Chapter 3

Investigations in the Ni-Mn-In and Ni-Mn-Sn alloys

In this Chapter we investigate the properties of Ni-Mn-In and Ni-Mn-Sn alloys, focusing particularly on the Ni$_{50}$Mn$_{34}$In$_{16}$ and Ni$_{50}$Mn$_{34}$Sn$_{16}$ alloys. These compositions were chosen from the phase diagram of the alloy systems published by Sutou et al. [3.1] (see Fig. 1.15 of Chapter 1) so that there is a transition from a ferromagnetic austenite (AST) phase to a ferromagnetic martensite (MST) phase as the temperature is lowered. With both the AST and MST phases being ferromagnetic, the alloys are expected to have interesting magnetic properties. Results of the measurements of the electrical resistivity ($\rho$), ac susceptibility ($\chi_{ac}$), dc magnetization ($M$) and heat capacity ($C$) as a function of temperature ($T$) and/or magnetic field ($H$) are presented in this Chapter. Our results confirm the presence of a temperature induced AST to MST phase transition in Ni$_{50}$Mn$_{34}$In$_{16}$ and Ni$_{50}$Mn$_{34}$Sn$_{16}$ alloys with lowering of the temperature. Our results also show that while in Ni$_{50}$Mn$_{34}$In$_{16}$ alloy MST-AST phase transition can also be induced by magnetic field, there is only weak signatures of such a transition in Ni$_{50}$Mn$_{34}$Sn$_{16}$ alloy. This magnetic field induced transition is correlated with the detailed nature of the temperature induced martensitic transition (MT) in the respective alloy. Further we have studied various physical properties of Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ and Ni$_{50}$Mn$_{35}$In$_{15}$ alloys. The results of these studies show that even in Ni-Mn-In alloys the nature of the MT is quite sensitive to the alloy composition.
3.1 Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} and Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} alloys: sample preparation and characterization

The alloys were prepared using the arc melting furnace technique described in section 2.1 of Chapter 2. Energy dispersive x-ray (EDX) analysis determined the actual compositions of Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} and Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} samples to be Ni\textsubscript{49.2}Mn\textsubscript{34.7}In\textsubscript{16.1} and Ni\textsubscript{49.8}Mn\textsubscript{33.5}Sn\textsubscript{16.7} respectively. In the subsequent discussion these alloys will be referred with their nominal compositions.

Fig. 3.1(a) and 3.1(b) present the room temperature x-ray diffraction (XRD) patterns of Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} and Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} respectively obtained with Cu K\textsubscript{α} radiation. The peaks in the XRD pattern of both the alloys can be indexed to the L2\textsubscript{1} structure. Type-I superlattice peaks, which are indicative of the presence of L2\textsubscript{1} ordering [3.2, 3.3], have been obtained along with the...
principal peaks. The peaks like (310), (321) and (332) observed in our data are ideally not allowed for stoichiometric composition with the L2₁ structure (peaks with \( h, k, l \) all odd or all even, only have non-zero intensity in stoichiometric L2₁ structure; see section 2.2.2 of Chapter 2). Their presence can be attributed to the site disorder in the samples as discussed in context with Heusler alloy structure in section 2.2.2 of Chapter 2. Average lattice constants calculated from prominent peaks are 6.011 Å and 5.999 Å for Ni₅₀Mn₃₄In₁₆ and Ni₅₀Mn₃₄Sn₁₆ respectively. These values match closely those reported for the same nominal composition of Ni–Mn–In alloy [3.4] and nearby composition of Ni–Mn–Sn alloy [3.5].

Rietveld fitting for the XRD pattern of the Ni₅₀Mn₃₄In₁₆ alloy using FULLPROF program [3.4] with L2₁ structure gives positions of the peaks correctly but does not match with the peak intensity/profile entirely. A better fit is obtained by taking into account also the possible B2 structure (see Fig. 2.7 and related discussion in section 2.2.2 in Chapter 2 for reduction of L2₁ structure into B2 with lattice constant half that of L2₁ structure). Such B2 structure may arise due to random distribution of Mn and In in this off-stoichiometric alloy. This Rietveld fitting is shown in Fig. 3.1(c). Lattice constant obtained from Rietveld fitting agrees with that obtained from the regular analysis mentioned above in the previous paragraph.

3.1.1 Temperature dependence of electrical resistivity of the Ni₅₀Mn₃₄Sn₁₆ and Ni₅₀Mn₃₄In₁₆ alloys

Fig. 3.2 presents resistivity (\( \rho \)) vs. \( T \) plot in the \( T \) range of 78–350 K for Ni₅₀Mn₃₄In₁₆ and Ni₅₀Mn₃₄Sn₁₆ measured in temperature ramping mode with ramp rate of 0.6 K/minute. In both the alloys there is a change in slope in \( \rho \) around 305 K with a lowering of \( T \). This is related with the paramagnetic (PM) to ferromagnetic (FM) transition in these alloys (this transition is inferred from temperature dependence of ac susceptibility and magnetization discussed in sections 3.1.2
Fig. 3.2: Temperature ($T$) dependence of electrical resistivity ($\rho$) of (a) Ni$_{50}$Mn$_{34}$In$_{16}$ and (b) Ni$_{50}$Mn$_{34}$Sn$_{16}$ alloys. Resistivity is normalized to its value at 300 K.

