Magnetic properties of Ga and Al-doped MnNiGe alloys

4.1 Introduction

In the previous chapter we have discussed how Fe doping at the Mn sites of MnNiGe alloy produces different magneto-functional properties. Now we are going to focus on Ge sites substitution with Ga (and Al) atoms in the MnNiGe alloy. We have prepared two samples with nominal compositions $\text{MnNiGe}_{0.928}\text{Ga}_{0.072}$ and $\text{MnNiGe}_{0.9}\text{Al}_{0.1}$ by the arc melting process. The magnetic properties of the samples will be discussed here. We will also investigate the impact of external hydrostatic pressure on the magnetic behavior of the Ga-doped sample.

4.2 Characterization

At room temperature both alloys are found to be in single phase hexagonal Ni$_2$In-type structure with space group $P6_3/mmc$. The room temperature XRD patterns with Rietveld refinement for both the alloys are shown in fig. 4.1. The lattice parameters and the goodness of fit ($\sigma$) and reliable parameters ($R_{WP}$ and $R_b$) of Rietveld refinement for both the samples are listed in table 4.1.
4.3 Results and discussions of MnNiGe$_{0.928}$Ga$_{0.072}$

4.3.1 Magnetization

The fig. 4.2(a) depicts the thermal variation of $M$ in ZFCH, FC and FCH protocols in presence of $H = 100$ Oe. $M(T)$ data show a sharp upturn on cooling at around 225 K, signifying the presence of PM to FM transition in the sample. On further cooling, $M(T)$ remains almost unchanged up to 150 K (during cooling only), followed by a rapid fall indicating the signature of MPT. The ZFCH data branch out from the FCH data below 150 K. The thermal hysteresis of about 30 K between FC and FCH data is an indication of the first order nature of the MPT. The sudden drop in the $M$ value around MPT is due to the FM-AFM transition associated with the MPT in Ga-doped MnNiGe alloys. [38]

To shed more light on the magnetic nature of the sample at different $T$ regions, we recorded isothermal $M$ data as a function of $H$ at selected constant temperatures (see fig. 4.2(b)). The linear nature of $M(H)$ data at 300 K confirms the PM nature of the high temperature austenite phase. However, for the isotherms below the FM
Table 4.1: Different parameters obtained from the Rietveld refinement of the room temperature XRD patterns.

Curie temperature \( (T_c) \) at 210 and 160 K, \( M \) rises with initial increase in \( H \) followed by a tendency of partial saturation at higher fields. This signifies typical FM-like austenite phase of the studied sample. Absence of complete saturation may be due to the presence of some other magnetic phase coexisting with the majority FM fraction. The magnetic moment of the sample at 50 kOe of applied \( H \) is found to increase with decreasing \( T \) in the high-\( T \) austenite phase. Interestingly, at 5 K, well below the MPT, the nature of the \( M(H) \) data is considerably different from that of the austenite phase. It shows “S” like behavior in the low field region and on further increase in \( H \), \( M \) starts to increase without showing any tendency of partial/complete saturation. This is a clear indication of the presence of a significant amount of AFM phase along with the FM fraction below MPT.

The parent MnNiGe alloy has layered structure. The inter layer Mn-Mn interaction (via Ge of the Ni-Ge layer) in the undoped alloy is reported to be spiral AFM in nature.\[13, 26, 27\] On the otherhand, Mn-Mn intra layer interaction is direct exchange type (short range) and due to the large intra layer Mn-Mn distance, it is non-magnetic in nature for the undoped alloy.\[13, 26, 27\] However, Ga doping at the Ge site breaks the spiral Mn-Ge-Mn inter layer interaction. In addition, Ga doping also induces FM interaction between Mn atoms of the same layer by reducing Mn-Mn distance. Even after Ga doping, there exists some unaltered Mn-Ge-Mn spiral AFM
Fig. 4.2: (a) Represents the temperature ($T$) dependence of magnetization ($M$) in presence of 100 Oe of applied magnetic field ($H$) in zero-field-cooled heating (ZFCH), field cooling (FC) and field-cooled heating (FCH) protocols respectively for MnNiGe$_0.928$Ga$_0.072$ sample. 

(b) Depicts the isothermal $M$ as a function of applied $H$ at different constant temperatures. 

interaction. This indicates the existence of a sizable AFM phase along with the majority FM fraction resulting in the partial saturating nature of the $M(H)$ isotherm in the FM austenite phase. On cooling below the MPT, formation of characteristic twin variants and change in lattice parameters (due to structural transition) result the loss of FM interaction among the Mn atoms in the same layer and AFM interaction starts to dominate.

