Chapter 7

Comparison of effect of Sn and Sb on physical properties

We have replaced Al partially with Sb and Sn in Ni-Mn-Al system and investigated effect on magnetism, entropy change and magnetoresistance in the vicinity of martensitic transformation. Both the samples had identical lattice parameters and the Mn contents, that are mostly responsible for magnetism in these systems, yet there is marked change in magnetic and functional properties of these systems. It was found that the magnetization increased in Sb alloy, while entropy change and magnetoresistance decreased compared to Sn alloy. These changes are attributed to the change in antiferromagnetic interaction as a result of variation in the Ni d - Mn d hybridization arising due to presence of different sp element.

In the present chapter we shall compare $Ni_2Mn_{1.36}Sn_{0.40}Al_{0.24}$ and $Ni_2Mn_{1.36}Sb_{0.40}Al_{0.24}$ systems. We will refer to them as Sn and Sb systems further on. The identical composition and lattice parameter of the system make these systems ideal to study the effect of Z atom (Sn and Sb in present case) on the magnetic and functional properties of these systems.

As mentioned in section 1.3.3, main contribution to magnetism in Ni-Mn-Z alloys comes from the magnetic interaction between the Mn atoms. The interaction is sensitive to the distance, is predominantly FM in austenitic phase and is competing FM/AFM in martensitic phase. Recent experimental and theoretical work on Ni_2Mn-In system indicates that the origin of AFM interaction in martensitic phase is superexchange in nature, these interactions mediate through Ni-3d orbital. It is AFM between an Mn atom in regular Mn site and another Mn atom in Z site, but is ferromagnetic when Z is present at its site [29,31]. Khan et al. has shown that replacement of Cr with Mn in $Ni_{50}Mn_{37-x}Cr_xSb_{13}$ (x= 1 to 6) lowers the AFM interaction and argued that it occurs because of weakening of Ni-Mn hybridization [59]. But decrease in Mn content along with increasing Cr content and chances of Cr occupying Ni, Mn and Z site leaves other possibilities which can affect magnetism, wide open. For example previous study by the same author on Ni-Mn-Sb system showed that exchange bias effect increases with increased in Mn content, showing that change in AFM interaction in Cr replaced system could possibly be outcome of decreasing Mn content [37]. To avoid confusion, here we have studied systems with Sn and Sb system, where Mn and Ni content both remained the same and system had almost identical lattice parameters. Hence such study will make comparison of Ni-Mn hybridization more pertinent and may lead to better understanding of magnetism in Ni-Mn-Z system.

Usually the comparison of magnetic property of the system with different fractions of Z element is hindered by the fact that the electron concentration and Mn-Mn distance (lattice parameter) both changes with change in composition. Since these are kept same here, our study will help better understand the underlying mechanism of the functional capabilities thus may pave the way for development of better FSMA.

7.1 Comparison

The resistivity measurements were performed using four probe techniques in 10 T and 14 T setup from Cryogenics.

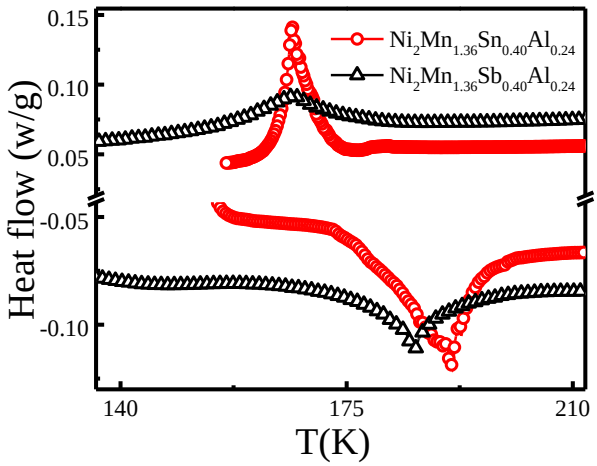

Figure 7.1 DSC curves obtained for Sn and Sb based samples in cooling and heating cycles performed at the rate of 10 K/min.