and 3.1.3 below). As $T$ is lowered further, $\rho$ exhibits an anomalous rise in both the alloys. A distinct thermal hysteresis is associated with this rise in resistivity. We will see in later sections that distinct features along with thermal hysteresis are also observed in the temperature dependence of $\chi_{ac}$ and $M$ of these alloys in the similar temperature range. Earlier, MT was reported in the same nominal composition of Ni–Mn–In alloy [3.5] and nearby composition of Ni–Mn–Sn alloy [3.6] in the same temperature range where this anomalous rise in $\rho$ is observed. So this feature can be attributed to the MT in these alloys. The associated thermal hysteresis is a manifestation of the first-order nature of this transition. The absence of any reversible region in the $\rho$ vs. $T$ plot in Fig. 3.2 for Ni$_{50}$Mn$_{34}$Sn$_{16}$ in the low $T$ side indicates that the MT is incomplete up to 78 K in this alloy. Though both the alloys undergo a MT around the similar temperature range, $\rho(T)$ shows significantly different behaviors across the MT in these alloys. While $\rho(T)$
increases over a wider T range in Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16}, the change in $\rho(T)$ is sharp and the transition extends over a relatively narrow T range in Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16}. This is indicative of a relatively broader MT in Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16}.

3.1.2 Temperature dependence of ac susceptibility of the Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} and Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} alloys

Fig. 3.3 presents $\chi_{ac}$ vs. T plot in the T range of 78–330 K for Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} and Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16}. In both the alloys there is a sharp rise in $\chi_{ac}$ around 305 K with a lowering of T, which is indicative of PM to FM transition in these alloys. The Curie temperatures ($T_C$) obtained from the point of inflection in the $\chi_{ac}$ vs. T plots are 305 and 306 K for Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} and Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} respectively. As T is lowered further, $\chi_{ac}$ exhibits an anomalous drop in both the alloys. A distinct thermal hysteresis is associated with this anomalous drop in $\chi_{ac}$. As mentioned earlier, MT has been reported in the same nominal composition of Ni–Mn–In alloy [3.5] and nearby composition of Ni–Mn–Sn alloy [3.6] in the same temperature range where this anomalous drop in $\chi_{ac}$ is observed. So this effect can be attributed to the MT in these alloys and the thermal hysteresis is related to the first-order nature of this transition. The absence of any reversible region in the $\chi_{ac}$ vs. T plot in Fig. 3.3 for Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} in the low T side indicates that the MT is incomplete up to 78 K in this alloy. It supports the inference drawn from the results of $\rho(T)$ measurements. Though Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} as well as Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} undergo an MT around the similar temperature range, the behavior of $\chi_{ac}(T)$ differs significantly across the MT in these alloys. While $\chi_{ac}$ decreases over a wider T range in Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16}, the change in $\chi_{ac}$ is sharp and the temperature hysteresis is relatively narrower in Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16}. This supports the inference drawn from results of resistivity measurement about the broader MT in Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16}. Further, in Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} $\chi_{ac}$ exhibits another feature within the MT region around 220 K where it shows a
local minimum followed by a local maximum with decreasing $T$. A possible explanation for these features in $\chi_{ac}$ is as follows. MT involves change in lattice parameters; as a result MST and AST phases may have different ferromagnetic characters and the Curie temperatures of the MST phase ($T_{CM}$) and of the AST phase ($T_{CA}$) may differ (a general discussion pertaining to $T_{CM}$, $T_{CA}$ and the MT temperature, can be found in [3.7].) In the present case $T_{CA}$ is the $T_C$ we have estimated from our experiment above. Now if $T_{CM}$ lies within the $T$ regime of MT, it will lead to a local minimum in the $\chi_{ac}(T)$ plot similar to what we have seen in Ni$_{50}$Mn$_{34}$Sn$_{16}$ (see Fig. 3.3). At the onset of MT near 240 K in Ni$_{50}$Mn$_{34}$In$_{16}$, the MST phase formed is in the paramagnetic state, so $\chi_{ac}$ decreases rapidly with lowering of $T$. As $T$ is lowered further, there is a paramagnetic to ferromagnetic transition in the MST phase within the $T$ regime of the MT and as a result $\chi_{ac}$ starts increasing, resulting in a local minimum. Below this PM to FM transition in the MST phase, $\chi_{ac}$

Fig. 3.3: Temperature ($T$) dependence of ac susceptibility ($\chi_{ac}$) of (a) Ni$_{50}$Mn$_{34}$Sn$_{16}$ and (b) Ni$_{50}$Mn$_{34}$In$_{16}$ alloys.
Fig. 3.4: Temperature ($T$) dependence of magnetization ($M$) of Ni$_{50}$Mn$_{34}$Sn$_{16}$ alloy ((a), (c) and (e)), and of Ni$_{50}$Mn$_{34}$In$_{16}$ alloy ((b), (d) and (f)) in various magnetic fields ($H$). The martensite start temperature of the austenite to martensite phase transition while cooling is indicated with vertical arrow. 

Figure 3.4:

- **Ni$_{50}$Mn$_{34}$Sn$_{16}$**
  - (a) $H=80$ kOe
  - (c) $H=1$ kOe
  - (e) $H=100$ Oe

- **Ni$_{50}$Mn$_{34}$In$_{16}$**
  - (b) $H=50$ kOe
  - (d) $H=1$ kOe
  - (f) $H=100$ Oe

decreases with decreasing $T$, which is possibly related to the difficulty in the magnetic domain rotation at low temperatures, and so $\chi_{ac}$ exhibits a local maximum. $T_{CM}$ lying in the temperature regime of the MT has been inferred from magnetization measurements for the same nominal composition of Ni–Mn–In alloy [3.5]. The absence of such a structure in $\chi_{ac}(T)$ in Ni$_{50}$Mn$_{34}$Sn$_{16}$ indicates that $T_{CM}$ of this alloy probably does not lie within its MT region.