4.3.2 Hydrostatic pressure effect on magneto-structural transition

We also examined the effect of $P$ on the magneto-structural properties of the studied alloy. FC and FCH magnetization data as a function of $T$ recorded at 100 Oe and at different constant $P$ are plotted in fig. 4.3(a). The FM-$T_c$ is found to be shifted towards higher $T$ with increasing $P$. About 5 K shift has been observed for the application of 4 kbar of pressure. On the other hand, the structural transition temperature remains almost unchanged with external $P$. However, a drastic increase in the magnetic moment of low-$T$ martensite phase has been observed. This is an
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Fig. 4.3: (a) Depicts the temperature variation of magnetization data in field cooling (FC) and field cooled heating (FCH) protocol at different applied hydrostatic pressure ($P$) in presence of 100 Oe of magnetic field for MnNiGe$_{0.928}$Ga$_{0.072}$ sample. (b) Shows isothermal variation of magnetization as a function of external magnetic field at 5 K in presence of different applied hydrostatic pressure.

indication of pressure induced AFM to FM transition in this alloy. To ascertain the presence of $P$-induced transition, we recorded isothermal variation of $M$ as a function of $H$ at 5 K (well below the MPT) under different constant applied $P$ as depicted in fig. 4.3(b). In presence of external pressure, $M(H)$ isotherm becomes FM like in nature with an initial increase in $M$ followed by a saturation with further increase in $H$. Application of external pressure also results a decrease in the lattice parameters and hence a decrease in the Mn-Mn intra layer distances. This makes the FM interaction strong enough to sustain ferromagnetism even below the MPT. Another possible explanation for this enhanced FM nature observed in high pressure condition is the partial suppression of huge volume expansion observed around the transition region and hence MPT. In presence of external $P$, due to the suppression of MPT, some of the austenite phase fraction (FM in nature) remain untransformed even at the lowest temperature of measurement (well below the MPT). Presence of such arrested FM austenite phase along with the AFM martensitic phase results a clear increase in the overall moment of the alloy.
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4.3.3 Magnetocaloric effect

Tempted by the observation of large change in magnetization near magnetic and structural transition, we have calculated the MCE (from Maxwell’s thermodynamical relation) of the sample using our magnetization data in ambient condition ($P = 0$ kbar) as well as in presence of external $P$ as depicted in fig. 4.4.

To calculate $\Delta S$ using Maxwell’s relation, isothermal $M(H)$ data at different constant $T$ are recorded in 5 K interval around the structural and magnetic phase transition regions, and are plotted in the main panel and inset of fig. 4.4(a) respectively. All the isotherms are recorded in a thermally demagnetized state, obtained
by cooling the sample from room temperature to 50 K and then heated back to the respective \( T \) of measurements in zero magnetic field. Between 125 and 170 K, we observed a clear signature of AFM to FM transition with increasing \( T \). Further increase in temperature results a decrease in saturation moment of the \( M(H) \) isotherm signifying FM to PM transition. The convoluted \( M \) versus \( T \) data at different \( H \), obtained from \( M(H) \) isotherms, for the present alloy are plotted in fig. 4.4(b). No mentionable shift has been observed both in structural and magnetic transition temperatures with increasing \( H \). Finally, the change in entropy due to the application of \( H \) has been calculated (by using equation 1.21 of chapter 1) and presented in fig. 4.4(c). In the present alloy, \( \Delta S \) is found to be positive (inverse MCE) around the first order structural phase transition with a peak value of 6.35 Jkg\(^{-1}\)K\(^{-1}\) (close to 160 K for \( H_0 = 50 \) kOe). On the other hand, it is negative (conventional MCE) near the PM to FM transition, with peak value \(-4.54\) Jkg\(^{-1}\)K\(^{-1}\) (close to 210 K for \( H_0 = 50 \) kOe).

### 4.3.4 Hydrostatic pressure effect on MCE

MCE in presence of different external \( P \) has also been investigated (see fig. 4.4(d)). Application of \( P \) results a drastic change in the MCE behavior of the alloy. No trace of inverse MCE (positive \( \Delta S \)) around the structural transition has been observed in presence of external \( P \). Possible reason behind this may be closely connected to the revival of FM interaction in the martensitic phase and hence a considerable decrease in the value of \( \Delta M \) around the MPT. However, only a small decrease in the peak value of negative MCE around the magnetic transition temperature is observed. On application of 4 kbar of external \( P \), peak value of \( \Delta S \) around the magnetic transition is found to be \(-3.86\) Jkg\(^{-1}\)K\(^{-1}\). In addition, a small increase in the peak width of negative MCE has also been observed (see fig. 4.4(d)). We also calculated the refrigeration capacity (RC) in ambient condition as well as in presence of external \( P \), of the studied alloy, which is a very important parameter for the development of MCE based refrigerator. For the present alloy, RC at 50 kOe is found to be -90.81 and
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4.4 Results and discussions of MnNiGe$_{0.9}$Al$_{0.1}$

