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2008 J. Phys.: Condens. Matter 20 505206

(http://iopscience.iop.org/0953-8984/20/50/505206)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 505206 (6pp) doi:10.1088/0953-8984/20/50/505206

Intermartensitic transitions in Ni–Mn–Fe–Cu–Ga Heusler alloys

Mahmud Khan[1], **Bhoj Gautam, Arjun Pathak, Igor Dubenko, Shane Stadler and Naushad Ali**

Department of Physics, Southern Illinois University, Carbondale, IL 62901, USA

Received 11 August 2008
Published 7 November 2008
Online at stacks.iop.org/JPhysCM/20/505206

Abstract

A series of Fe doped $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ Heusler alloys have been investigated by means of x-ray diffraction, magnetizations, thermal expansion, and electrical resistivity measurements. In $Ni_2Mn_{0.75}Cu_{0.25}Ga$, martensitic and ferromagnetic transitions occur at the same temperature. Partial substitution of Mn by Fe results in a decrease of the martensitic transition temperature, T_M, and an increase of the ferromagnetic transition temperature, T_C, resulting in separation of the two transitions. In addition to the martensitic transition, complete thermoelastic intermartensitic transformations have been observed in the Fe doped $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ samples with $x > 0.04$. An unusual transition is observed in the alloy with $x = 0.04$. The magnetization curve as a function of increasing temperature shows only one first-order transition in the temperature range 5–400 K, which is identified as a typical coupled magnetostructural martensitic transformation. The magnetization curve as a function of decreasing temperature shows three different transitions, which are characterized as the ferromagnetic transition, the martensitic transition and the intermartensitic transition.

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

1. Introduction

Ferromagnetic materials undergoing first-order phase transitions in a magnetically ordered state are of great importance. Very often interesting phenomena such as giant magnetoresistance [1, 2], large magnetocaloric effects [3–6], etc, are associated with such phase transitions, that are very significant from both applications and scientific viewpoints. Already, many ferromagnetic materials have been discovered. Only a very small proportion of these materials have been reported to undergo first-order transitions while in a ferromagnetic state.

The Heusler alloy Ni_2MnGa with the cubic $L2_1$ structure is one such material that is well known for exhibiting a first-order martensitic phase transformation while in a ferromagnetic state [7]. Large strains can be produced in the martensitic phase of this alloy by the application of a magnetic field [8–12]. This characteristic makes Ni_2MnGa very promising for potential application as a magnetic field-controlled actuator material. In addition to undergoing the martensitic transformation, Ni_2MnGa undergoes a first-order intermartensitic transformation at temperatures lower than the martensitic transformation temperature, T_M. The intermartensitic transformation is a phase transition between the modulated (M-type) and the unmodulated (T-type) martensite at lower temperature [13–17]. In previous reports, the intermartensitic transformation showed both non-thermoelastic and thermoelastic behaviors. In the non-thermoelastic case, the transition was observed only while cooling or heating and not for both. In a thermoelastic situation the intermartensitic transformation was observed while cooling at a temperature T_I, and a reverse intermartensitic transformation was observed while heating at a temperature T_R [16, 17]. The temperature hysteresis ($\Delta T_I = T_I - T_R$) of the intermartensitic transformation was found to be much larger than that of the martensitic transformation. In the intermartensitic phase of this single crystal, a large strain of 5% was achieved with a small applied field of 0.2 T [17]. This strain is much larger than that observed in the martensitic phase.

Observations of complete thermoelastic intermartensitic transformations in polycrystalline Ni–Mn–Ga based Heusler alloys are very rare, and therefore such observations are interesting from both scientific and applications points of view.

[1] Author to whom any correspondence should be addressed. Present Address: Materials and Engineering Physics, Ames Laboratory, Iowa State University, Ames, IA 50010, USA.

