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Magnetic and transport properties of the $Ni_{2-x}Mn_{1+x}Ga$ alloys

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Abstract. Magnetization and transport measurements have been performed to study the martensitic and pre-martensitic transitions for a series of ferromagnetic Heusler $Ni_{2-x}Mn_{1+x}Ga$ alloys. Both magnetization and resistivity measurements show a clear jump at the martensitic transition and a discontinuous slope change at the pre-martensitic transition. The characteristic temperatures correspond well with those derived from previous direct structural results from neutron scattering, electron microscopy and ultrasonic studies. The martensitic transition temperature decreases with increasing Mn concentration.

The ferromagnetic Heusler alloy $Ni_{2-x}Mn_{1+x}Ga$ with $x = 0$ was first studied in the early 1980s [1]. For the stoichiometric Ni_2MnGa, the alloy was found to be ferromagnetic with a Curie temperature of 376 K. A martensitic phase transition from a cubic structure to a complex tetragonal structure at 202 K on cooling was observed from microscopy and neutron scattering measurements, with a corresponding jump in magnetization at the same temperature. The potential of the $Ni_{2-x}Mn_{1+x}Ga$ alloys as shape memory materials has led to much more careful studies of the structural transition. Recent studies using x-ray, electron and neutron scattering, ultrasound attenuation and magnetic measurements reveal structural anomalies at temperatures above the martensitic transition [2–9]. Work on alloys with non-stoichiometric compositions shows that both the Curie temperature and the martensitic transition can be varied with the concentration x [10–12]. However, it is generally believed that except the magnetic jump that occurred at the martensitic transition and magnetic anomalies associated with the pre-martensitic transition [9], there is no transport evidence corresponding to the structural transitions [10–12].

In this paper, we report the first direct magnetic and transport characterizations of the pre-martensitic transition for several concentrations of the $Ni_{2-x}Mn_{1+x}Ga$ alloy. Magnetization M as a function of temperature T at various applied fields H shows a jump at the martensitic transition T_m and an anomalous temperature dependence at the pre-martensitic transition T_1. Transport measurements reveal a corresponding jump in resistivity at T_m and a change of slope at T_1. The results demonstrate clearly the presence of one or more pre-martensitic structural transitions in these alloys.

Samples are prepared with the conventional arc-melt process with the stoichiometric composition of starting materials [1]. Structural analysis confirms the single-phase, crystalline nature of the alloy. Magnetization measurements are performed on several samples using a SQUID magnetometer. The magnetization data on three samples with $x = 0.04$, 0 and -0.08, and mass $m = 3.1$ mg, 9.1 mg and 7.2 mg, respectively, are reported here. Thermal

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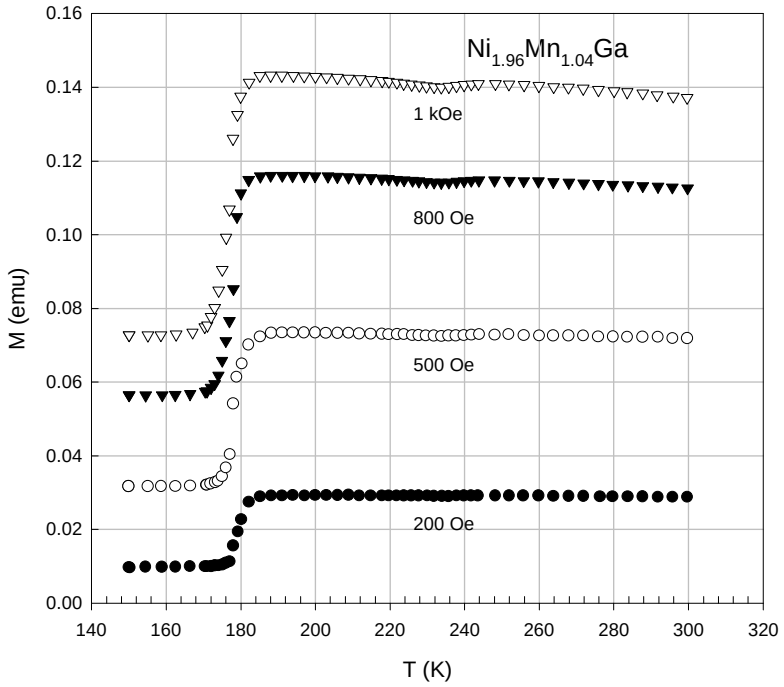

Figure 1. Magnetization as a function of temperature at various low magnetic fields for a $Ni_{1.96}Mn_{1.04}Ga$ sample.