The $M(T)$ behavior of the MnNiGe$_{0.9}$Al$_{0.1}$ alloy is similar to the Ga-doped sample. During cooling in presence of $H = 100$ Oe, the sample undergoes a second order PM to FM transition around 200 K. On further cooling the FM state transforms to AFM state in association with MPT around 115 K. The thermal hysteresis of about 20 K between FC and FCH data indicates the first order nature of the MPT. In order to get an understanding on the effect of magnetic field on the martensitic transition, the thermomagnetic variation at different fields is shown in fig. 4.5(a). It can be seen that the martensitic transition shifts to lower temperatures with increase in field. For the sample, $M_S$ is 106 K in a field of 1 kOe, which decreases to 102 K at 50 kOe.
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Fig. 4.6: (a) Presents the standard Arrott plot of the MnNiGe$_{0.9}$Al$_{0.1}$ sample. (b) Shows change in entropy ($\Delta S$) as a function of temperature ($T$), calculated from the magnetization data for MnNiGe$_{0.9}$Al$_{0.1}$ alloy.

These observation indicates that in presence of magnetic field the austenite state is preferred.

To understand the magnetic nature of the studied sample we have recorded the isothermal magnetization data as a function of $H$ at different constant $T$ on the heating leg (see fig. 4.5(b)). Linear variation of $M$ with $H$ at 300 K indicates the paramagnetic nature of the sample. At 200 K, which is at the region of ferromagnetic transition, presence of ferromagnetic state is observed in paramagnetic background. A ferromagnetic state is confirmed from the 150 K $M$-$H$ curve with the saturation moment of $\sim 55$ emu/g. $M$ shows nonlinear variation of $H$ at 100 K and 5 K and does not saturate with the higher value of $H = 50$ kOe. This indicates the antiferromagnetic nature of the sample at low temperatures.

Another way to check the order of the phase transition is Arrott plot analysis. According to Banerjee criteria, negative slope in Arrott plot indicates the first order nature of the phase transitions, whereas second order phase transition is determined by the positive slope. [164] Fig. 4.6(a) shows the Arrott plot obtained from the isothermal $M(H)$ data of the Al-doped sample. Clear negative slopes observed for 105 K to 115 K (which are around the MPT) data confirm the first order nature of the MPT.
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On the other hand, positive slope is seen for the curves around the 200 K indicating the second order nature of the PM to FM phase transition present in the alloy.

Large change in magnetization, both around the magnetic and structural phase transition, tempted us to investigate the MCE of the sample. The $\Delta S$ calculated from Maxwell’s relation is found to be positive around the region of first order phase transition, with a peak value $\Delta S_{\text{max}} = 15 \text{ J/kg-K}$ at 115 K for $H = 50 \text{ kOe}$. However, it is negative near the second order phase transition, with peak value $\Delta S_{\text{max}} = -5 \text{ J/kg-K}$ at 190 K for $H = 50 \text{ kOe}$ (see fig. 4.6(b)). The corresponding RC values are 150.4 J/kg and 142.92 J/kg respectively.

4.5 Summary and Conclusion

The present study indicates that the alloys MnNiGe$_{0.928}$Ga$_{0.072}$ and MnNiGe$_{0.9}$Al$_{0.1}$ depict both positive and negative MCE around the structural and magnetic transitions respectively. The studied alloys are fascinating examples among the MM$'$X alloys having both inverse and conventional MCE. Ga/Al doping in MnNiGe alloy induces ferromagnetism in otherwise antiferromagnetic alloy by affecting the lattice parameters and hence the bond lengths between different atoms. The alloys are found to lose their FM nature below MPT in ambient condition. Application of external $P$ results the revival of FM interaction below the MPT region. External $P$ has a drastic effect on the MCE behavior of the material also. The inverse MCE is found to be vanishingly small in presence of external $P$. However, a considerable increase in the RC value around the conventional MCE region has also been noticed. This indicates that the studied alloys become more efficient magnetic refrigerant around their conventional MCE region in presence of external pressure. Present work reveals that the studied alloys are good addition to the family of presently available intermetallic alloys having MCE.