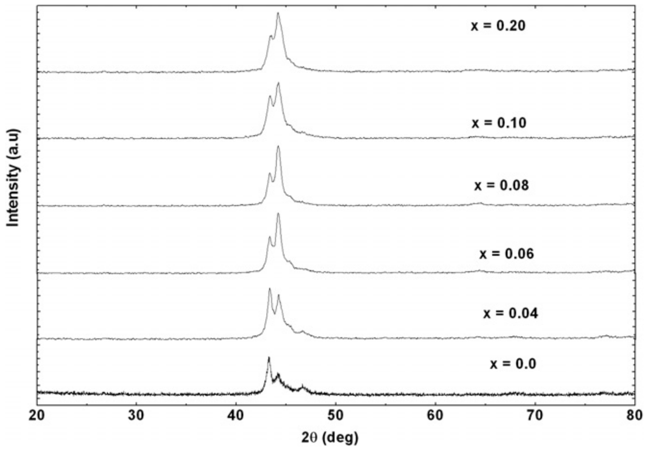

Figure 1. Room temperature powder XRD patterns of $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$.

It was reported earlier that partial substitution of Mn by Cu in Ni_2MnGa results in increase of T_M and decrease of T_C [18], and for some critical concentration ($Ni_2Mn_{0.75}Cu_{0.25}Ga$), T_M and T_C coincide, resulting in a single magnetostructural phase transition. In the vicinity of this transition, a large magnetic entropy change has been observed in $Ni_2Mn_{0.75}Cu_{0.25}Ga$ [19].

In this paper, we present the results of an experimental study performed on an Fe doped $Ni_2Mn_{0.75}Cu_{0.25}Ga$ Heusler alloy system, where the Mn atoms were partially replaced by Fe. Magnetic measurements that were performed on the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ alloy system revealed the existence of complete thermoelastic intermartensitic transformation.

2. Experimental details

The $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ samples were prepared by conventional arc melting techniques, where the elements Ni, Mn, Fe, Cu, and Ga of 4N purity were repeatedly melted under an argon atmosphere. The weight loss of each sample after melting was less than 0.3%. For homogenization, after melting, the samples were wrapped in Ta foil and annealed in vacuum at 850 °C for 24 h.

X-ray diffraction (XRD) measurements were done at room temperature using a GBC MMA (mini-materials analyzer) x-ray diffractometer that used Cu Kα radiation and Bragg–Brentano geometry. The magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer manufactured by Quantum Design Inc. The measurements were performed in a temperature range of 5–400 K and in fields up to 50 kOe. Thermal expansion measurements were conducted using the capacitance dilatometry method in temperature ranges of 80–350 K. Direct current resistivity was measured, using the four-probe method, over the same temperature range as the magnetization.

3. Results and discussion

The room temperature XRD patterns of the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ are shown in figure 1. The distorted peaks of

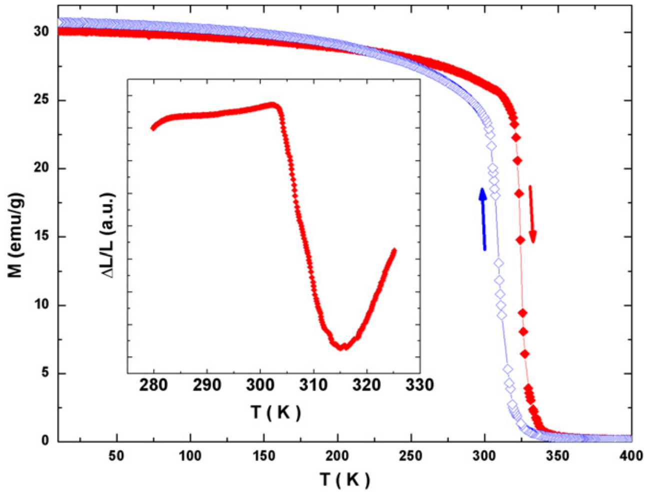

Figure 2. Magnetization as a function of increasing and decreasing temperature for $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ ($x = 0.0$) obtained at a field of 1 kOe. The insets show the curves for thermal expansion as a function of increasing temperature for the respective alloy.