The XRD patterns obtained at room temperature for Sn and Sb samples were given in the Chapter 3. Rietveld refinement of the sample showed that it was in austenitic phase with $L2_1$ structure and lattice parameter of 0.593 nm for both samples [35]. Structural transformation temperatures were determined form DSC curves which are shown together in Figure 7.1 for comparison. The M_s, M_F, A_S and A_F temperatures were found to be 189 K, 154 K, 158 K and 207 K respectively for $Ni_2Mn_{1.36}Sb_{0.40}Al_{0.24}$ and were 171K, 158 K, 168K, and 196K, respectively for $Ni_2Mn_{1.36}Sn_{0.40}Al_{0.24}$. The M_S of the Sb alloy is slightly higher than that of Sn alloy [35]. This was consistent with the fact that with increase in electron concentration the transformation temperature increases.

As per a phenomenological theory of martensitic transformation, thermal hysteresis at MT with higher slope indicates presence of boundary friction, elastic strain energy and interfacial energy [98,134]. It was found that thermal hysteresis at MT in case of Sn system was 10 K ($\Delta T_H = A_S - M_F$) where as it was 4 K for Sb system. Narrower thermal hysteresis in case of Sb alloy indicates that there is lesser boundary friction compared to Sn alloy. The slope of transformation was found to be greater in case of Sb alloy. The larger elastic strain energy and interfacial energy resist the martensitic and reverse transformation, thus increasing the slope of transformation. This indicates that Sb system

will have better phase transition response time and more strain energy across MT [98,134].

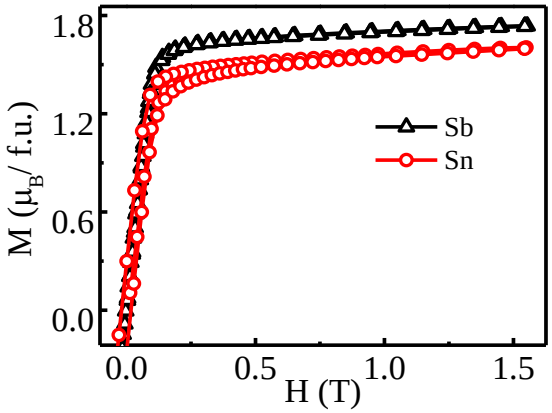

Figure 7.2 M-H measured at 300 K for Sn and Sb samples.

The T_C of Sb alloy was determined to be 355 K, whereas that of Sn alloy was 326 K [35] (Sections 3.1 and 3.2). Higher T_C in case of Sb alloy shows that Sb in the system enhanced ferromagnetic exchange. M-H measurements were performed at 300 K up to a field of 1.5 T for both the samples and the obtained results are shown in Figure 7.2. It can be seen that the magnetic moment of Sn system is 1.60 μ_B /f .u. and that of Sb system is 1.73 μ_B /f .u., which is higher in case of Sb system. As mentioned earlier in Ni_2Mn-Z system magnetism is mostly carried by Mn atom. Both the systems were in ordered $L2_1$ structures with the same Mn-Mn distances and contents of Ni and Mn were same for both, so only difference is that they have different atoms at the Z sites. The presence of different atoms at Z site affected p-d hybridization between Ni and Z (also Ni and Mn) differently, which in turn affected the interaction among the different Mn atoms. This possibly gave rise to different magnetizations in these two systems.

