Role of Ni-Mn hybridization in the magnetism of the martensitic state of Ni-Mn-In shape memory alloys

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Abstract – Extended X-ray Absorption Fine Structure (EXAFS) studies on Ni\textsubscript{50}Mn\textsubscript{25}\textsubscript{x}In\textsubscript{25}\textsubscript{−x} have been carried out at the Ni and Mn K-edge as a function of temperature. Thermal evolution of nearest-neighbor Ni-Mn and Mn-Mn bond distances in the martensitic phase gives a clear evidence of a close relation between structural and magnetic degrees of freedom in these alloys. In particular, the study highlights the role of Ni 3d-Mn 3d hybridization in the magnetism of the martensitic phase of these alloys.

The presence of competing magnetic interactions in the martensitic state has been demonstrated by the presence of exchange bias phenomena in Ni\textsubscript{50}Mn\textsubscript{25}\textsubscript{x}Z\textsubscript{25}\textsubscript{−x} (Z = In, Sn, Sb) alloys [1–4]. In contrast to Ni\textsubscript{2}MnGa-based alloys [5] a drop in magnetization is observed in these alloys upon structural transformation and has been attributed to enhancement of antiferromagnetic interactions in the martensitic phase [6–12]. Transformation from the high-temperature austenitic to the low-temperature martensitic phase with zero or greatly reduced magnetization in Ni\textsubscript{50}Mn\textsubscript{25}\textsubscript{x}Z\textsubscript{25}\textsubscript{−x} gives rise to a number of interesting effects such as inverse magnetocaloric effect, [13,14] giant strain due to field-induced reverse martensitic transformation [15,16] and giant magneto resistivity [17,18].

Understanding the magnetism of the martensitic state of alloys with excess Mn has been a challenge. While in a \textit{X}_{2}\textit{YZ}-type Heusler alloy, ferromagnetism arises due to the Ruderman-Kittel-Kasuya-Yoshida (RKKY) exchange interaction between Mn atoms occupying the \textit{Y} sublattice (Mn(Y)), the origin of antiferromagnetic interactions in Heusler alloys with excess Mn has been a matter of debate. On the one hand the antiferromagnetism is believed to be a result of RKKY interactions between Mn atoms in the \textit{Z} sublattice (Mn(Z)) and those in the \textit{Y} sublattice [12]. The second study proposes superexchange interactions arising due to hybridization between Ni 3d and Mn 3d bands as the origin of antiferromagnetic interactions [19,20]. The magnetic state in these alloys is then a result of competition between the ferromagnetic and antiferromagnetic interactions leading to an observation of exchange bias effect. A proper understanding of the mechanism of magnetism of the martensitic phase is still to be achieved. Experimental studies have related the change in magnetic ordering of the martensitic phase to the changes in bond distances between the constituent atoms in these alloys [21]. X-ray Absorption and X-ray magnetic circular dichroism studies on Ni\textsubscript{2}MnGa-type alloys have highlighted the role of hybridization between Ni and Ga atoms in martensitic transformation and the intimate connection between structural and magnetic transformations [22] indicating the importance of local structure in influencing the magnetic interactions in these alloys.

Furthermore, in alloys with excess Mn, EXAFS studies have shown the presence of local structural distortions even in the austenitic phase and that there is a charge transfer from Ni 3d band to Mn 3d band [23,24]. Therefore a better understanding of temperature variation of near-neighbor bond distances in the martensitic phase of such Heusler alloys is required. Such a study will help to elucidate the magnetic interactions at play in the martensitic phase. It is with this aim that EXAFS studies at the Ni and Mn K-edges as a function of temperature in
Fig. 1: (Color online) X-ray diffraction patterns (upper panel) and magnetization data (lower panel) recorded in a field of 100 Oe during ZFC, FC and FH cycles for Ni$_{50}$Mn$_{25}$In$_{25}$ (IN25) and Ni$_{50}$Mn$_{35}$In$_{15}$ (IN15).

Fig. 2: (Color online) Variation of amplitude of the FT of the Ni K-edge EXAFS as a function of temperature in IN25 and IN15.

the range $30K \leq T \leq 300K$ in case of two alloys of type Ni$_{50}$Mn$_{25+x}$In$_{25-x}$ with $x = 0$ and 10 have been carried out. Here, the $x = 0$ alloy has a stable crystal structure and serves as a reference point while the other alloy undergoes a martensitic transformation at about 265 K. The results obtained clearly point to the role of the nearest-neighbor Ni-Mn bond distance in the magnetism of these alloys in the martensitic phase.