### 3.1.3 Temperature dependence of magnetization of the Ni$_{50}$Mn$_{34}$Sn$_{16}$ and Ni$_{50}$Mn$_{34}$In$_{16}$ alloys

We have measured the temperature dependence of the magnetization in constant magnetic field for both the Ni$_{50}$Mn$_{34}$In$_{16}$ and Ni$_{50}$Mn$_{34}$Sn$_{16}$ alloys with field cooled cooling (FCC) and field cooled warming (FCW) protocols. In the FCC protocol $H$ was applied at 300 K
and $M$ was measured while cooling down to the lowest temperature of measurement. After the FCC measurements, $M$ was measured while warming up the sample in the presence of the same applied $H$ and this protocol is called the FCW. Figure 3.4 presents $M$ vs. $T$ curves for Ni$_{50}$Mn$_{34}$In$_{16}$ and Ni$_{50}$Mn$_{34}$Sn$_{16}$ measured in FCC and FCW protocols in the $T$ range 5–300 K and in various applied magnetic fields. We first discuss $M(T)$ curves in a magnetic field of 100 Oe (Figs. 3.4(e) and 3.4(f)). At $T = 300$ K Ni$_{50}$Mn$_{34}$In$_{16}$ and Ni$_{50}$Mn$_{34}$Sn$_{16}$ both are in the ferromagnetic phase as $T_C > 300$ K for these alloys. In the case of Ni$_{50}$Mn$_{34}$In$_{16}$, with lowering of $T$ there is a rapid fall in $M$ between 240 and 215 K. At 215 K there is a sharp minimum in $M$, which is followed by an appreciable increase in $M$ with further lowering of $T$. Also there is a thermal hysteresis in $M$. The sharp decrease in $M$ around 240 K and thermal hysteresis can be attributed to the MT occurring in this alloy. It is established that, depending upon the values of $T_{CM}$, $T_{CA}$ and MT temperature, the $M$ vs. $T$ curve of a ferromagnetic Heusler alloy can exhibit quite different features [3.7]. The sharp local minimum in $M$ around 215 K followed by a noticeable increase in $M$ with decreasing $T$ have the explanation that $T_{CM}$ lies within the $T$ regime of MT which we have already inferred from $\chi_{ac}$ data. Ni$_{50}$Mn$_{34}$Sn$_{16}$ also exhibits a decrease in $M$ with lowering in $T$ around 240 K and a thermal hysteresis, which can be attributed to MT occurring in this alloy. But $M(T)$ curve of Ni$_{50}$Mn$_{34}$Sn$_{16}$ shows no extra feature in the MT region like that in Ni$_{50}$Mn$_{34}$In$_{16}$. Further the increase in $M$ with decreasing $T$ below the MT region in Ni$_{50}$Mn$_{34}$Sn$_{16}$ is relatively small. This finds the explanation that in this alloy $T_{CM}$ is well above the $T$ regime of the MT. As a result there is no feature in the MT region and the increase in $M$ with decrease in $T$ in the MST phase is also small because this $T$ range is far below $T_{CM}$. This type of relationship between $T_{CM}$ and the MT temperature regime is reported for a nearby composition of Ni–Mn–Sn alloy [3.6]. $M(T)$ curves in higher magnetic field in both the alloys
reveal that transition temperatures of the MT shift to lower $T$ with increasing $H$. This shift is much larger in Ni$_{50}$Mn$_{34}$In$_{16}$ as compared that in Ni$_{50}$Mn$_{34}$Sn$_{16}$. Also $M$ in the AST phase has a higher value as compared to that in the MST phase in both the alloys. The MT in both the alloys has the similarity that the MST phase has a lower value of $M$ than the respective AST phase, in other words $M$ has positive temperature coefficient across the MT in both the alloys. However, the change in magnetization across the martensitic transition is much larger in Ni$_{50}$Mn$_{34}$In$_{16}$ as compared to that in Ni$_{50}$Mn$_{34}$Sn$_{16}$. The probable reason for the change in spontaneous magnetization can be the change in exchange interaction across the MT because of different lattice parameters in AST and MST phases. It should be noted here that an excess of Mn in these off-stoichiometric alloys as compared with the stoichiometric Ni$_2$MnIn and Ni$_2$MnSn, leads to occupation of a number of 4(b) sites in the L2$_1$ structure by Mn atoms [3.8]. There is an incipient antiferromagnetic (AFM) coupling between the magnetic moments of these excess Mn atoms and the magnetic moments of the Mn atoms occupying sites corresponding to the stoichiometric composition. This incipient AFM coupling can be strengthened further in the MT phase [3.8, 3.9]. Also the characteristic temperatures of the MT shift towards the lower $T$ side with increasing $H$ in both the alloys. On the other hand the MT in these alloys is somewhat different in character. The nature of variation of $M$ across the MT highlights the basic difference between the MT in these alloys. It is clear that the transition is rather broad in Ni$_{50}$Mn$_{34}$Sn$_{16}$. Also the jump in value of $M$ across the MT is smaller in Ni$_{50}$Mn$_{34}$Sn$_{16}$ than in Ni$_{50}$Mn$_{34}$In$_{16}$. Furthermore, the shift in temperatures of the MT with $H$ is substantially smaller in Ni$_{50}$Mn$_{34}$Sn$_{16}$. A smaller shift of MT temperature in Ni–Mn–Sn alloy as compared to that in Ni–Mn–In alloy has been observed for other compositions of these alloy systems [3.10].
3.1.4 Temperature dependence of heat capacity of the Ni$_{50}$Mn$_{34}$Sn$_{16}$ and Ni$_{50}$Mn$_{34}$In$_{16}$ alloys