These samples transform from a predominantly FM state (austenitic) to a state with lower magnetization state (martensitic) within a window of few Kelvins. This results in large change in magnetization (ΔM) across martensitic transformation giving rise to properties like magnetocaloric effect and giant magnetoresistance. The magnetocaloric effect was calculated from isothermal magnetization measurement using modified Maxwell's relation as given in the Section 4.1.1 and 4.1.2 for these samples. The obtained value of entropy change (ΔS_M) is given in Figure 7.3 for Sn and Sb alloys. The maximum of ΔS_M

obtained in case of Sn alloy was 5.6 $Jkg^{-1}K^{-1}$ and was 0.365 $Jkg^{-1}K^{-1}$ in Sb alloy. The refrigerant capacity (RC) values for the field of 1.5 T were 25.2 and 6.8 J kg^{-1} respectively for Sn and Sb alloys as shown in Section 4.1.1and 4.1.2.

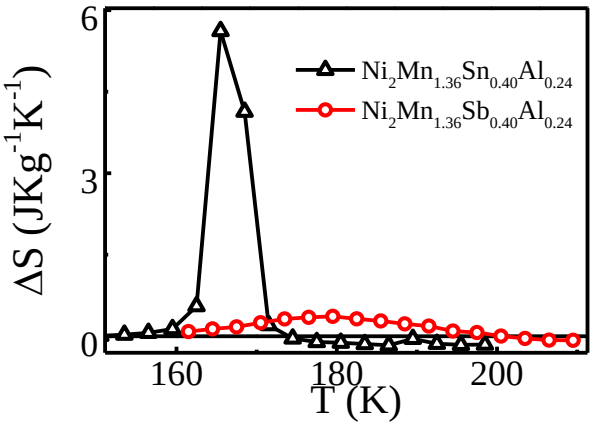

Figure 7.3 Entropy changes due to application of field of 1.5 T calculated from modified Maxwell relation.

The ΔM obtained from the M-H curve in Sn alloy was 19.5 emu/g and in the other case was only 4 emu/g (Section 4.1.1 and 4.1.2), it can be seen that even though magnetization was higher in case of Sb system the value of ΔM was much smaller. As mentioned earlier increased Ni-Mn hybridization leads to AFM interaction, between the Mn atoms occupying Mn site and Z site, in martensitic phase. The replacement of Sn with Sb most probably weakens the hybridization between the Mn-Ni-Mn thus resulting in enhancement of ferromagnetism in the Sb alloy compared to the Sn alloy. The effect is more pronounced in the martensitic phase and as a result of it the value of ΔM is lower in case of Sb alloy. The lower value of ΔM thus results in lower value of ΔS_M and RC in the Sb sample.

To throw some more light in this matter, transport measurements on these samples were done next. The resistivity measurements were performed in cooling and heating cycles for these samples. Figure 7.4 (a) and (b) shows the curves obtained when resistivity measurements performed in zero applied dc magnetic field for both, and in fields of 10 T and 14 T for Sn and Sb alloy respectively. The resistivity showed sharp changes upon structural transformations. Resistivity of the martensitic phase is higher than austenitic phase by 37 % and 32 % for Sn and Sb alloy. The structural transformation to martensitic

phase enhanced the AFM interaction, this changes the density of state at Fermi surface. The different magnetic ordering (AFM) and crystal structure in the martensitic phase compared to austenitic phase established different type of electronic band structures. This gives rise to super zone gap upon martensitic transformation thus leading to increase in resistance [59,183,184]. The lower value of change in resistivity across MT ($\Delta\rho_{M-A}$) in Sb alloy shows that change in AFM interaction upon MT is small in this system. The resistivity curve measured under non zero field, shifted to lower temperature. The shift is large in Sn alloy compared to Sb alloy. The lowering of transformation temperature with field can be understood from Clausius-Clapeyron relation [18]. As the magnetization change in Sb alloy was much smaller than Sn alloy, the resulting shift in transformation temperature is also lower. The change in MT temperature with field also results is large magnetoresistance (MR= $[\rho(H, T) - \rho(0, T]/\rho(0, T))$ [185,186]. The MR obtained for both samples are given in the Figure 7.4 (c) and (d). For Sn alloy the maximum MR of 36 % is observed for the applied field of 10 T whereas the maximum for Sb alloy much lower at 5 % for the field of 14 T, even though both alloys have slightly different change of $\Delta\rho_{M-A}$ upon MT. Therefor the MR results are consistent with the magnetic measurements.