The alloys of composition Ni$_{50}$Mn$_{25}$In$_{25}$ (IN25) and Ni$_{50}$Mn$_{35}$In$_{15}$ (IN15) were prepared by arc melting the constituents taken in stoichiometric ratio. The buttons obtained after several melts were sealed in a quartz tube and annealed for 48 hours at 750 °C and later quenched in ice cold water. The ingots were then cut in suitable sizes for further measurements. The samples were characterized by X-ray diffraction (XRD) for phase purity and structure. Energy dispersive analysis by X-rays (EDAX) was employed to check the composition ratios. The constituent atomic ratios obtained for the two samples were Ni = 50.5, Mn = 25.3, In = 24.2 for IN25 and Ni = 51.3, Mn = 33.7 and In = 15.0 for the IN15 sample. Magnetization as a function of temperature and field was recorded using a MPMS SQUID magnetometer in the temperature interval 5 K–350 K and field of 100 Oe. For this measurement the samples were cooled in zero applied field from room temperature to 5 K, upon which the field was applied and magnetization was recorded during warming (ZFC), cooling (FC) and subsequent warming (FH) without removing the applied field. EXAFS measurements at the Mn and Ni K-edges each at six temperatures in the interval 30 K to 300 K were performed at the Photon Factory beamline 12 C. Typically, for EXAFS, the scan was cut from −300 eV to 1000 eV with respect to the edge energy in steps of 5 eV in the pre-edge region (−300 eV to −50 eV), 1 eV in the edge region (−50 eV to 100 eV) and 2 eV in the rest of the region (100 eV to 1000 eV). Absorbers were prepared by sandwiching an appropriate number of sample-coated scotch tape layers such that the edge jump ($\Delta\mu(E)$) $\leq 1$. Data analysis was carried out using IFEFFIT [25] in ATHENA and ARTEMIS programs [26]. Here theoretical fitting standards were computed with FEFF6 [27,28]. The data in the $k$ range of (2–12) Å$^{-1}$ and $R$ range 1 to 3 Å for Ni EXAFS and 1 to 5 Å for Mn EXAFS was used for analysis.

X-ray diffraction patterns recorded at room temperature (293 K) and magnetization measured during ZFC, FC and FH cycles are plotted in fig. 1. The diffraction pattern for IN25 shows superstructure reflections of the $L2_1$ phase indicating an ordered structure with a lattice constant $a = 6.067$ Å. The corresponding magnetization data also shows a clear ferromagnetic transition at $T_c = 306$ K. In the case of IN15 the XRD pattern shows extra reflections which can be indexed to the orthorhombic martensitic phase in addition to those belonging to the cubic austenitic phase. This can be related to the proximity of room temperature to martensitic transformation temperature in this sample. The magnetization measurements indicate the austenitic finish ($A_f$) temperature for this sample to be 290 K and the martensitic start ($M_s$) temperature to be 240 K. Magnetization curve also shows that the sample undergoes paramagnetic-to-ferromagnetic transition in the austenitic phase at $T^{A}_c = 310$ K and another magnetic ordering transition in the martensitic phase at $T^{M}_c = 200$ K. Therefore it is quite clear that while IN25 is structurally and magnetically stable alloy, IN15 undergoes structural (martensitic) transition as well as a change in its magentic ordering at low temperatures. A comparative study of local structure around the magnetic ions will help in understanding the role of near-neighbor interactions in the magnetism of these two alloys.

The magnitude of the Fourier transform (FT) of the Ni K-edge EXAFS signals recorded at different temperatures for both the alloys is plotted in fig. 2. With the lowering
of temperature, the amplitude of the EXAFS oscillations should increase due to decrease in the Debye-Waller contribution to $\sigma^2$. This is clearly evident in the case of IN25 in fig. 2 wherein the peak in the FT spectra of EXAFS becomes sharper with decrease in temperature. Whereas, for IN15, the FT amplitude shows a sudden decrease in the temperature interval $300 \, \text{K} < T \leq 250 \, \text{K}$. This being the region of martensitic transformation, a decrease in FT peak amplitude can be related to the structural disorder present in the alloy. The second feature visible from fig. 2 is the change in the position of the first peak, in the temperature interval $300 \, \text{K}$ to $250 \, \text{K}$ in the FT spectra of the IN15 alloy. The position of the peak in FT spectra corresponds to the bond distance between the absorbing and scattering atom and therefore a change in its position indicates a variation in bond distance.