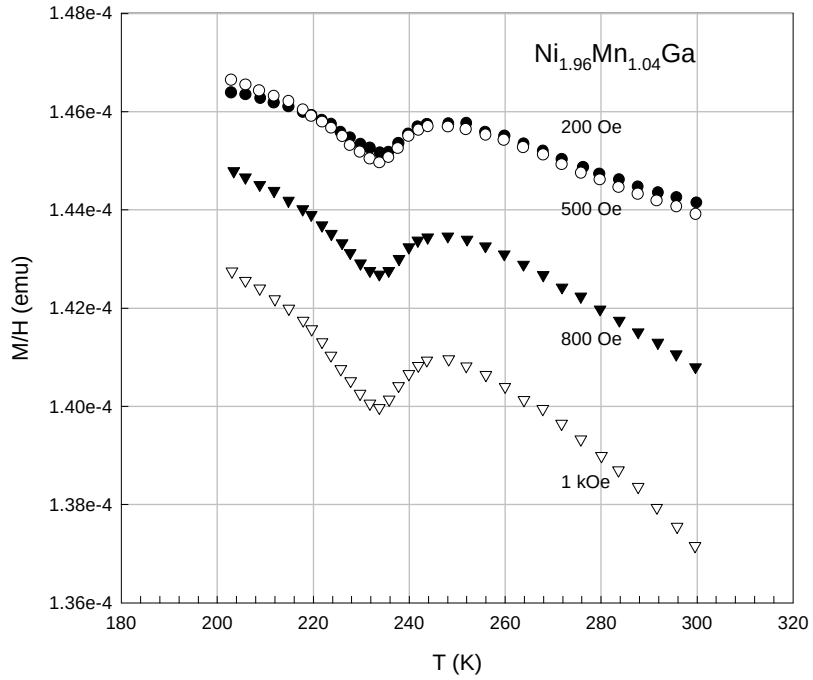

Figure 2. An expanded view of *M/H* at temperatures above the martensitic transition for the $Ni_{1.96}Mn_{1.04}Ga$ sample.

hystereses in the magnetization and resistivity measurements were observed for cooling down and warming up of the sample, most probably due to the grains and dislocations of the alloy. Most of the data presented here were collected during the process of warming up from below T_m and the sample was cooled in zero field each time from about 320 K. For a sample cooled in a field, an overall larger magnetization was observed than if it was cooled in zero field. The transport measurements were done on samples cut from the same pieces using the standard four-probe technique with a typical excitation current of 100 μA. The signal was fed through a transformer amplifier to minimize the noise of the lock-in amplifier.

Shown in figure 1 is an overlay of magnetizations as a function of temperature at various small fields $H = 200$, 500, 800, 1000 Oe for a $Ni_{1.96}Mn_{1.04}Ga$ sample. At the martensitic transition, a jump in magnetization at around 180 K is clearly observed. A large jump in $M(T)$ at T_m is characteristic of martensitic transition of the ferromagnetic Heusler alloy. The magnitude of the jump increases with increasing field in the field range. Below T_m, M is nearly flat. Above T_m, a small dip-like structure is observed.

To allow us to look at the dip structure more carefully, the linear susceptibility, M/H, is plotted for temperature above T_m in figure 2. The dip structure is now seen clearly at a temperature around 235 K. The rise in M above 235 K is somewhat similar to the jump observed at T_m, except that the magnitude of the jump is about 2% of $\Delta M(T_m)$. Notice that the temperature at which the dip occurs does not vary with the magnetic field.

At higher fields $H = 1$, 2, 3, 4 kOe, the dip gradually disappears, as shown in figure 3. Above 2 kOe, $M(T)$ decreases monotonically with increasing temperature. At 4 kOe, M is nearly saturated.

