Local atomic arrangement and martensitic transformation in Ni$_{50}$Mn$_{35}$In$_{15}$: an EXAFS study

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Abstract
Ni$_{50}$Mn$_{35}$In$_{15}$ is a newly found ferromagnetic shape memory alloy that displays exotic properties such as inverse magnetocaloric effect and large magnetoresistance at moderate field values. Since the Mn content in this compound is more than the stoichiometric (X$_2$YZ) Heusler composition, the magnetic and electronic properties of this material are decided to a large extent by the distribution of constituent atoms in the available sites. In this work, we present extended x-ray absorption fine structure (EXAFS) measurements on the bulk Ni$_{50}$Mn$_{35}$In$_{15}$ which reveal the local structural change that occurs upon phase transformation. The change in the bond lengths between different atomic species helps in understanding the types of interactions which are responsible for driving such Ni–Mn based systems towards martensitic transformation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Ni–Mn based Heusler alloys are magnetic materials that exhibit structural transformation of the martensitic type with large magnetic field induced strains and can be exploited for tremendous technological applications [1, 2]. These materials also offer an excellent opportunity to investigate the various aspects of magnetic and structural phase transformations in a single system [3, 4]. As a magnetic field controlled shape memory effect is realized in these materials upon martensitic transformation, they are commonly referred to as ‘ferromagnetic shape memory alloys’ or FSMAs. Recently, martensitic transformations were observed in ferromagnetic alloys with the composition Ni$_{50}$Mn$_{35-x}$Z$_{x}$ where Z = In, Sn, Sb. The phase diagram of these systems indicates that with concentrations up to $\sim$16 at% Z element, a transformation from the high temperature austenitic phase to a low symmetry martensitic phase can be achieved with the lowering of temperature [5]. In particular, the Sn and In alloy series have been in focus [6–11] and are known to exhibit exotic properties that promise various innovative applications. A giant inverse magnetocaloric effect has been reported in Ni–Mn–Sn alloys (18 J kg$^{-1}$ K$^{-1}$ at 5 T) where the application of the magnetic field adiabatically cools the sample [6], whereas a large magnetoresistance at moderate field values has been observed in Ni$_{50}$Mn$_{35}$In$_{15}$ at temperatures very close to room temperature [11]. In particular, Ni$_{50}$Mn$_{35}$Sn$_{15}$ has a cubic L2$_1$ structure at room temperature and transforms martensitically at $T_M \approx$ 200 K, while Ni$_{50}$Mn$_{35}$In$_{15}$ is reported to have different structures at room temperature [5, 8]. The investigation of the magnetic properties show that the overall magnetic exchange in both the parent and product phases is ferromagnetic with a Curie temperature ($T_C$) of 319 K for Ni$_{50}$Mn$_{35}$Sn$_{15}$ [7] and of 304 K for Ni$_{50}$Mn$_{35}$In$_{15}$ [8]. In addition, the magnetization studies show that the structural transformation in these alloys could be induced by both temperature and magnetic field [8, 9] placing them in the class of FSMAs.

For the development of new FSMAs and to classify the best alloys for practical applications, certain important properties of these alloys have been mapped with their composition. At least for the much studied prototype Ni–Mn–Ga alloys a correlation between structural transformation temperature ($T_M$), martensitic crystal structure and the average number of

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valence electrons per atom \((e/a)\) has been established \[12\]. For the near-stoichiometric Ni–Mn–Ga alloys, the compositional dependence of \(T_M\) is determined and it is found to increase linearly with an increase in the \(e/a\) value \[13\]. The role of \(e/a\) in relation to the martensitic transformation temperature in Ni–Mn–Ga alloys has been discussed at length by Entel et al \[4\]. Keeping in view the dependence of \(T_M\) on \(e/a\) it is interesting to compare the two systems: Ni\(_{50}\)Mn\(_{35}\)Sn\(_{15}\) that has an \(e/a\) value of 8.05 and Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\) with \(e/a = 7.9\). In spite of Ni\(_{50}\)Mn\(_{35}\)Sn\(_{15}\) having a slightly higher \(e/a\) value, it undergoes a martensitic transition at a much lower temperature as compared with Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\). At such a point, understanding the correlation between the structural aspect of martensitic phase and the transformation temperature, \(T_M\), becomes important. With this aim, Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\) has been studied for its structural properties in the austenitic and martensitic phases using extended x-ray absorption fine structure (EXAFS) measurements at Mn and Ni K-edges and compared with our results on Ni\(_{50}\)Mn\(_{35}\)Sn\(_{15}\) \[14\].