In order to extract structural parameters like bond distances and $\sigma^2$ EXAFS spectra at Ni and Mn K-edges were fitted using the respective structural models. In case of IN25 spectra at all temperatures were fitted using correlations based on the L21 structure (cubic model) while the EXAFS spectra in case of IN15, barring those at $300 \, \text{K}$ were fitted using correlations based on the orthorhombic structure described in ref. [7]. The $300 \, \text{K}$ EXAFS spectra in IN15 were fitted using the cubic model. Further in case of IN15, the coordination spheres involving Mn/In atoms as back-scatters at the same bond distance were fitted as two separate correlations consisting entirely of Mn and In atoms with the coordination number fixed as per their composition ratio. The fitting to the EXAFS data at two representative temperatures, $300 \, \text{K}$ and $30 \, \text{K}$ at the Ni and Mn K-edges are shown in figs. 3 and 4, respectively.

In the $X_2YZ$-type Heusler structure, $X$(Ni) atom is equidistant from $Y$(Mn) and $Z$(In). This is indeed true in case of IN25. The Ni-Mn and Ni-In bond lengths obtained from Ni EXAFS at $300 \, \text{K}$ are equal at 2.62 $\text{Å}$ and in good agreement with the bond distances calculated from lattice constant obtained from XRD. There is also a good agreement of other bond distances obtained from EXAFS analysis with those calculated from lattice constant. The values of bond lengths ($R$) and the corresponding mean square radial distortion ($\sigma^2$) obtained from fitting at $300 \, \text{K}$ are given in table 1. In case of IN15 however, the Ni-Mn and Ni-In distances are different at $2.55 \, \text{Å}$ and $2.62 \, \text{Å}$, respectively, even at $300 \, \text{K}$ (see table 1). A difference in these bond distances in the austenitic phase indicates the presence of local structural disorder which has been shown to be due to the presence of excess Mn in the alloy [29]. The substituted Mn at the Z site being smaller in size compared to In, is displaced from its position giving rise to a local structural distortion. Therefore a shorter Ni-Mn distance implies Mn(Z) is closer to Ni than Mn(Y) or In. Such a disorder in the nearest-neighbor bond distances of Ni was also seen in Ni$_{50}$Mn$_{35}$Sn$_{15}$ in its austenitic phase [23]. Furthermore, in IN15, there is an Mn-Mn bond distance at about 3 $\text{Å}$ between Mn(Y) and Mn(Z) atoms. The bond distance between the two Mn atoms occupying the same sublattice is 4.2 $\text{Å}$. Given the fact that ferromagnetism in both the alloys is due to the RKKY interaction between Mn atoms in their own sublattice while the antiferromagnetism in IN15 could be either due to the RKKY interaction between Mn(Y) and Mn(Z) or due to Ni-Mn hybridization [12,20] it is prudent to examine the temperature variation of Ni-Mn and Mn-Mn bond distances in IN15 and compare them with similar ones in IN25 and Ni-In bond distance in IN15. Such a comparison is provided in figs. 5 and 6.
Table 1: Results of the fits to the Ni and Mn edge EXAFS data for IN25 and IN15 at 300 K. $R$ refers to the bond length and $\sigma^2$ is the thermal mean-square variation in the bond length. The fittings were carried out in the $k$ range: 2 to 12 Å$^{-1}$ with $k$ weight = 3 and $R$ range 1–3 Å for the Ni $K$-edge and 1–5 Å for the Mn $K$-edge. Figures in parentheses indicate the uncertainty in the last digit.

| Atom and Coord. No. | IN25 | | Atom and Coord. No. | IN15 |
|---------------------|------|------|---------------------|------|
| Ni $K$-edge         |      |      | Mn $K$-edge         |      |
| Mn $\times$ 4       | 2.621(3) 0.013(1) | Mn $\times$ 5.44 2.563(4) 0.014(1) |
| In $\times$ 4       | 2.621(3) 0.009(1) | In $\times$ 2.56 2.622(3) 0.006(1) |
| Ni $\times$ 12      | 3.027(3) 0.036(5) | Ni $\times$ 12 3.03(3) 0.029(4) |
| Mn $\times$ 4       |      |      | Mn $\times$ 2.2 2.858(7) 0.004(1) |
| Mn $\times$ 2       | 2.836(7) 0.007(1) | Mn $\times$ 12 4.22(6) 0.028(4) |
| Ni $\times$ 8       | 4.99(1) 0.022(4) | Ni $\times$ 8 4.99(1) 0.022(4) |

Fig. 5: (Color online) Variation of different Mn-Mn bond lengths as a function of temperature in IN25 and IN15.