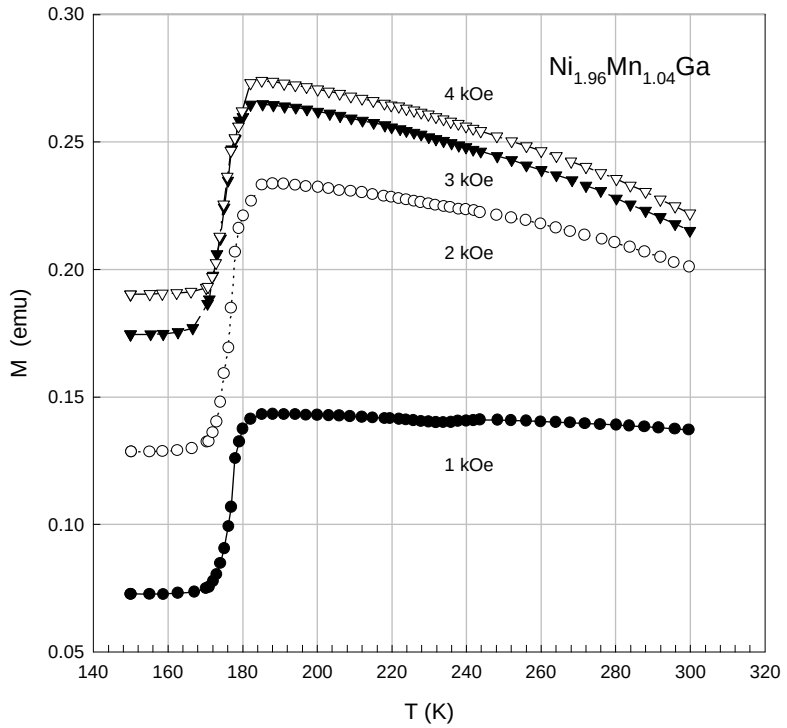

Figure 3. Magnetization as a function of temperature at higher fields for the $Ni_{1.96}Mn_{1.04}Ga$ sample.

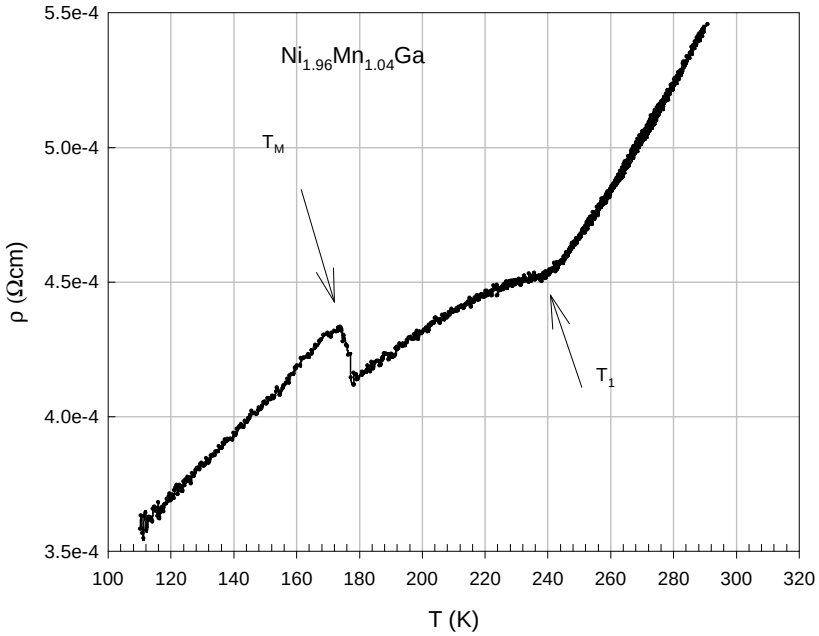

Figure 4. Resistivity as a function of temperature for the $Ni_{1.96}Mn_{1.04}Ga$ sample.