2. Experimental details

Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\) was prepared by repeated melting of appropriate quantities of the constituent elements of 4 N purity under an argon atmosphere in an arc furnace. The sample bead so obtained was annealed at 800 K for 48 h followed by quenching in ice water. Subsequent energy dispersive x-ray (EDX) analysis confirmed the composition of the sample to be close to nominal with Ni = 50.17, Mn = 34.59 and In = 15.24. Small pieces were cut from the sample bead using a low speed diamond saw and the remainder was crushed into very fine powder using a motor and a pestle. The temperature dependence of magnetization was studied using a vibrating sample magnetometer with a low field value of 100 Oe and in the temperature range 50–330 K. The room temperature crystal structure was determined by x-ray powder diffraction (XRD) recorded on a Rigaku D-MAX IIC diffractometer with Cu Kα radiation. EXAFS measurements at Ni and Mn K-edge were recorded at room temperature and liquid nitrogen temperature, in the transmission mode, on the EXAFS-1 beamline at the ELETTRA Synchrotron Source using Si(1 1 1) as a monochromator. Data analysis was carried out using IFEFFIT \[15\] in ATHENA and ARTEMIS programs \[16\]. Theoretical fitting standards were computed with ATOMS and FEFF6 programs \[17, 18\].

3. Results

\(M(T)\) measurements were carried out in a field of 100 Oe over the temperature range 50–330 K in cooling/warming cycles as can be seen from figure 1. The first warmup followed by cooling and subsequent heating data are indicated in the figure as ZFC (zero-field cooled), FC (field-cooled) and FH (field-heated), respectively. A steep rise in magnetization is observed at \(T_C = 305\) K in all the three data sets indicating a transition to the magnetically ordered state. With a further decrease in temperature, a sudden drop in magnetization takes place at 302 K, a signature that marks the formation of the new structural phase. However, magnetization drops to almost zero. Such a drastic change can be due to the formation of crystallographic variants of the new phase that temporarily disturbs the established ferromagnetic orientation. A large hysteresis follows in the temperature range 265–310 K between FC and subsequent FW magnetization curves which strongly supports the occurrence of a first-order structural transition within this temperature interval. Thus the initial rise and the subsequent fall in magnetization observed upon the lowering of temperature are signatures of magnetic \((T_C = 305\) K) and concomitant martensitic \((T_M \approx 302\) K) phase transformations. Below 200 K, an irreversible behaviour between the ZFC and FC curves is observed indicating some degree of frustrated spin alignment. The frustration of spins may result from the competition between the underlying ferromagnetic coupling and an incipient antiferromagnetic coupling between Mn atoms present at two different crystallographic positions \[19\]. The subsequent FW curve retraces the FC curve over this temperature range. The ZFC magnetization increases slowly with the rise in temperature and forms a ‘peak-like’ feature at \(\sim 175\) K. Such a feature is assigned to ferromagnetic ordering of the martensitic phase \[8\]. A distinct splitting between the three curves is observed in the region 250–310 K. This splitting can be attributed to the start and finish of martensitic transition.

The XRD profile for Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\) is shown in figure 2. The room temperature structures for Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\) have been reported by Krenke et al \[8\]. Here with decreasing In concentration from \(x = 25\), the structure changes from L2\(_1\) to B2 at \(x = 16\) and to modulated structures for lower values of \(x\). Recently, Pathak et al have reported structures of Ni\(_{50}\)Mn\(_{35}\)–In\(_{x}\) \((x = 15–16)\) \[20\] and the XRD profile of our sample matches closely with the ones reported here. It must be mentioned here that from figure 2 it is difficult to assign a pure B2 order as the profile and also earlier reports hint at mixed structures for this composition \[5, 8, 20\]. Fitting the XRD profile to a B2 structure \((Sp.gr. = Pm\bar{3}m)\) gives a lattice parameter of 3.020 ± 0.001 Å.