IN25 is a ferromagnet with $T_c = 306$ K and has a stable crystal structure, thus there is very little or no variation in the bond distance between Mn atoms Mn(Y)-Mn(Y) in the range 300 K to 30 K. On the other hand, the Mn(Y)-Mn(Y) bond distance in IN15 increases in the transformation region (300 K–200 K) and then decreases at lower temperatures. The increase in Mn(Y)-Mn(Y) bond distance can be related to the weakening of ferromagnetism due to martensitic transformation. Therefore any decrease in this bond length at lower temperature should lead to the strengthening of ferromagnetism. This is indeed the case. The Mn(Y)-Mn(Y) bond distance decreases below 200 K and the magnetization curve too shows a build-up of ferromagnetism. Magnetic hysteresis studies reported on similar composition are also in agreement with this hypothesis [4]. Thus variation of bond distances obtained from EXAFS can explain the evolution of ferromagnetic interactions quite well. As regards to the origin of antiferromagnetic interactions, it can be seen from fig. 5 that the behavior of Mn(Y)-Mn(Z) bond distance is similar to that of Mn(Y)-Mn(Y) indicating an enhancement of the strength of antiferromagnetic interactions at low temperatures. Does this mean antiferromagnetism is also due to RKKY interactions? Is there any role at all of the nearest-neighbor interaction in the magnetism of the martensitic phase?

To seek answers to these questions, the variation of Ni-Mn bond distance as a function of temperature is plotted and compared with the Ni-In bond length in IN15 and the Ni-Mn/In bond distance in IN25 in fig. 6. Expectedly, in case of IN25, the equal Ni-Mn and Ni-In bond distances show almost no variation as a function of temperature. On the other hand, due to structural instability in IN15 the Ni-In bond length shows a change near $T_M$ and then remains fairly constant at lower temperature. If the Ni-Mn nearest-neighbor correlation had no role to play.
in the magnetism of these alloys its variation should be
similar to the Ni-In bond length. However, the variation
of the Ni-Mn bond distance in IN15 is not only different
from that of Ni-In and Mn-Mn bond lengths, but it is also
very interesting. Firstly, the variation cannot be explained
on the basis of the variation of the Mn(Y)-Mn(Z) bond
distance as the two are distinctly different from each other.
If the two were related, then the temperature depend-
ence of both these bond distances should be similar.
Secondly, the variation of Ni-Mn quite closely replicates
the behaviour of the ZFC magnetization curve. The Ni-Mn
bond distance first decreases quite sharply in the martens-
itic transformation region and then increases below 250 K
culminating into a broad hump centred around 100 K. A
shorter Ni-Mn bond distance implies a stronger hybridiza-
tion between these two atoms. This will lead to a charge transfer from the nearly full Ni 3d band to the half-filled
Mn 3d band forcing the latter to be closer to $E_F$. Coupled
with destabilization of structural order due to martensitic
transformation it results in complete or partial destruc-
tion of ferromagnetism. This explains the observed large
decrease in magnetization seen at $T_M$. The increase in
the Ni-Mn bond distance below 250 K results in the strength-
ening of magnetism as evidenced from reordering of Mn
spins and a magnetic transition in the martensitic state
at $T^M$. Below 100 K, the Ni-Mn bond distance shows a
tendency to decrease which results in the strengthening
of antiferromagnetic interactions. The observed exchange
bias effect at lower temperatures in these alloys supports
this argument [4]. These facts clearly bring out the impor-
tance of hybridization between nearest neighbors in the
magnetism of the martensitic state. While it seems from
the EXAFS studies that Mn(Y)-Mn(Y) interactions are
solely responsible for ferromagnetic interactions, the anti-
ferromagnetic interactions are a result of the increase in
the hybridization of Ni 3d states with Mn 3d states due to
the shortening of the Ni-Mn bond length.

In summary, EXAFS studies carried out on
Ni$_{30}$Mn$_{25+3}$In$_{25-x}$ as a function of temperature have
been used to study the evolution of nearest-neighbor
Ni-Mn, Ni-In and Mn-Mn bond distances. The tempera-
ture dependence of these bond lengths suggest that the
ferromagnetic interactions depend on the distance
between Mn atoms occupying the Y sublattice of the
X$_2$YZ Heusler structure. It is the hybridization between
Ni 3d and Mn 3d that plays a crucial role in the strength
of the antiferromagnetic interactions in the martensitic
phase.

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