Heat capacity has been measured for both of these alloys while warming in zero magnetic field. $C$ vs. $T$ data in zero magnetic field in $T$ range 5–300 K is presented in Fig. 3.5 for Ni$_{50}$Mn$_{34}$In$_{16}$ and Ni$_{50}$Mn$_{34}$Sn$_{16}$. The peaks in $C(T)$ correspond to the MT in these alloys. Ni$_{50}$Mn$_{34}$In$_{16}$ shows a sharp peak in $C$ while the peak in $C$ of Ni$_{50}$Mn$_{34}$Sn$_{16}$ is much broader. This supports our earlier inference from resistivity and magnetic measurements that the MT in Ni$_{50}$Mn$_{34}$Sn$_{16}$ is relatively broad.

Fig. 3.5: Temperature ($T$) dependence of heat capacity ($C$) of (a) Ni$_{50}$Mn$_{34}$Sn$_{16}$ and (b) Ni$_{50}$Mn$_{34}$In$_{16}$ alloys in zero magnetic field.
3.1.5 Magnetic field induced phase transition in the Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} and Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} alloys

Fig. 3.6 presents isothermal \(M(H)\) curves up to a maximum magnetic field of 80 kOe for Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} and Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} alloys. We have performed \(M(H)\) measurements at each temperature of interest starting from an initial state, which was prepared by cooling the samples from 300 K to the target temperature in zero magnetic field. Then isothermal \(M(H)\) measurements were performed by changing \(H\) from zero to 80 kOe and then back to zero. Figs. 3.6(a) and 3.6(b) present isothermal \(M(H)\) curves at representative temperatures in \(T\) regimes well outside the MT region. Figs. 3.6(c) and 3.6(d) present \(M(H)\) curves within the MT region. Isothermal \(M(H)\) curves are reversible in the \(T\) regime away from the MT region in both the alloys. This indicates the soft ferromagnetic character of the MST phase as well as the AST phase of these alloys. In the crossover regime of AST to MST phase transition, the isothermal \(M(H)\) curves exhibit a marked hysteresis. This hysteresis is not related to the ferromagnetic character of MST and AST phases but is a result of the magnetic field-induced first-order phase transition from MST phase to AST phase. In a ferromagnetic material the hysteresis arises due to domain wall pinning and/or anisotropy and has maximum width at \(H = 0\). In such a case the width of the hysteretic region increases with the lowering of temperature. But in the present case the hysteresis is almost zero at \(H = 0\). Further in the present case the hysteresis vanishes both on the lower and higher temperature sides of the MT regime. The distinct rise in \(M\) with increasing \(H\) and the associated hysteresis mentioned above are typical signatures of a magnetic field-induced first-order phase transition [3.11]. Such hysteresis related to magnetic field-induced phase transition is reported in other magnetic systems [3.12, 3.13] and also in Ni–Mn–In [3.5] and some Ni–Mn–Sn [3.14] alloys. Presence of magnetic field induced MST to AST phase transition in Ni-Mn-In alloy has been verified from neutron diffraction measurements in
increasing magnetic field \([3.9]\). In \(\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}\), the magnetic field induced phase transition leads to change in magnetization to the extent of the difference in the magnetization between the MST and the AST phases. However, in \(\text{Ni}_{50}\text{Mn}_{34}\text{Sn}_{16}\) the magnetic field induced phase transition is not able to change magnetization to the extent of difference in the magnetization between the MST and the AST phases. Thus the magnetic field-induced phase transition is much weaker in \(\text{Ni}_{50}\text{Mn}_{34}\text{Sn}_{16}\) than in \(\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}\). In \(\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}\) at certain temperatures the magnetic field induced MST to AST phase transition is completed in a magnetic field of 80 kOe. However, in \(\text{Ni}_{50}\text{Mn}_{34}\text{Sn}_{16}\) it appears that the magnetic field induced MST to AST phase transition is not completed up to magnetic field of 80 kOe.

\[\text{Fig. 3.6}:\] Representative isothermal magnetization \((M)\) vs. magnetic field \((H)\) curves of \(\text{Ni}_{50}\text{Mn}_{34}\text{Sn}_{16}\) alloy \((a)\) and \((c)\) and of \(\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}\) alloy \((b)\) and \((d)\) at constant temperatures. \(M(H)\) curves in \((a)\) and \((b)\) are in the temperature regime well away from martensitic transition region while those in \((c)\) and \((d)\) are within the temperature regime of the martensitic transition.
3.1.6 Possible reason for the difference in magnetic field induced martensite to austenite phase transition in the Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} and Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} alloys