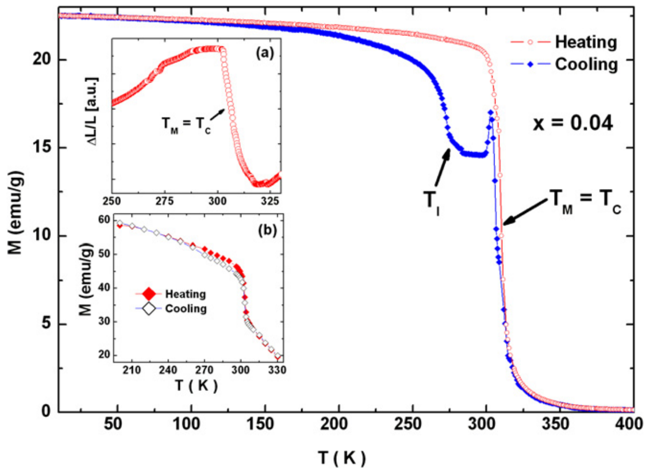

Figure 3. Magnetization as a function of increasing and decreasing temperature for $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ ($x = 0.04$) obtained at a field of 1 kOe. The insets show the curves for thermal expansion as a function of increasing temperature for the respective alloy.

each of the sample as shown in the figure suggest that each of the samples exhibits mixed martensitic and austenitic phases at room temperature. Materials that undergo first-order structural transition are very likely to show the presence of mixed structures near their structural transformation temperatures. Since martensitic transformation is a first-order structural transformation, the presence of mixed phases in the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ system can be attributed to the T_M of each sample in the system being close to room temperature.

Figure 2 shows the curves for magnetization as a function of increasing and decreasing temperature ($M(T)$) measured in an applied field of 1 kOe, for the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ alloy with $x = 0.0$. The inset of figure 2 shows the curve for thermal expansion as a function of increasing temperature for the respective alloy. The only transition observed in the $M(T)$ curves of the alloy is the magnetostructural transition at $T_M = T_C$. The observed characteristics of the $M(T)$ curve and

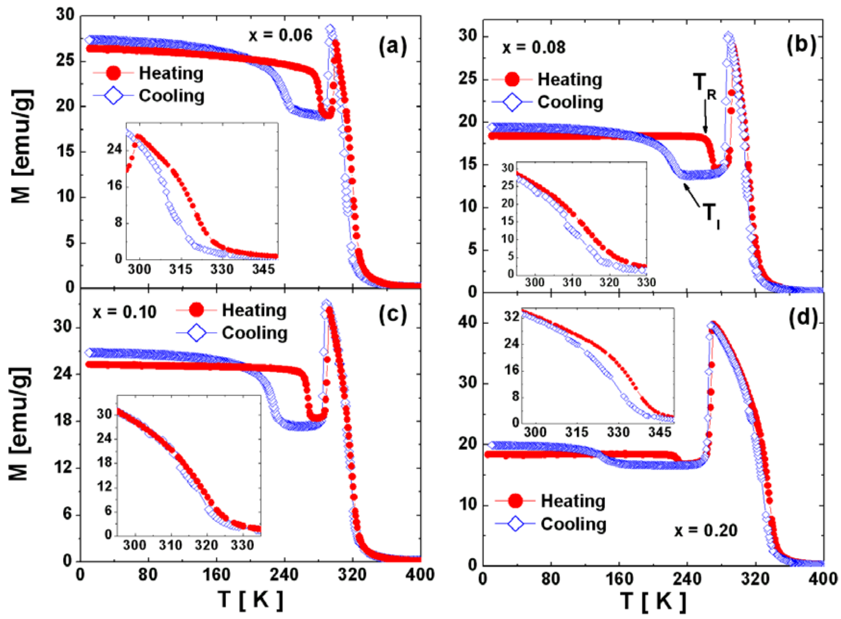

Figure 4. Magnetization as a function of increasing and decreasing temperature for $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ for (a) $x = 0.06$, (b) $x = 0.08$, (c) $x = 0.10$, and (d) $x = 0.20$, obtained at a field of 1 kOe.

thermal expansion curve of the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ alloy with $x = 0.0$ are very similar to those which have already been reported in earlier literature [19].