![Figure 1](image-url)
Generally, in the cubic phase $XYZ$ Heusler alloys are known to crystallize in the highly ordered $L2_1$ structure that consists of four face-centred cubic (fcc) sublattices. In the $L2_1$ unit cell $X$ atoms occupy the $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ position, while $Y$ and $Z$ atoms, respectively, occupy the $(0, 0, 0)$ and $(0, \frac{1}{2}, 0)$ positions. When $Y$ and $Z$ atoms occupy the above-mentioned sites absolutely at random causing a $Y-Z$ disorder, the alloy is known to have a $B2$ structure. This disordered phase can be represented by a CsCl type structure with $X$ atoms at the centre of the cube and $Y$ and $Z$ atoms sharing the corners. In the case of Ni$_{50}$Mn$_{35}$In$_{15}$, Ni atoms occupy the body-centred position and Mn and In atoms occupy the corners of the cube.

EXAFS were recorded at Mn and Ni K-edge in the austenitic and martensitic phases by carrying out the measurements at room temperature and liquid nitrogen temperature, respectively. The room temperature EXAFS data were fitted with the $B2$ crystal structural model. The coordination spheres involving Mn/In atoms as backscatters 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 is shown in figure 3 and the values of the parameters for the fit are mentioned in table 1. Parameters such as the bond length and the corresponding thermal mean square variation in the bond length for different correlations are obtained. The bond lengths calculated on the basis of the lattice parameters obtained from the XRD profile are compared with values obtained from the EXAFS analysis. Certain striking anomalies in the crystal structure are observed from the EXAFS analysis of both the Mn and Ni edge data. The second correlation representing the scattering between Mn (absorber) and Mn/In (backscatterer) atoms gives different values for Mn–In and Mn–Mn bonds. This difference in the bond distances is also represented by a CsCl type structure with $X$ atoms at the centre of the cube and $Y$ and $Z$ atoms sharing the corners. When compared with the bond distance calculated from the XRD profile, it is seen that the Ni–In and Ni–Ni bond distances match with the calculated values within the error bars while considerable deviation is observed for the Ni–Mn bond distance. Further, this Ni–Mn bond distance differs from the value obtained from Mn EXAFS for the same (Mn–Ni) correlation. Ideally, the Ni–Mn bond length as obtained from Ni K-edge and Mn K-edge data should have been equal as it involves the same pair of atoms. The difference in this correlation as observed from the EXAFS analysis agrees with the argument that atoms move from their crystallographic positions over varied amplitudes of displacement with Mn atoms being displaced more than the other constituent atoms.

Another striking feature in the Ni K-edge data is the difference in the Ni–Mn and Ni–In bond distances. If the crystal structure had to be perfectly cubic then Ni atoms, being at the body-centred position, would have been equidistant from In and Mn. The unequal Ni–Mn and Ni–In bond distances in Ni$_{50}$Mn$_{35}$In$_{15}$ are related to the interplay between a static structural disorder and proximity to martensitic transformation temperature. It may be noted that $T_M \sim 302$ K for Ni$_{50}$Mn$_{35}$In$_{15}$ is close to the temperature of the EXAFS measurement (295 K). The transformational effects get very intense as $T_M$ is approached and any measurement in the narrow region of temperature around $T_M$ is known to be affected. The influence of such effects on the parameters obtained from the EXAFS analysis has already been observed for Ni$_{52}$Mn$_{38}$Ga that has $T_M \sim 285$ K [21]. Hence the room temperature EXAFS of Ni$_{50}$Mn$_{35}$In$_{15}$ reflects the anomalies associated with martensitic transformation such as unequal movement of constituent atoms and discrepancies in the bond distances for similar atomic correlations.

The local structure of the martensitic phase of Ni$_{50}$Mn$_{35}$In$_{15}$ was fitted using correlations derived from the $L1_0$ structure. The bond distance and $\sigma^2$ values obtained from the low temperature EXAFS analysis are included in table 1 and the fitted spectra are shown in figure 4. Martensitic transformation results in splitting of the bonds that were degenerate in the cubic cell due to lowering of the crystal symmetry. Such splittings are evident from the Mn–Mn and Mn–Ni correlations in the Mn edge and Ni–Ni correlations in the Ni edge (see table 1). However, for the nearest neighbour
Figure 3. Magnitude and real component of Fourier transform (FT) of EXAFS spectra in $R$ space (left panel) and real component of FT in the back transformed $k$ space (right panel) for Mn and Ni K-edge in Ni$_{50}$Mn$_{35}$In$_{15}$ obtained at room temperature. The fitting to the data is shown as differently coloured lines.