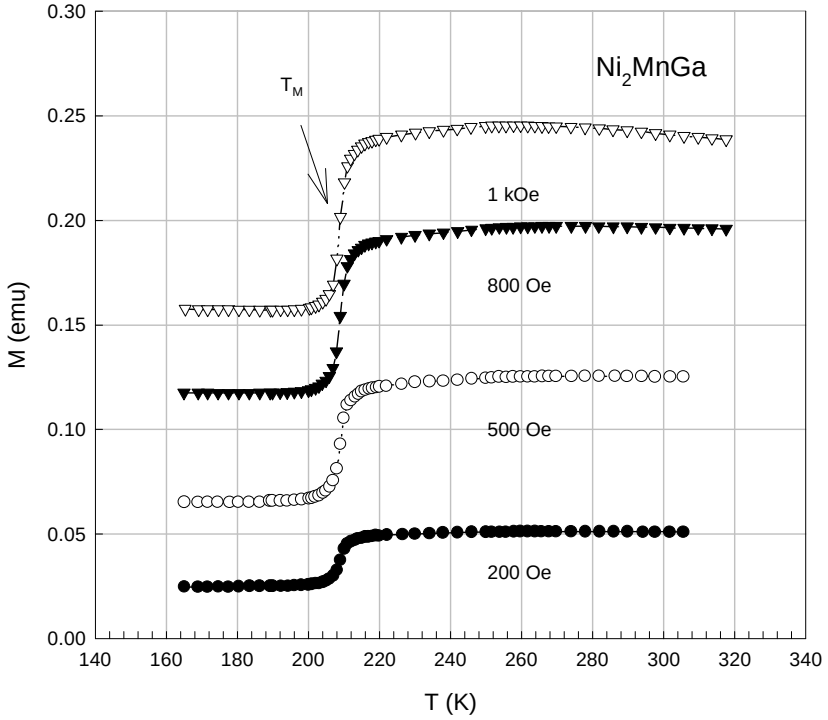

Figure 5. Magnetization as a function of temperature at various low magnetic fields for a Ni_2MnGa sample.

Shown in figure 4 is a plot the resistivity as a function of temperature for a sample cut from the same piece. The temperature dependence can be described as approximately three linear regions except at the transitions. A large jump near 180 K corresponds well to the martensitic transition observed magnetically. This is a natural consequence of a first-order structural transition. At a higher temperature T_1, near 240 K, a change in the slope of the resistivity is clear. A linear extrapolation would imply a small jump at T_1 as at T_m. T_1 is nearly the same as the dip temperature observed in $M(T)$ at low fields. The close correspondence demonstrates unambiguously a secondary process above the martensitic transition or a pre-martensitic transition for the $Ni_{1.96}Mn_{1.04}Ga$ sample.

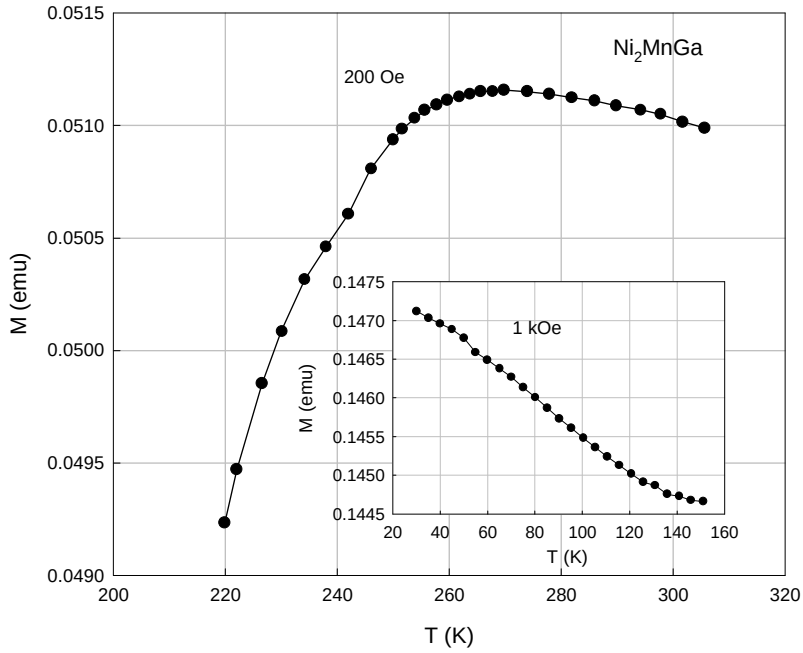

Figure 6. An expanded view of $M(T)$ at 200 Oe at $T > T_m$ for the Ni_2MnGa sample. The inset is a plot of $M(T < T_m)$.

For a sample with the stoichiometric composition Ni_2MnGa, similar measurements were carried out. Shown in figure 5 is an analogous temperature dependence of the magnetization at small fields. The martensitic transition characterized by the jump in M is now at around 210 K—an increase of 30 K above the T_m of the $x = 0.04$ sample. Similarly the jump in M increases with field at small values of H, with T_m independent of the applied field. Above T_m, unlike in the case for the $Ni_{1.96}Mn_{1.04}Ga$ compound, $M(T)$ goes through a broad peak structure rather than a dip. An expanded view of the magnetization at 200 Oe is shown in figure 6 for T above 220 K. $M(T)$ increases with T and peaks at around 260 K and decreases for $T > 260$ K. The inset shows a typical temperature dependence of the magnetization at 1 kOe at low temperatures $T < T_m$. $M(T)$ decreases monotonically with increasing T before the martensitic transition is reached.