The $M(T)$ curves of the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ alloy with $x = 0.04$ obtained while heating and cooling show different characteristics (see figure 3). In the $M(T)$ curve of the alloy with $x = 0.04$ obtained while heating up from 5 K, only one transition, the coupled T_M and T_C one, near 310 K is apparent. The $M(T)$ curve of the sample obtained while cooling down shows that three different transitions near 305 K, 301 K, and 272 K are observed, each of which corresponds to T_C, T_M, and T_I for the alloy, respectively. The characteristic of the $M(T)$ curve obtained while cooling is similar that of $Ni_{52}Mn_{24}Ga_{24}$ single crystal, where XRD measurements confirmed the existence of a intermartensitic transition in the crystal. Therefore the observations made for the $M(T)$ curves of the alloy with $x = 0.04$ suggest that, as the sample is heated up, the intermartensitic, martensitic, and ferromagnetic transitions occur at temperatures very close to each other, appearing to be a single phase transition. However, as the sample is cooled down, the transitions separate due to the different thermal hystereses of the transitions. As mentioned earlier, the temperature hystereses of the martensitic and intermartensitic transitions are different. Each of the $M(T)$ curves obtained while heating and cooling at 5 T shows only one transition at T_C, with the presence of minor temperature hysteresis (see inset (b) of figure 3). No intermartensitic transition is observed in the $M(T)$ curves at 5 T. The sharp jump in the thermal expansion curve of the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ ($x = 0.04$) alloy near T_M suggests that the transition at T_M is a first-order phase transition (see inset (a) of figure 3).

Figure 4(a) through (d) show the 1 kOe $M(T)$ curves of $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ ($0.06 \leqslant x \leqslant 0.20$). The inset of each figure shows the features of the curves in the vicinity of T_C for each respective alloy. Each of the alloys exhibits an intermartensitic transformation at a temperature, T_I, during cooling. The reverse intermartensitic transformation is observed at a temperature T_R in the $M(T)$ curves obtained while heating up from 5 K. The observed temperature hysteresis of the transition in each of the curves suggests that the transition is of first order. It also shows that the transition is completely thermoelastic, which is usually observed for single crystals of Ni–Mn–Ga based alloys [16, 17]. It is also clear in figure 4 that the temperature hysteresis of the martensitic transition is much smaller than that of the intermartensitic transition. This is a typical behavior of such transitions [16, 17]. Besides that at the martensitic and intermartensitic transitions, temperature hysteresis is also observed at T_C for each respective alloy, showing the presence of first-order transitions in the vicinity of T_C. This suggests that the martensitic transformations that take place at T_M are incomplete and reach completion at T_C. It should be noted that although T_M for the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ alloy with $x = 0.20$ is around 268 K, which is quite well below room temperature, the presence of mixed austenitic and martensitic phases was evident in the XRD data for the alloy (see figure 1). This can be explained by the presence of thermal hysteresis at T_C observed in the $M(T)$ curves of the alloy (see figure 4(d)), which shows the presence of a first-order phase transition (most probably a martensitic transformation) in the vicinity of T_C.

In figure 5, the thermal expansion curves of the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ ($0.06 \leqslant x \leqslant 0.08$) alloys are shown. The inset of each figure shows the respective regions of the curves where the intermartensitic transformations take place. The step-like transitions at T_R and T_M in the thermal expansion curves of the alloys clearly show that both the intermartensitic and martensitic transformations are first order in nature.

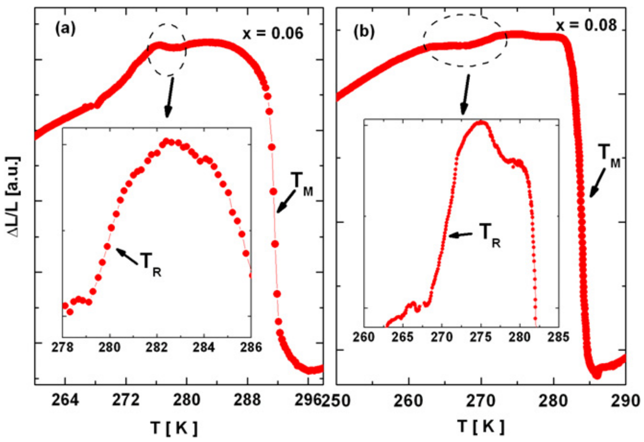

Figure 5. Curves of the thermal expansion of the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ alloys with (a) $x = 0.06$ and (b) $x = 0.08$, as a function of increasing temperature. The insets show the magnified regions of the circled parts in the thermal expansion curves of the alloys, respectively.