Table 1. Mn and Ni K-edge EXAFS analysis of Ni$_{50}$Mn$_{35}$In$_{15}$ in the cubic and martensitic phases. $R_{\text{calc}}$ refers to the bond distance calculated for the B2 cell from the lattice parameters obtained from the XRD profile. $R$ is the bond length as obtained from the EXAFS analysis and $\sigma^2$ is the corresponding thermal mean square variation in the bond length. The analysis were carried out in the $k$ range: (2–12) Å$^{-1}$ with $k$-weight: 3 and $R$ range: (1–5) Å for Mn edge and (1–3) Å for Ni edge. Figures in parentheses indicate uncertainty in the last digit.

| Atom and coord. no. | Cubic B2 phase | Martensitic phase |
|---------------------|----------------|-------------------|
|                     | $R_{\text{calc}}$ (Å) | $R$ (Å) | $\sigma^2$ (Å$^2$) | $R_{\text{calc}}$ (Å) | $R$ (Å) | $\sigma^2$ (Å$^2$) |
| **Mn K-edge**       |                |               |               |                      |          |                  |
| Ni1 × 8             | 2.615          | 2.567(3)      | 0.0115(3)    | Ni1 × 8              | 2.568(3) | 0.0079(3)         |
| In1 × 1.8           | 3.020          | 2.886(5)      | 0.0058(5)    | In1 × 1.8            | 2.879(6) | 0.0046(6)         |
| Mn1 × 4.2           | 3.020          | 2.911(5)      | 0.0108(6)    | Mn1 × 4.2            | 2.896(6) | 0.0094(7)         |
| Mn2 × 12            | 4.270          | 4.274(4)      | 0.035(7)     | Mn1 × 8              | 4.19(1)  | 0.016(2)          |
| MS$^6$ × 4.8        | 5.230          | 5.10(3)       | 0.013(4)     | Mn2 × 4              | 4.40(2)  | 0.012(2)          |
| MS$^8$ × 11.2       | 5.230          | 5.17(5)       | 0.0129(7)    | Ni2 × 8              | 4.736(7) | 0.009(8)          |
| Ni1 × 6             |                |               |               | Ni3 × 16             | 4.918(8) | 0.0080(9)         |
| **Ni K-edge**       |                |               |               |                      |          |                  |
| Mn1 × 5.6           | 2.615          | 2.580(4)      | 0.0128(5)    | Mn1 × 5.6            | 2.558(3) | 0.0068(4)         |
| In1 × 2.4           | 2.615          | 2.634(4)      | 0.0070(4)    | In1 × 2.4            | 2.70(1)  | 0.009(1)          |
| Ni1 × 6             | 3.020          | 3.13(6)       | 0.038(9)     | Ni1 × 2              | 2.797(7) | 0.0038(8)         |
|                     |                |               |               | Ni2 × 4              | 3.13(8)  | 0.027(13)         |

$^a$ Mn$\rightarrow$In3$\rightarrow$Ni1$\rightarrow$Mn.

$^b$ Mn$\rightarrow$Mn3$\rightarrow$Ni1$\rightarrow$Mn.

interactions, the difference between the split bonds is very small and cannot be resolved by EXAFS. In such instances we have used single correlations in the fittings, for example, in the case of the first and second neighbour scatterings in both Mn and Ni EXAFS data. The first Mn–Ni bond distance as obtained from the Mn edge data remains unchanged from its room temperature value, while from the Ni edge data the same bond distance decreases from 2.580 to 2.558 Å. As mentioned above, such differences in bond distances involving the same pair of atoms can be attributed to the movement of atoms from their crystallographic position. It may be noted that, while the Mn–Ni distance obtained from Mn EXAFS remains unchanged, the same bond distance obtained from Ni EXAFS decreases from 2.58 to 2.56 Å with the decrease in temperature. Furthermore, the Ni–In bond increases by almost 0.07 Å in comparison with its room temperature value. This implies that within the tetrahedral arrangement around Ni atoms, the large movement of Mn atoms causes the Ni–Mn bonds to shrink at the cost of Ni–In bonds leading to a stronger Ni–Mn hybridization.
4. Discussion

