PHYSICAL REVIEW B VOLUME 58, NUMBER 17 1 NOVEMBER 1998-I

Magnetic properties of the premartensitic transition in Ni_2MnGa alloys

F. Zuo and X. Su
Department of Physics, University of Miami, Coral Gables, Florida 33124

K. H. Wu
Department of Mechanical Engineering, Florida International University, Miami, Florida 33196

(Received 2 June 1998)

Magnetization as a function of field and temperature for a ferromagnetic Heusler alloy Ni_2MnGa is reported. Magnetization above the Martensitic transition displays a field-dependent peak effect, a direct magnetic evidence of premartensitic phase. At low fields, the peak effect occurs at a temperature consistent with the observations of the micromodulated structure transition seen from neutron scattering, electron microscopy, and ultrasonic studies in this compound. At high fields, the peak effect is suppressed. The strong field dependence of the peak temperature suggests a large magnetoelastic interaction in the intermediate phase.
[S0163-1829(98)09537-X]

The ferromagnetic Heusler alloy $Ni_{2-x}Mn_{1+x}Ga$ with $x=0$ was first studied in the early 1980's.[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. Later studies on alloys with nonstoichiometric compositions show that both the Curie temperature and the Martensitic transition can be varied with x.[2–4] Recent interest in the $Ni_{2-x}Mn_{1+x}Ga$ alloys as shape memory materials has lead to much more careful studies of the structural transition. It has been reported that the Martensitic transition is proceeded by a premartensitic transition as observed from several experiments such as x-ray, electron- and neutron-scattering, and ultrasound measurements.[5–11] However, it is generally believed that there is no magnetic anomaly corresponding to the premartensitic transition.[2–4]

In this paper, we report direct magnetic characterizations of the premartensitic transition for the stoichiometric Ni_2MnGa alloy. Magnetization M as a function of temperature T at various applied field H shows clear evidence of a premartensitic transition. The premartensitic transition is characterized by a peak in $M(T)$ well above the Martensitic transition temperature T_m. The premartensitic transition temperature T_p is found dependent on the applied field. The field dependence of T_p demonstrates a large magnetoelastic effect in the premartensitic or intermediate state.

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 superconducting quantum interference device magnetometer. The data reported here are for a small rectangular sample of 9 mg. Thermal hysteresis in magnetization as well as in the T_m was observed between cooling down and warming up of the sample, most likely due to the grains and dislocations of the alloy. Most of the data presented here are collected during the warming up process from below T_m and the sample was cooled in zero field each time from about 320 K. For a sample cooled in field, an overall larger magnetization was observed than if cooled in zero field.

Shown in Fig. 1 is a plot of the magnetization as a function of temperature for temperatures above T_m. It is clear that the magnetization peaks at about $T_p \sim 270$ K, above which magnetization decreases with increasing temperature. The continued increase in $M(T)$ for $T_p > T > T_m$ demonstrates an incomplete Martensitic transition at T_m. The intermediate state defined between T_p and T_m spans over 60 K in temperature. The inset in Fig. 1 is the magnetization over a broader temperature range. A large jump in $M(T)$ at $T_m = 210$ K is characteristic of Martensitic transition of the ferromagnetic Heusler alloy.

Figure 2 shows a similar plot of magnetization versus

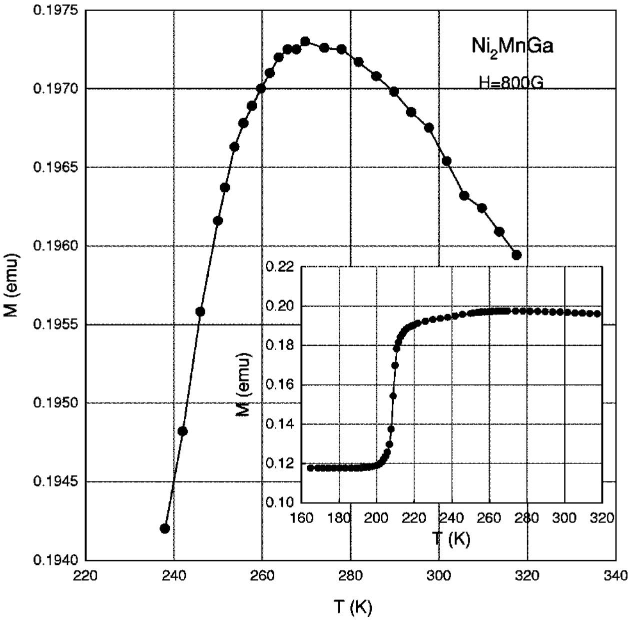

FIG. 1. Magnetization as a function of temperature at $H=800$ G. The inset is a plot over a broader temperature range.