Figure 7 shows the high-field temperature dependence of the magnetization. With increasing field, the jump at T_m decreases for $H > 2$ kOe. At $H = 10$ kOe, M is completely saturated. The bump-like structure above T_m shifts toward smaller temperatures with increasing field. The inset is a replot of the magnetization as a function of temperature at 10 kOe. The

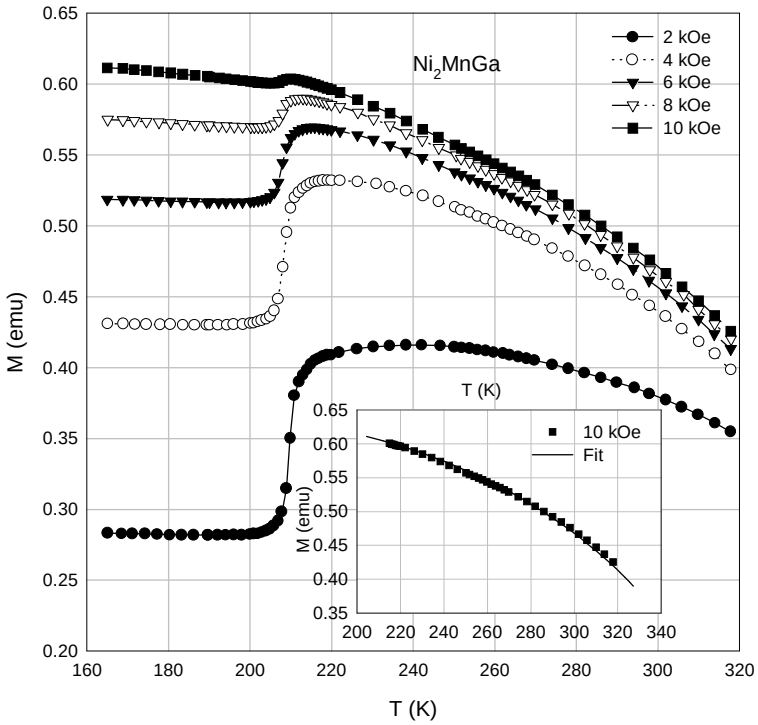

Figure 7. Magnetization as a function of temperature at higher fields for the Ni_2MnGa sample. The inset shows $M(T)$ at 10 kOe and the curve is a fit.

solid curve is a fit to the mean-field theory of the magnetic moment as a function of temperature. For a ferromagnetic material, the magnetic moment can be described by $M(T) = M_0 m(T)$; here $m(T) = \tanh[T_c m(T)/T]$ [13]. The curve fit gives $M_0 = 0.65$ emu and a Curie temperature of about 378 K, consistent with direct high-temperature measurements on this compound. The saturation magnetic moment M_0 gives an effective magnetic moment of about 3.3 Bohr magnetons per Mn atom, in agreement with the earlier magnetic measurement [1]. The excellent fit to the data suggests that the intermediate phase or pre-martensitic phase is essentially absent in a field of 10 kOe. Notice also that T_m is hardly changed by fields up to 10 kOe. Careful analysis of the field dependence of the secondary-peak temperature has been presented elsewhere [9].

Resistivity for the stoichiometric compound as a function of temperature in zero field is plotted in figure 8. Again, the data are piecewise linear in temperature. At $T_m \sim 210$ K, a jump in ρ is well correlated with the jump in M at T_m. At a higher temperature $T_1 \sim 250$ K, an abrupt change in $\mathrm{d}\rho/\mathrm{d}T$ is clear. 250 K is slightly below 260 K at which a bump was observed magnetically at 200 Oe. The difference may be attributed to the field dependence of T_1 at small H.

With decreasing Mn concentration, the martensitic transition is pushed toward a higher temperature. Shown in figure 9 is a similar magnetization versus temperature plot at various fields for a $Ni_{2.08}Mn_{0.92}Ga$ compound. Indeed, T_m is increased to about 230 K as determined from the jump in M. Above T_m, the behaviour of the magnetization is somewhat similar to that of the stoichiometric compound, with noticeable bumps in M. With increasing field, the bump feature gradually disappears.