So, we see that upon substituting Sn with Sb, the overall magnetization of austenitic phase increased but the change in magnetization across MT decreased. The effect of substitution is even more pronounced on the functional properties like MCE and MR where they decreased by an order of magnitude. The increase in magnetization of Sb alloy shows that the AFM interaction in the sample weakened in austenitic phase. The lowering of ΔM, MCE and MR further shows that the decrease in AFM interaction was more pronounced in martensitic phase than in austenitic phase. The AFM interaction in martensitic phase had been attributed to Ni 3*d* - Mn 3*d* hybridization, which was sensitive to distance. The XRD results showed that the lattice parameters did not change upon substitution of Sn with Sb. The replacement of Sn with Sb led to increase in the density of electrons in conduction band, it was argued by Khan et al. that change in electron concentration influenced metallic radii of Mn [59,187]. The radii of Mn decreased with increase in electron concentration which would reduce the Ni-Mn distance compared to

Sn system then in Sb system, thus the Mn-Ni-Mn hybridization decreased, reducing the AFM interaction in the Sb sample.

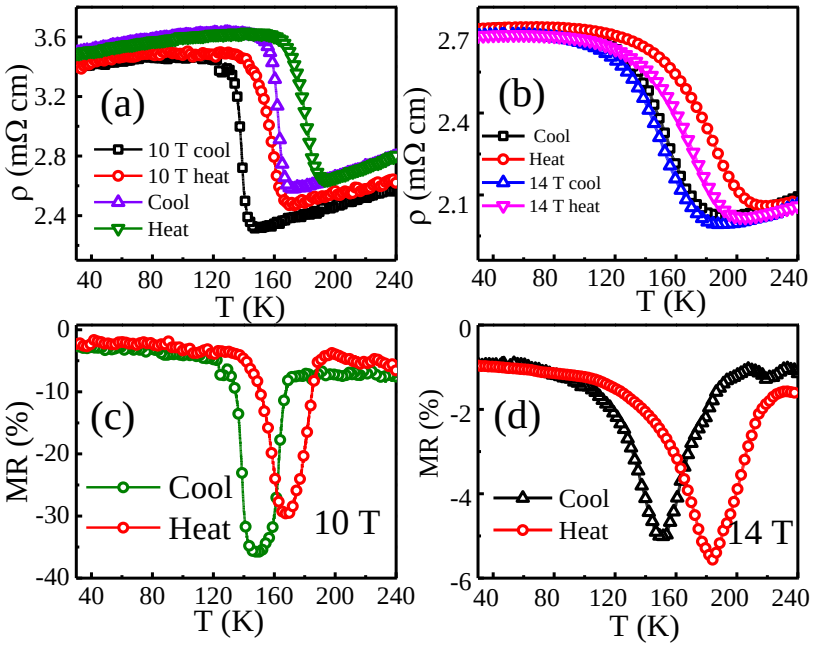

Figure 7.4 (a) and (b) shows resistivity measurement performed in the zero applied dc magnetic field and field of 10 T and 14 T for Sn and Sb alloy respectively. (c) and (d) shows MR obtained for respective alloys.

7.2 Discussion

In summary, we have shown that it is possible to obtain large fraction $L2_1$ phase by replacing Al with other *sp* elements having larger radii. Such replacement also offers us a way to control the magnetic and functional properties of these systems. We have also shown that the different s*p* element can change the Ni-Mn and Ni-Z hybridization and thus effect the magnetism and related properties. The presence of Sb weakens the AFM interaction (hybridization) in sample leading to increase in magnetism of both austenitic and martensitic phase, the effect being more pronounced in martensitic phase, leading to decrease in magnitude of ΔM, MCE and MR by more than an order of magnitude.