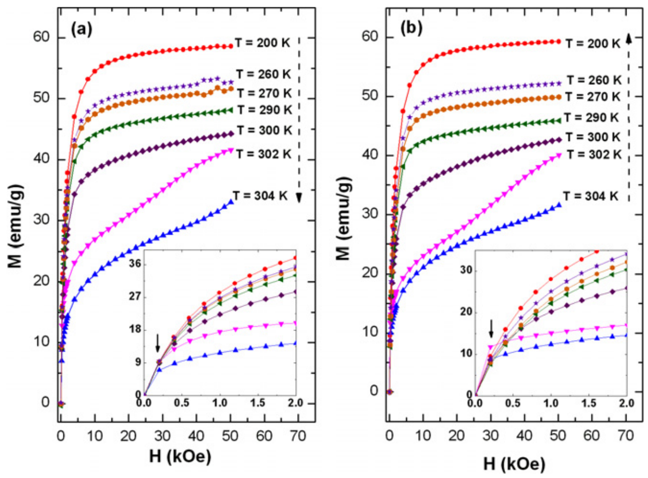

Figure 6. Isothermal magnetization curves of the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ alloy ($x = 0.04$) obtained at different (a) increasing temperatures and (b) decreasing temperatures. The insets show the respective magnetization curves in the lower field regions.

As was shown in figure 3, the $M(T)$ curves of $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ with $x = 0.04$ obtained while cooling and heating showed different behaviors. In order to explore the field dependence of the magnetization of the alloy while the temperature is increased and decreased, isothermal magnetization measurements were performed at different temperatures while the temperatures were raised from 200 to 400 K, and then decreased from 400 to 200 K. Figures 6(a) and (b) show some of the isothermal magnetization, $M(H)$, curves obtained at temperatures ranging from 200 to 304 K, while the temperature was increasing and decreasing, respectively. The inset of each figure shows the $M(H)$ curves in the lower field region. It can be clearly seen in the figures that the increasing temperature and decreasing temperature $M(H)$ curves obtained at 302 and 304 K show different behaviors (see the insets of figure 6). The $M(H)$ curves obtained while heating show hard magnetic behavior whereas the $M(H)$ curve obtained while cooling shows easy magnetic behavior. This characteristic clearly shows that the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ with $x = 0.04$ alloy undergoes different magnetostructural transitions while being heated up and cooled down.

Figures 7(a) and (b) shows the Arrott plots of the $M(H)$ curves of the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ with $x = 0.04$ obtained near T_C. Figure 7(a) shows the plots while heating up and figure 7(b) shows the plots obtained while cooling down. The S shaped curves shown in the figures clearly demonstrate the first-order nature of the transitions at T_C. Like the $M(H)$ curves shown in figure 6, the Arrott plots in the temperature range from 301 to 304 K obtained while heating and cooling exhibit different characteristics. This again reveals that $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ with $x = 0.04$ undergoes different magnetostructural transitions while being heated up and cooled down.

The magnetic entropy changes as functions of increasing and decreasing temperatures for the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ ($x = 0.04$) alloy are shown in figure 8. The maximum