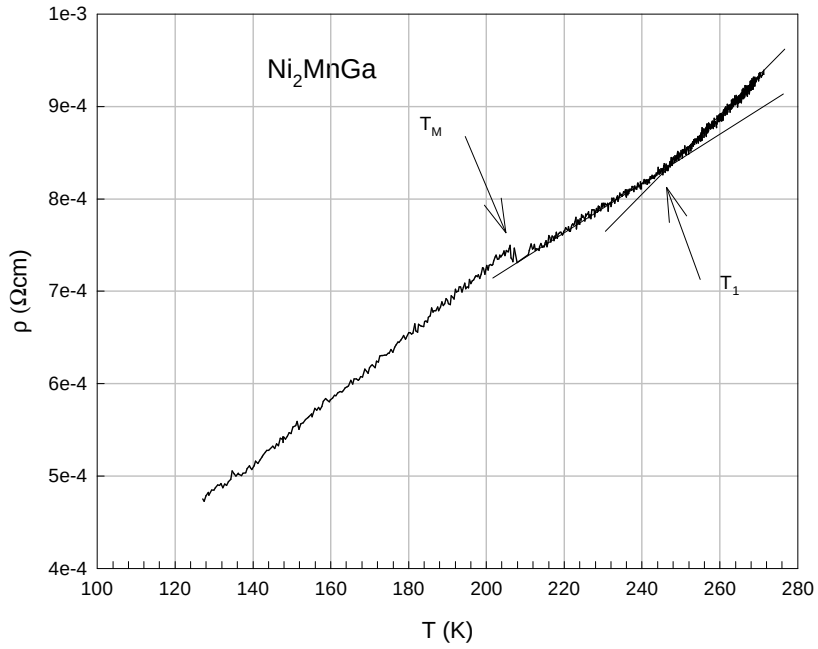

Figure 8. Resistivity as a function of temperature for the Ni_2MnGa sample.

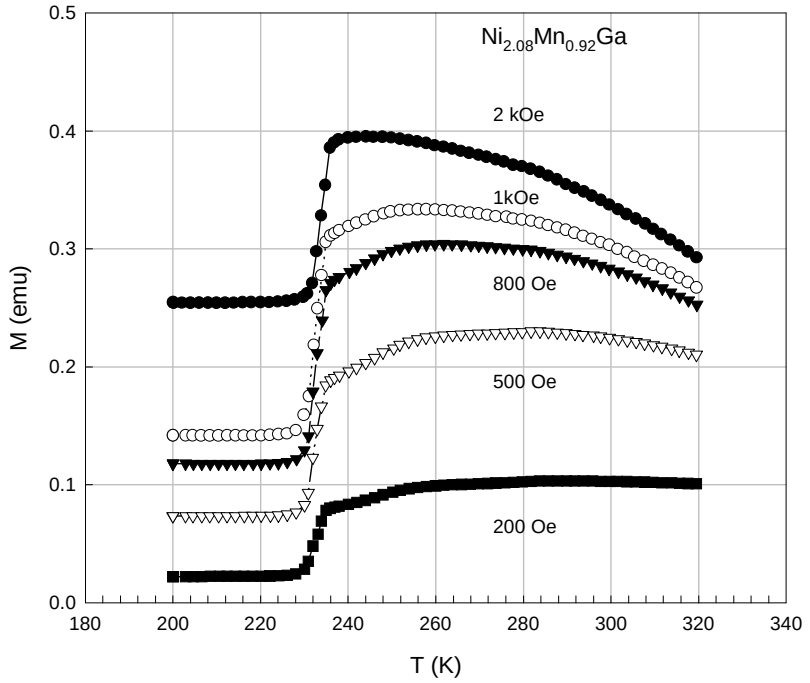

Figure 9. Magnetization as a function of temperature at various magnetic fields for a $Ni_{2.08}Mn_{0.92}Ga$ sample.

