximum PR is observed at the martensite transition i.e. around $T_M$ for all pressures.

Inset of Figure 3.2.3(a) reveals that for $x=0$, negative PR increases gradually with pressure and the maximum -PR of 34 % is observed at 232 K for 30 kbar pressure. For $x=0.15$, a pronounced peak of PR is observed at $T_M$ and the application of pressure increases the +PR (inset of Figure 3.2.3(b)). The maximum +PR of 17% is observed at 154 K for the pressure of 28 kbar. The observed negative (positive) PR is due to the decrease (increase) in $\rho$ with pressure for $x=0$ (0.15) are shown in inset of Figure 3.2.3(a&b). Thus one could confirm that the PR of polycrystalline $\text{Ni}_2\text{MnGa}$ responds well with hydrostatic pressure. The PR behaviour is also observed in $\text{Ni}_{45}\text{Co}_{5}\text{Mn}_{37.5}\text{In}_{12.5}$ single crystal under uniaxial stress and a maximum PR of 122% was reported [27]. Hence, the Ni-Mn-Ga Heusler alloys are very much potential applications in spintronics area by exhibiting sign changes of PR.
Figure 3.2.3  Temperature dependence of piezoresistance at different pressures for (a) Ni$_2$MnGa, (b) for Ni$_{1.85}$Mn$_{1.15}$Ga alloys. PR vs P for Ni$_2$MnGa and Ni$_{1.85}$Mn$_{1.15}$Ga are shown in insets of Figure 3(a) and 3(b), respectively.

Figure 3.2.4 (a&b) shows variation of both residual resistivity ($\rho_0$) and electron scattering factor (A) with pressure for $x=0$ and 0.15. The $\rho_0$ and (A) are obtained by fitting the simple electrical resistivity equation, $\rho = \rho_0 + (AT^2)$ in the low temperature region 4-200 K and 4-130 K for $x=0$ and 0.15 respectively, and the fitted plots are shown in the inset of Figure 3.2.4 (a&b). The $\rho_0$ occurs in the present alloys is due to the impurities or defects. The (A) value at low temperature represents the electron-electron scattering [39]. From Figure 3.2.4 (a), the value of both $\rho_0$ and A decreases with the application of pressure for $x=0$. In contrast, for $x=0.15$ both $\rho_0$ and (A) increases with the application of pressure. The contrasting variation of (A) implies that the application of pressure suppresses (enhances) the electron-electron scattering for $x=0$ (0.15). For $x=0.15$, the static disorder due to the excess Mn atoms that occupy the Ni sites possibly responsible for increases in both the $\rho_0$ and (A) with pressure [40]. Another factor that might increase (A) could be related to the spin fluctuations due to Fermi surface nesting under pressure [41, 42].
Figure 3.2.4  Pressure variation of both residual resistivity ($\rho_0$) and electron scattering factor ($A$) for (a) Ni$_2$MnGa (b) Ni$_{1.85}$Mn$_{1.15}$Ga alloy. $\rho_0$ vs $T^2$ for Ni$_2$MnGa and Ni$_{1.85}$Mn$_{1.15}$Ga are shown in insets of Figure 4(a) and (b), respectively.

3.2.4 Conclusion

In summary, Ni$_2$MnGa and Ni$_{1.85}$Mn$_{1.15}$Ga alloys exhibit negative and positive piezoresistivity respectively, when subjected to hydrostatic pressure of 30 kbar and 28 kbar, respectively. The rate of change of $T_M$ and resistivity with respect to pressure has been calculated and shows positive values for both the samples. The $\rho_0$ and ($A$) are found to be decreased with pressure for Ni$_2$MnGa, which exhibit metallic behaviour, but both increase for Ni$_{1.85}$Mn$_{1.15}$Ga and it may be related to static disorder effects and spin fluctuations. These materials have tremendous potential applications in sensors and spintronics.
References