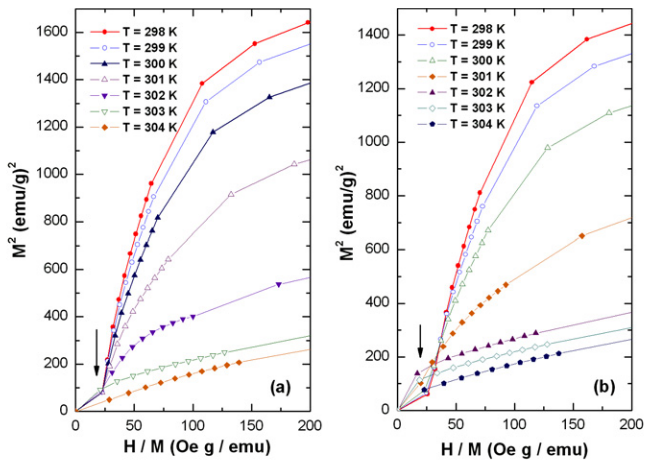

Figure 7. Arrott plots of the $M(H)$ curves of $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ with $x = 0.04$ obtained near T_C while (a) temperature was increased and (b) temperature was decreased.

magnetic entropy change, ΔS_m, obtained while heating is -40.7 J kg^{-1} K^{-1}, whereas the maximum while cooling is -26.7 J kg^{-1} K^{-1}. This difference in maximum ΔS_m values can be attributed to the single magnetostructural transition that takes place while heating and multiple transitions that take place while cooling. A peak in the vicinity of the intermartensitic transition temperature is also observed in the curve for ΔS_m as a function of decreasing temperature (see the inset of figure 8). No peak is observed in this temperature region in the curve for ΔS_m as a function of increasing temperature.

The curves for resistivity as a function of increasing temperature ($R(T)$) for $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ are shown in figure 9. The $R(T)$ curve of the sample with $x = 0.04$ shows only one transition near 310 K, which is consistent with the transition temperature shown for the $M(T)$ curve of the alloy (see figure 3). Every other alloy in the series shows two

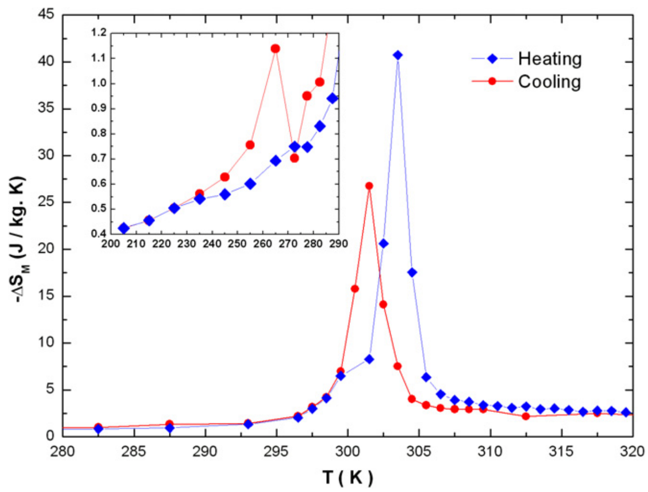

Figure 8. Magnetic entropy changes of the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ alloy ($x = 0.04$) obtained as functions of increasing and decreasing temperatures. The inset shows the same for temperature regions 200–290 K.

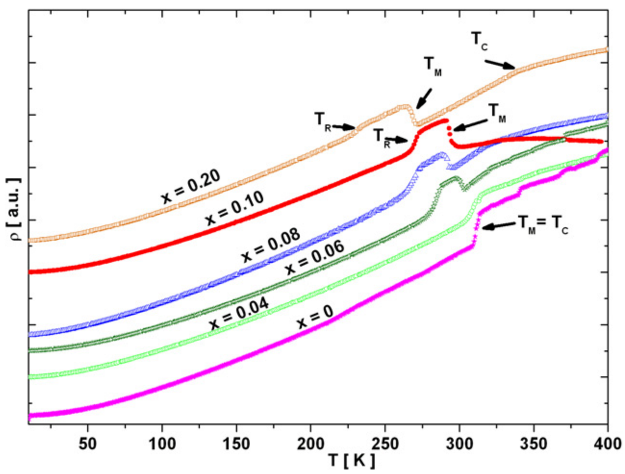

Figure 9. Electrical resistivity as a function of increasing temperature for $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ ($0.04 \leqslant x \leqslant 0.20$).