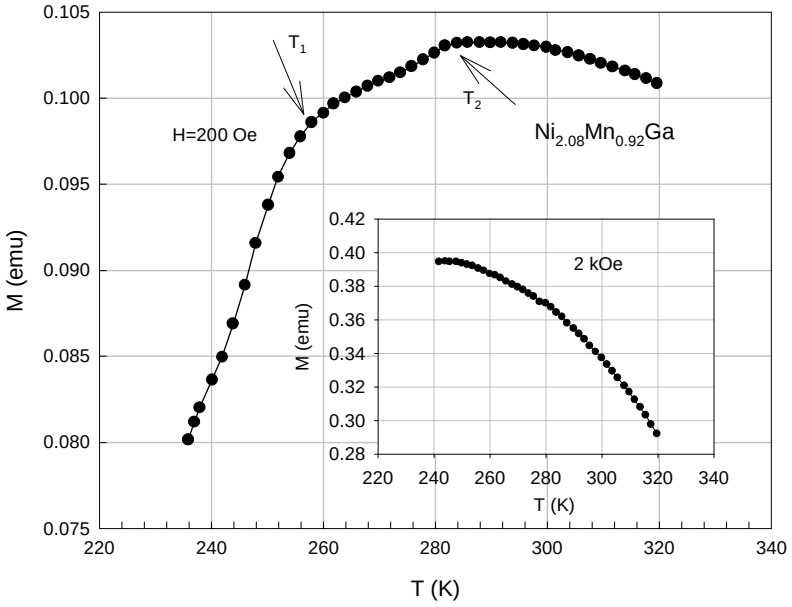

Figure 10. An expanded view of $M(T)$ at 200 Oe at $T > T_m$ for the $Ni_{2.08}Mn_{0.92}Ga$ sample.

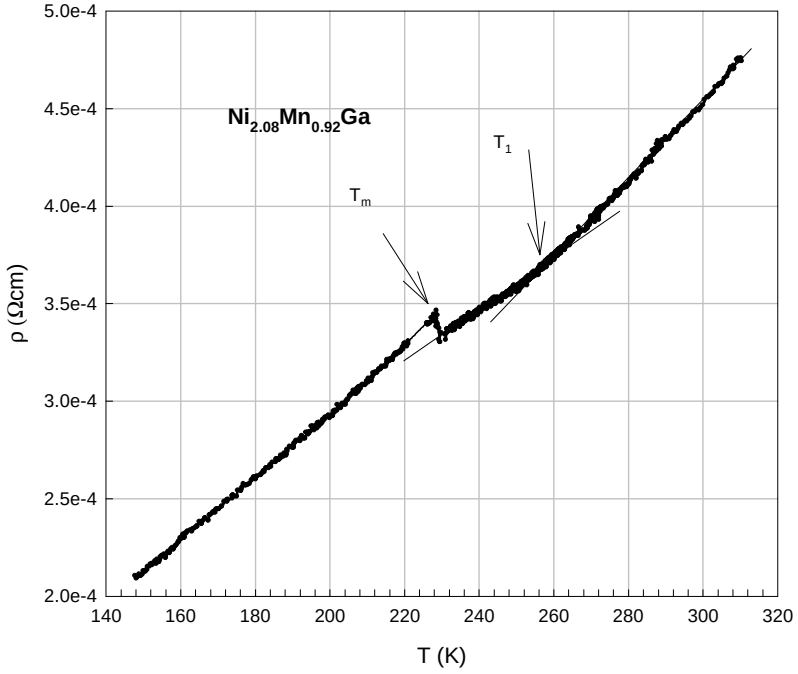

Figure 11. Resistivity as a function of temperature for the $Ni_{2.08}Mn_{0.92}Ga$ sample.

Figure 10 is an expanded view of the high-temperature anomaly for $Ni_{2.08}Mn_{0.92}Ga$. The magnetization at 200 Oe rises rapidly with increasing temperature to about 260 K, at which

point a change in the slope dM/dT is evident. At a second temperature T_2, about 280 K, M starts to decrease with further increasing temperature. The inset compares the behaviour at a higher field of 2 kOe. Here, $M(T)$ is seen to be clearly decreasing monotonically with temperature.

The corresponding resistivity measurement shows a jump at 230 K, as shown in figure 11. A slope change at a temperature between 250 and 260 K is seen, correlating with the 260 K anomaly in $M(T)$. However, no discernible change in $\rho(T)$ at 280 K is observed within the resolution of our measurements. This may be related to the fact that the magnetic anomaly at 280 K is relatively small and thermal fluctuations are more important for transport measurements at high temperatures.