We have noticed that while Ni\textsubscript{50}Mn\textsubscript{34}Sn\textsubscript{16} alloy shows only a weak signature of magnetic field induced MST to AST phase transition, this transition is quite prominent in Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16} alloy. This difference can be correlated with the character of the phase transition in the respective alloy. First we recall from Chapter 1 (see section 1.4.2) that the MT is characterized by four characteristic temperatures: MST start temperature $T_{MS}$, MST finish temperature $T_{MF}$, AST start temperature $T_{AS}$ and AST finish temperature $T_{AF}$. In the present case the magnetization in MST phase is smaller as compared to that in AST phase. Hence, $T_{MS}$ can be determined as the temperatures where magnetization starts decreasing while cooling the sample and $T_{MF}$ can be taken as the temperature where the thermal hysteresis in magnetization goes to zero in the low temperature side. Similarly, $T_{AS}$ can be taken as the temperatures where the magnetization starts increasing while warming the sample and $T_{AF}$ can be taken as the temperature where the temperature hysteresis in magnetization ceases to exist in the higher temperature side. $T_{MF}$ ($T_{AF}$) will be the limit of supercooling (superheating) in terms of standard phenomenology of a first-order phase transition [3.15]. It is worthwhile noting here that the AST to MST phase transition while cooling the sample as well as the MST to AST phase transition while warming the sample takes place over a finite width of temperature. This suggests the disorder-influenced nature of the transition [3.16, 3.17] (as discussed in section 1.3.4 of Chapter 1). Further, it is observed in Fig. 3.4 that $T_{MS}$ is greater than $T_{AS}$. This indicates the presence of a landscape of transition onsets in the present alloy [3.18]. We will explore this issue further in Chapter 5.
From the temperature dependence of the electrical resistivity, ac susceptibility, magnetization and heat capacity, we note the following points about the transition in these Ni$_{50}$Mn$_{34}$Sn$_{16}$ and Ni$_{50}$Mn$_{34}$In$_{16}$ alloys.

(i) The MT in Ni$_{50}$Mn$_{34}$Sn$_{16}$ alloy is quite broad as compared to that in Ni$_{50}$Mn$_{34}$In$_{16}$ alloy so the temperature span of $T_{MS}$ to $T_{MF}$ (also $T_{AS}$ to $T_{AF}$) is relatively larger in Ni$_{50}$Mn$_{34}$Sn$_{16}$ (see Figs. 3.2-3.5).

(ii) The temperature regime of MT as well reverse MT in both the alloys shifts to lower temperature side with increasing magnetic field. Thus the characteristic temperatures $T_{MS}$, $T_{MF}$, $T_{AS}$ and $T_{AF}$ shift to lower temperature side with increasing magnetic field (see Fig. 3.4). However this shift in Ni$_{50}$Mn$_{34}$In$_{16}$ alloy is much larger. Fig. 3.7 shows schematic variation of these temperatures with magnetic field. The magnetic field dependence of these characteristic temperatures will be discussed in detail in Chapter 5.

Fig. 3.7: Schematic showing magnetic field induced martensite to austenite phase transition in systems where characteristic temperature decrease with increasing field. Phase transition starts at magnetic field value $H_1$ and finishes at $H_2$. 

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The above two points help to understand qualitatively why there is a prominent magnetic field induced MST to AST phase transition in Ni$_{50}$Mn$_{34}$In$_{16}$, while this magnetic field induced transition in Ni$_{50}$Mn$_{34}$Sn$_{16}$ is quite weak. Consider the schematic shown in Fig. 3.7. When magnetic field is increased from zero isothermally, at certain magnetic field value $H_1$, $T_{AS}$ line is crossed resulting in the start of the MST to AST phase transition. At a certain higher magnetic field $H_2$, the $T_{AF}$ line is crossed resulting in the finish of the MST to AST phase transition. Such a transition is observed in Fig. 3.6. It is obvious from the schematic that a larger shift in characteristic temperatures with magnetic field and a smaller width of transition, will facilitate the magnetic field induced MST to AST phase transition. If the shift of characteristic temperatures is too small, a larger magnetic field is required to start the magnetic field induced transition. Over and above this, if the width of transition is also large, a still larger magnetic field is required to complete this transition. As noted above Ni$_{50}$Mn$_{34}$In$_{16}$ has a larger shift of characteristic temperature and a smaller width of transition as compared to that in Ni$_{50}$Mn$_{34}$Sn$_{16}$ which helps the magnetic field induced MST to AST phase transition in Ni$_{50}$Mn$_{34}$In$_{16}$ alloy. On the other hand, Ni$_{50}$Mn$_{34}$Sn$_{16}$ alloy with a smaller shift of characteristic temperature with magnetic field and a larger width of transition will require a much higher magnetic field than 80 kOe.

3.2 Sensitivity of the magnetic field induced phase transition in the Ni-Mn-In alloys to the composition

The above discussion on the experimental results suggests that Ni-Mn-In alloys are likely to exhibit a prominent magnetic field induced transition. In this direction we have investigated two more members of Ni-Mn-In family with nominal compositions: Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ and
Ni$_{50}$Mn$_{35}$In$_{15}$. The results of this investigation show that in Ni-Mn-In family the transition is also more sensitive to composition than indicated in the previously reported phase diagram (Fig. 1.15 of Chapter 1).