The understanding of atomic rearrangements that occur upon martensitic transformation and hence hybridization that results due to the phase change is vital in determining the physical properties of such FSMA. In the local structural study of Ni–Mn–Ga alloys it has been shown that at low temperature Ni–Ga hybridization grows stronger in comparison with Ni–Mn causing tetrahedral distortions within the L10 sub-cell of the parent L21 structure [21]. Such p–d hybridization that develops between X and Z atoms of the XYZ Heusler structure in the low temperature phase leads to redistribution of electrons causing the band Jahn–Teller effect. On the other hand, EXAFS measurements on Ni50Mn35Sn15 present unequal Ni–Mn and Ni–Sn bond lengths that result in a stronger hybridization between Ni and Mn occupying the Z-sites [14]. From the study of these two systems, it may be deduced that in the Ni–Mn based Heusler alloys, it is the strong hybridization between the X and Z species which results in the alteration of the band structure at the Fermi level and leads to martensitic transformation. In Ni50Mn35In15 the results are similar, namely, Ni–Mn bond lengths are shorter than Ni–Sn. This points to the fact that there exists some Mn-d and Ni-d hybridization. It is this d–d hybridization that is responsible for martensitic transformation in Ni50Mn35In15.

A martensitic transformation occurs when the Fermi surface touches the Brillouin zone boundary [22]. Thus, any variation in factors such as chemical pressure (as a result of a difference in the atomic sizes) and the e/a value can cause the alteration of the Fermi surface driving such systems towards structural instabilities. A linear dependence of the $T_M$ on e/a has indeed been observed for the Ni–Mn–Ga alloys [12, 13]. However, in the present case, Ni50Mn35Sn15 that has an e/a value of 8.05 undergoes a martensitic transition at a much lower temperature as compared with Ni50Mn35In15 with e/a = 7.9. One of the main distinctions between these two systems is the size difference between In and Mn in Ni50Mn35In15 and Sn and Mn atoms in Ni50Mn35Sn15. The size difference between In and Mn atoms being larger results in a greater amount of disorder. This disorder also affects the hybridization in the martensitic phase. In Ni50Mn35Sn15 the Ni–Mn and Ni–Sn bond lengths obtained from the EXAFS analysis are 2.57 Å and 2.61 Å, respectively, giving a difference of 0.04 Å, whereas as it can be seen from table 1 the difference between Ni–Mn and Ni–In bond lengths is 0.14 Å. This clearly indicates more structural disorder in Ni50Mn35In15 than in Ni50Mn35Sn15. In Ni50Mn35In15, Ni is enclosed in a cubic cage of Mn and In atoms. Ideally, both Mn and In should have been equidistant from Ni regardless of either B2 or L21 order. The higher Mn concentration results in a local structural disorder due to the size difference leading to a shorter Ni–Mn bond length. It has been shown earlier that a shorter Ni–Ga bond length in Ni2MnGa results in the distortion of the tetrahedral cage around Ni atoms which leads to redistribution of electrons causing a band Jahn–Teller effect [21]. In the case of Ni–Mn–In, the much larger difference between Ni–Mn and Ni–In bond lengths results in a higher distortion of the Mn tetrahedra surrounding Ni. Such a distortion is responsible for the rearrangement of d electrons within the hybrid band resulting in the lifting of degeneracy and lowering of the symmetry. This distortion being stronger in the case of Ni50Mn35In15 as compared with Ni50Mn35Sn15 results in a higher martensitic transition temperature.

5. Conclusion

The local structure of a new FSMA, Ni50Mn35In15, was studied using the EXAFS technique. A comparison of the bond
distance values between different atomic constituents in the austenitic and martensitic phases is made. A substantial off-centre distortion of the tetrahedral arrangement around Ni atoms leads to a shorter Ni–Mn bond length in the martensitic phase. This distortion is larger in Ni50Mn35In15 than in a similar composition, Ni50Mn35Sn15, and in direct relation to the observed martensitic transformation temperatures in the two compounds.

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