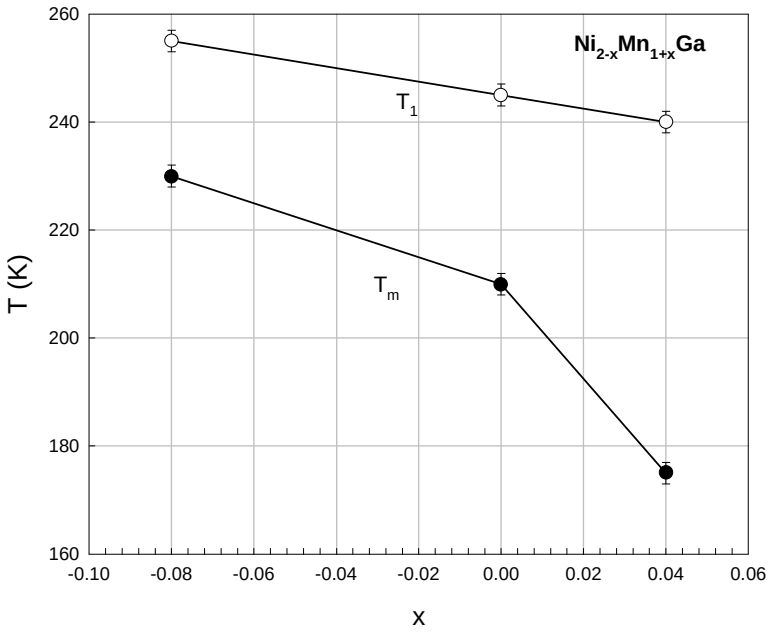

Figure 12. T_m and T_1 as functions of concentration x.

Figure 12 summarizes the concentration dependence of the martensitic and pre-martensitic transition temperatures. Clearly, both T_m and T_1 decrease with increasing x.

T_m decreasing with increasing Mn concentration is consistent with the previous reports on the concentration dependence of the structure transition [11]. The magnetic properties are dominated by the interaction of Mn atoms, where most of the magnetic moments reside as observed from neutron scattering experiments [1]. Qualitatively, with increasing Ni concentration, the distance between the Mn atoms increases, thus resulting in a reduced exchange interaction and lower Curie temperature. At the same time, the electron density and the structural transition temperature increase.

Careful structural studies, such as those by means of neutron scattering, ultrasound attenuation and transmission electron microscopy, have been reported, mostly for the stoichiometric compound. It has been shown that there is significant TA_2 phonon softening at wave vector $q \approx 0.33$ at temperatures well above that of the martensitic transition [3]. The studies established the existence of a weakly first-order structural transition at $T_1 \sim 265$ K and a pre-martensitic phase for a temperature between T_m and 265 K. The pre-martensitic phase

is approximately fcc with a modulation corresponding to a wave vector of $\frac{1}{3}$[110]. Below T_m, the structure is approximately tetragonal. The presence of the intermediate phase is also supported by ultrasonic attenuation and velocity measurements, where the elastic constant stiffens and the attenuation decreases drastically below 265 K [5]. The correspondence of the martensitic and pre-martensitic transition temperatures with our magnetic and transport measurements on the Ni_2MnGa compound supports strongly the presence of a pre-martensitic transition. Furthermore, the field dependence of the pre-martensitic transition temperature for the stoichiometric compound suggests a large magneto-elastic interaction for the pre-martensitic phase [9].

For the non-stoichiometric compounds, the data suggest the presence of two possible pre-martensitic transitions for the $Ni_{2.08}Mn_{0.92}Ga$ composition, at 280 K and 260 K respectively. The 260 K transition may be of the same nature as for the Ni_2MnGa. For the $Ni_{1.96}Mn_{1.04}Ga$ compound, the dip-like field dependence of the magnetization suggests that the pre-martensitic transition may have a different origin, although the possibility of a small secondary phase with a large T_m cannot excluded from our measurements.

In summary, magnetization and transport measurements show jumps and discontinuous slope changes at temperatures corresponding to the martensitic and pre-martensitic transitions. The martensitic transition temperature increases with increasing Ni concentration and is independent of the applied field up to 10 kOe. The agreement of the transition temperatures of the stoichiometric compound with other direct structural studies suggests the possible presence of more than one pre-martensitic transition for the non-stoichiometric compounds and calls for careful direct structural studies on these compounds to allow us to achieve an understanding of the physics of these materials.

Acknowledgments

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