3.2.1 Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ and Ni$_{50}$Mn$_{35}$In$_{15}$ alloys: sample preparation and characterization

These alloys were also prepared in an arc melting furnace and given similar heat treatments as Ni$_{50}$Mn$_{34}$In$_{16}$. It was found that the samples with the nominal compositions Ni$_{50}$Mn$_{35}$In$_{15}$ and Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ had the average compositions of Ni$_{49.7}$Mn$_{35.1}$In$_{15.2}$ and

![Graph a](image1.png)

![Graph b](image2.png)

**Fig. 3.8:** The x-ray diffraction patterns for the (a) Ni$_{50}$Mn$_{35}$In$_{15}$ and (b) Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ alloy samples at room temperature.
Ni_{48.6}Mn_{35.1}In_{16.3} respectively as determined with EDX analysis. These EDX analyses were performed at nearly twenty locations on the samples. However, EDX may not be a suitable tool for resolving the very small composition differences in the Ni, Mn, and In concentrations as the error bar for EDX is of the order of 3 at. % for this alloy system. The chemical compositions of the samples were also determined through x-ray fluorescence (XRF) studies using a homemade spectrometer [3.19]. According to the XRF results, the samples with the nominal compositions Ni_{50}Mn_{35}In_{15} and Ni_{50}Mn_{34.5}In_{15.5} had the actual compositions of Ni_{50.1}Mn_{34.9}In_{15.1} and Ni_{49.3}Mn_{35.2}In_{15.6} respectively. The error bar for XRF is of the order of 0.2 at. % for these alloys. We will henceforth refer to these alloy samples as In-15 and In-15.5, respectively, based on the nominal composition alone.

The XRD pattern obtained for the In-15 sample is shown in Fig. 3.8. All the XRD peaks for this sample could be indexed for an orthorhombic crystal structure. Six XRD peaks (Nos. 1, 3, 4, 5, 6, and 7, starting from the left of the figure) in the 2θ range of 20°–80° match well with those observed by Pathak et al. [3.20], obtained for a sample of the same nominal composition. The positions of some of the peaks of our sample (Fig. 3.8(a)), appear to match with an unindexed XRD pattern reported by Bhobe et al. [3.21] for a sample of the same nominal composition. In spite of the matching of the most intense XRD peak, the XRD pattern presented in Fig. 3.8(a) looks quite different from that of Bhobe et al [3.21]. This difference is probably because of the fact that the actual composition (determined from EDX study) of the sample of Bhobe et al. [3.21] was Ni_{50.17}Mn_{34.59}In_{15.24}. The lattice parameters for our In-15 sample are found to be \( a = 17.678 \, \text{Å} \), \( b = 10.66 \, \text{Å} \), and \( c = 4.632 \, \text{Å} \), which are closer to the parameters reported by Pathak et al. [3.20] for the same nominal composition. Bhobe et al. [3.21], however,
have attempted to fit their XRD pattern to a B2 structure with a lattice parameter of 3.02 Å. The orthorhombic crystal structure derived from the XRD pattern of our sample indicates that the sample is in the MST phase at room temperature. Figure 8(b) shows the XRD pattern obtained for the In-15.5 sample. The XRD peaks corresponding to both the L2$_1$ and the orthorhombic structures were found in this pattern, indicating that both the AST and the MST phases are present in the sample at room temperature. The lattice parameters obtained from the analysis of the XRD results are $a = 6.020$ Å for the L2$_1$ phase, and $a = 18.156$ Å, $b = 10.786$ Å, and $c = 4.555$ Å for the orthorhombic phase. The lattice parameter for the L2$_1$ phase is quite close to that of our Ni$_{50}$Mn$_{34}$In$_{16}$ sample studied earlier (see section 3.1 of this Chapter). On the other hand, the lattice parameters for the orthorhombic phase are close to that of our In-15 sample mentioned above.

3.2.2 Temperature dependence of electrical resistivity of the Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ and Ni$_{50}$Mn$_{35}$In$_{15}$ alloys

Fig. 3.9(a) shows the temperature dependence of electrical resistivity $\rho(T)$ of In-15.5 in zero magnetic field. The temperature dependence of $\rho(T)$ depicted in Fig. 3.9(a) is quite similar to that of our Ni$_{50}$Mn$_{34}$In$_{16}$ alloy reported earlier. In zero magnetic field, a change in slope in the $\rho(T)$ curve is observed at around 312 K while cooling. A very similar kink in the temperature dependence of electrical resistivity was earlier observed in Ni$_{50}$Mn$_{34}$In$_{16}$ at the Curie temperature of that alloy. The kink in the present $\rho(T)$ curve could thus be the signature of the Curie temperature of the In-15.5 sample. On further cooling, a sharp rise in the electrical resistivity is observed near 250 K, which is also associated with distinct thermal hysteresis. As discussed earlier, in context with Ni$_{50}$Mn$_{34}$In$_{16}$, the sharp change in resistivity and the associated thermal hysteresis is attributed to the first-order AST–MST phase transition in the present sample. It is
Fig. 3.9: Temperature ($T$) dependence of resistivity ($\rho$) of the (a) $\text{Ni}_{50}\text{Mn}_{34.5}\text{In}_{15.5}$ and (b) $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ alloys in zero magnetic field.

Noted that outside this phase transition regime the temperature coefficient of electrical resistivity is positive, commensurate with the metallic nature of the present sample.