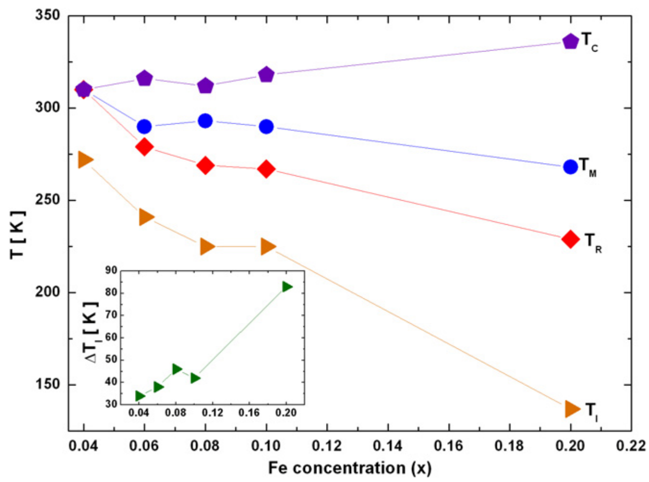

Figure 10. Martensitic transformation temperature (T_M), intermartensitic transformation temperature (T_I), reverse intermartensitic transformation temperature (T_R), and Curie temperature (T_C) as a function of Fe concentration (x). The inset shows the temperature hysteresis of the intermartensitic transformation, ΔT_I, as a function of Fe concentration (x).

distinct transitions, at T_R and T_M (see figure 4). A slope change, typical for a second-order phase transition, is also observed in the $R(T)$ curves at T_C. The shapes of the resistivity curves are very similar to those of Ni–Mn–Ga Heusler alloys exhibiting intermartensitic transitions [16, 17].

Figure 10 shows the transition temperatures T_I, T_R, T_M, and T_C, as a function of Fe concentration (x). The inset of figure 10 shows the temperature hysteresis, ΔT_I, of the intermartensitic phase transition. With increasing Fe concentration, T_I, T_R, and T_M are found to decrease, which is consistent with the result reported in [20], where the partial substitution of Mn with Fe results in a decrease of T_M. The increase of T_C with Fe concentration, as shown in figure 6, is due to the enhanced exchange interaction caused by Fe doping. Figure 5 also shows that, as Fe concentration increases, ΔT_I for the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ system also increases.

Wang *et al* [16] showed that the intermartensitic transformation arises due to a certain level of internal stress built up in the alloy. The internal stress cause some distortion in the lattice and thus compel the parent (cubic) phase to take a totally different martensitic transformation path during cooling, giving rise to the intermartensitic transformation. Taking this explanation into consideration, the observed intermartensitic transformations in the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ system can be explained in terms of internal stress developing in the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ alloy system due to Fe doping. It is very likely that adding a fifth element to the four-element compound $Ni_2Mn_{0.75}Cu_{0.25}Ga$ will assist in the formation of some distortion in the lattice of the compound. Such distortion in the lattice will be accompanied by some internal stress. If this stress exceeds the critical stress, which is typically about 13.8 ± 1.08 MPa, as reported in [16], the observation of intermartensitic transformation will be probable. Most probably the additions of Fe in the $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ have facilitated such a phenomenon. However, a detailed temperature dependent structural analysis including determining the occupancies of the specific elements is needed in order to establish the factors that caused the intermartensitic transformation in $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$.

4. Conclusion

In conclusion, complete thermoelastic intermartensitic transformations have been observed in Fe doped $Ni_2Mn_{0.75-x}Fe_xCu_{0.25}Ga$ Heusler alloys in the concentration range $0.04 < x \leqslant 0.20$. By varying the degree of Fe doping, the intermartensitic transition temperatures can be controlled over a wide range of temperatures. The alloy with $x = 0.04$ exhibits an unusual property that is revealed by magnetization measurements. Only one transition is observed in the $M(T)$ curve obtained as a function of increasing temperature, while the $M(T)$ curve as a function of decreasing temperature shows three different transitions.

Acknowledgments

This research was supported by a Research Opportunity Award from the Research Corporation (RA0357), and by the Office of Basic Energy Sciences, Material Sciences Division of the US Department of Energy (contract No. DE-FG02-06ER46291).

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