Figure 9(b) shows the electrical resistivity of In-15 as a function of temperature in zero magnetic field. In the zero magnetic field measurement, there is a sharp increase in resistivity below 365 K during cooling. Below 350 K, the resistivity continues to increase gradually until 150 K below which it decreases with the lowering of temperature. There is a clear thermal hysteresis in resistivity between 350 and 375 K. There is no signature of thermal hysteresis in any other temperature regime of measurement. As discussed for Ni-Mn-In alloys above, these off-stoichiometric Heusler alloys are known to undergo a first-order AST to MST phase transition with the lowering of temperature. It has been inferred from the XRD data in section
3.2.1 that the In-15 sample is in the MST phase at room temperature. Thermal hysteresis of an experimental observable is usually a signature of a first-order phase transition [3.15]. We, therefore, attribute the sharp rise in resistivity near 365 K, and the associated thermal hysteresis to the first-order nature of the AST–MST phase transition in the sample. As discussed earlier, the end points of the thermal hysteresis demarcate the limits of metastability (supercooling and superheating) [3.15] of this first-order AST–MST phase transition. It is clear from Fig. 3.9(b) that below 350 K the sample is certainly in the MST phase, a finding supported by XRD measurements as well. In Fig. 3.9(b) it is observed that within this MST phase the In-15 sample has a negative temperature coefficient of resistivity between 350 and 150 K. This is quite anomalous since metallic samples are expected to have a positive temperature coefficient of resistivity arising from electron–phonon scattering [3.22]. The resistivity maximum observed in Fig. 3.9(b) at around 150 K is quite interesting. The $\rho$ vs. $T$ results on a Ni$_{50}$Mn$_{35}$In$_{15}$ (nominal composition) sample has been recently reported by Bhobe et al. [3.23] Their sample exhibits a sharp rise in resistivity below 300 K (nearly 365 K in our case), which has been interpreted as an indication of the AST–MST phase transition. A broad maximum is also seen in their $\rho(T)$ curve close to 165 K, though its significance is not clear from their work. Clearly, the characteristic features observed in the $\rho(T)$ for the sample of Bhobe et al., occurs at temperatures different from those of the In-15 alloy. Furthermore, thermal expansion measurements reported by Pathak et al. [3.20] show a MT near 310 K for the same In-15 composition. This apparent mismatch between the results obtained by various authors highlights the need of characterizing the Ni–Mn–In family of alloys with a technique that can resolve very small differences in the actual composition. The effect of the anti-site disorder involving Ni and Mn also needs to be investigated, which could be important in deciding the nature of magnetic interaction in these
samples. Recently, a sharp rise in resistivity near and above 300 K and a broad maximum in $\rho(T)$ at a lower temperature has also been observed in some Ni$_{50}$Mn$_{25+x}$Sb$_{25-x}$ alloys [3.24] and Ni$_{50}$Mn$_{35}$In$_{15}$X (X = Si,Ge,Al) alloys [3.25]. While the sharp rise in resistivity has been interpreted as the indication of the AST–MST phase transition, the reason for the broad maximum was not stated. On the other hand, a somewhat similar broad maximum in $\rho(T)$ observed earlier in a Co$_2$NbSn shape memory alloy has been interpreted as the signature of the Curie temperature of that material [3.26]. We will see in later discussion that in the temperature regime between 350 and 250 K there is no magnetic ordering in zero magnetic field. We have performed the temperature dependent resistivity measurement in presence of 80 kOe magnetic field and found that there is almost no effect of magnetic field on the resistivity in the temperature regime between 350 and 250 K. This indicates the absence of any kind of magnetic ordering in this temperature regime even in the presence of magnetic field. We conjecture that the negative temperature coefficient of resistivity between 350 and 250 K may be related to the strain and disorder present in the system. The In-15 alloy being in the MST phase below 350 K, it is quite likely to be strained with respect to the AST phase. The effect of strain in the presence of twin boundaries in the MST phase could probably enhance the scattering of electrons and lead to such anomalous resistivity.

3.2.3 Temperature dependence of magnetization of the Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ and Ni$_{50}$Mn$_{35}$In$_{15}$ alloys

Fig. 3.10(a) shows the $M$ vs. $T$ curve (measured in FCW protocol) of the In-15.5 sample for $H = 100$ Oe. Qualitatively similar $M$ vs. $T$ curve has been observed previously in the Ni$_{50}$Mn$_{34}$In$_{16}$ alloy. The rise in $M$ around 312 K indicates a PM-FM transition in the alloy. This feature can be correlated with the kink on the $\rho(T)$ curve of the same sample observed at
around 312 K, and supports our earlier conjecture that this kink indicates the Curie temperature of the AST phase of In-15.5. The sharp drop in $M$ around 260 K has an associated thermal hysteresis (not shown in the Fig. 3.10), and this is correlated with the first-order nature of AST-MST phase transition.

Fig. 3.10(b) shows the $M$ vs. $T$ curve of the In-15 sample for $H = 100$ Oe obtained using the FCW protocol. The rise in $M$ near 150 K indicates PM to FM transition in the alloy. We have already inferred that in this temperature regime the sample is in MST phase. The magnetic character of AST phase (in In-15 alloy, AST phase appears at $T \geq 375$ K) could not be investigated because the high temperature range is not available in vibrating sample magnetometer (VSM) used for these investigations.

3.2.4 Magnetic field induced phase transition in Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ and Ni$_{50}$Mn$_{35}$In$_{15}$ alloys

Like Ni$_{50}$Mn$_{34}$In$_{16}$ alloy, isothermal $M(H)$ curves at temperatures away from the MST-AST phase transition in In-15.5 alloy show characteristics of a soft ferromagnet and within the
temperature regime of transition exhibit signature of magnetic field induced MST to AST phase transition. For example, Fig. 3.11(a) shows the isothermal $M$ vs. $H$ curve of the In-15.5 sample for $T = 230$ K starting from zero field cooled state. There is a clear signature of a magnetic field induced phase transition at about 25 kOe on the virgin magnetization curve. As discussed earlier in context of Ni$_{50}$Mn$_{34}$In$_{16}$ alloy, this transition is associated with a hysteresis which is quite different in nature compared to the hysteresis observed in the M(H) curves of a ferromagnet. The magnetic field hysteresis associated with this transition is attributed to the first-order nature of this magnetic field induced phase transition.

Fig. 3.11(b) shows the $M$ vs. $H$ curves for In-15 alloy obtained at 80, 120, 170, and 350 K. The $M$ vs. $H$ curves obtained above 150 K do not exhibit any signature of technical saturation. Absence of any spontaneous magnetization above $T = 150$ K has been confirmed using $M^2$ vs. $H/M$ plot or Arrott plot [3.27] constructed from the isothermal $M(H)$ curves.

![Figure 3.11](image.png)

**Fig. 3.11:** Isothermal magnetic field ($H$) dependence of magnetization ($M$) of the (a) Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ and (b) Ni$_{50}$Mn$_{35}$In$_{15}$ alloy samples.
3.2.5 Possible reason for contrasting magnetic behavior of the Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ and Ni$_{50}$Mn$_{35}$In$_{15}$ alloys

Our observations in Ni$_{50}$Mn$_{50-y}$In$_y$ (y = 15.5 and 15) show that the Ni-Mn-In alloy system is more sensitive to the composition in this regime of y (In-content) than what is apparent from the earlier phase diagram [3.1]. A concentration differences as low as 0.5 at. % causes a drastic difference in the properties of the alloy. While in case of y = 15.5 a magnetic field induced transition is clearly observed, there is no detectable signature of any magnetic field induced phase transition in the y = 15 alloy even up to magnetic fields as high as 80 kOe. The reason behind such extreme dependence of the functional properties of the alloys on the composition is not understood at present. However, it is known that the Ni–Mn–In off-stoichiometric Heusler alloys In is partially replaced by Mn at the 4(b) site of the stoichiometric compound [3.9], and the magnetic and structural transitions in this alloy system are sensitive to this off-stoichiometry [3.1]. We speculate that the sharp contrast of magnetic behavior between the y = 15.5 and y = 15 alloys may be related to the random distribution of Mn and In at the 4(b) site, though we had followed the same well documented preparation technique for both the alloys [3.5]. As discussed earlier, in Ni-Mn-X alloys, the Mn atoms occupying sites corresponding to the stoichiometric composition Ni$_2$MnX, are coupled ferromagnetically. On the other hand, in the off-stoichiometric alloys there is an incipient antiferromagnetic coupling between these Mn atoms (occupying proper Mn sites) and the excess Mn atoms (occupying In sites in present case). This incipient antiferromagnetic coupling might get strengthened in the MST phase [3.8, 3.9]. The excess Mn atoms can also have some magnetic coupling among themselves which will depend on their distribution at In sites. In Chapter 6 we will see that the magnetic properties strongly affect the AST-MST phase transition in these alloys. Recently, the effects of random distribution
of Mn and Fe in the 4(b) site of the Co$_2$Mn$_{1-x}$Fe$_x$Si Heusler alloys were probed by $^{55}$Mn nuclear magnetic resonance (NMR) [3.28, 3.29]. Such NMR studies could also be very informative in the present systems.

### 3.3 Conclusion

From the various experimental studies on the Heusler alloys Ni$_{50}$Mn$_{34}$Sn$_{16}$ and Ni$_{50}$Mn$_{34}$In$_{16}$ alloys, it is found that both the alloys undergo a martensitic transition from an austenite phase to a martensite phase with decreasing temperature in a similar temperature regime. Thermal hysteresis associated with a first-order phase transition has been observed in the temperature dependence of the physical properties. It has been found that the transition in Ni$_{50}$Mn$_{34}$Sn$_{16}$ alloy takes place over a comparatively broader temperature regime. Further we observed that the AST phase has larger value of magnetization as compared to that in the MST phase in both the alloys. It is also found that in both the alloys the transition shifts to lower temperature with increasing magnetic field. However, this shift is much larger in Ni$_{50}$Mn$_{34}$In$_{16}$ alloy. Further, isothermal magnetization measurements as a function of applied magnetic field show a prominent magnetic field induced MST to AST phase transition in Ni$_{50}$Mn$_{34}$In$_{16}$ alloy, while there is only weak signature of such magnetic field induced phase transition in Ni$_{50}$Mn$_{34}$Sn$_{16}$ alloy. The magnetic field induced phase transition has been correlated with the width of the transition and the shift of characteristic temperatures of the AST-MST phase transition in these alloys. Moreover, results of investigations on Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ and Ni$_{50}$Mn$_{35}$In$_{15}$ alloys show that while Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ alloy also undergoes magnetic field induced MST-AST phase transition, Ni$_{50}$Mn$_{35}$In$_{15}$ alloy exhibit no detectable signature of magnetic field induced transition up to magnetic field of 80 kOe. This dependence of field induced transition in the off-stoichiometric Ni-Mn-In Heusler alloys on the
small change in the composition may have origin in the random distribution of Mn and In atoms at 4(b) lattice site.

**Publications based on this Chapter:**

1. Magnetocaloric effect in Heusler alloys Ni$_{50}$Mn$_{34}$In$_{16}$ and Ni$_{50}$Mn$_{34}$Sn$_{16}$.


   **Sharma V. K.**, Chattopadhyay M. K., Kumar R., Ganguli T., Tiwari P., and Roy S. B.

2. Contrasting magnetic behavior of Ni$_{50}$Mn$_{35}$In$_{15}$ and Ni$_{50}$Mn$_{34.5}$In$_{15.5}$ alloys.