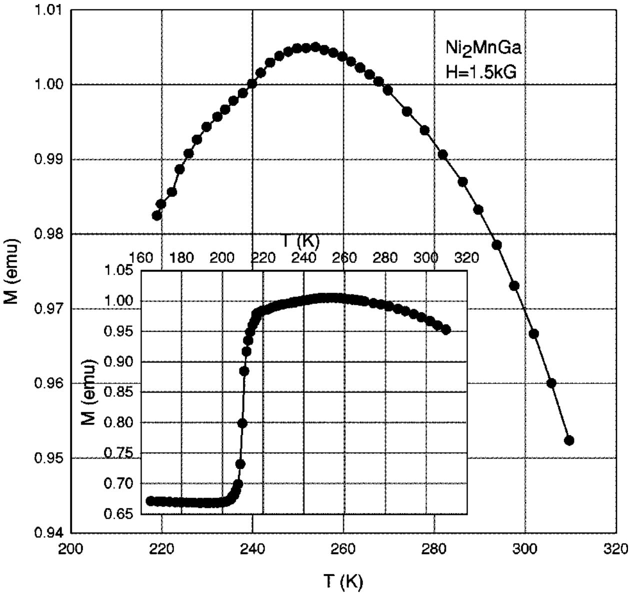

FIG. 2. Magnetization as a function of temperature at $H=1.5$ kG. The inset is a plot over a broader temperature range.

temperature for an applied field of 1.5 kG. The overall characteristics are very similar to the $M(T)$ at 800 G. However, the peak temperature is now at about 250 K, a decrease of 20 K from the peak temperature at $H=800$ G. Magnetization above T_p decreases much faster than that at 800 G. The inset shows the magnetization through the same Martensitic transition at $T_m=210$ K.

Figure 3 shows an overlay of magnetizations at higher applied fields from $H=2$ kG to 10 kG. The curves from the bottom up correspond to $H=2$, 4, 6, 8, and 10 kG, respectively. The overall data are consistent with $M(T)$ at smaller H with a downward shift in T_p and a stronger temperature dependence above T_p. The Martensitic transition temperature is hardly changed for fields up to 1 T. Magnetizations at $H=8$ and 10 kG are almost overlapping at high temperatures, indicating magnetic saturation at these fields and temperatures.

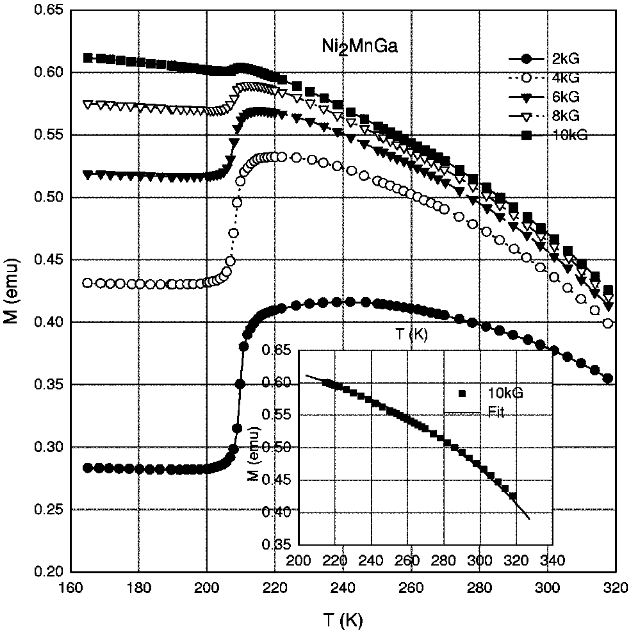

FIG. 3. Magnetization as a function of temperature at several high fields $H=2$, 4, 6, 8, and 10 kG. The inset is a plot of magnetization at 10 kG and a model fit.

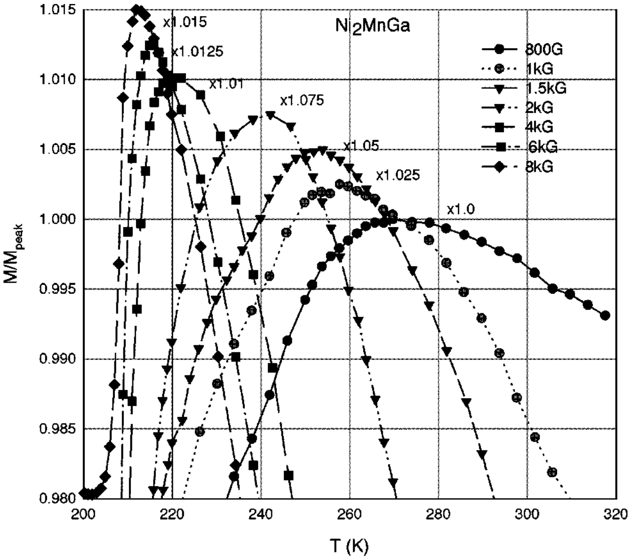

FIG. 4. Normalized magnetizations at various fields as a function of temperature near the peak temperatures.

The inset in Fig. 3 is a replot of the magnetization as a function of temperature at 10 kG. The solid line 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 $M(T)=M_o m(T)$, here $m(T)=\tanh[T_c m(T)/T]$.[12] The line fit gives a $M_o=0.65$ emu and the Curie temperature about 378 K, consistent with direct high-temperature measurements on this compound. The saturation magnetic moment M_o gives an effective magnetic moment of about 3.3 Bohr magneton per Mn atom, in agreement with the earlier magnetic measurement.[1] The excellent fit to the data suggests that the intermediate phase or premartensitic phase is essentially absent in a field of 1 T.

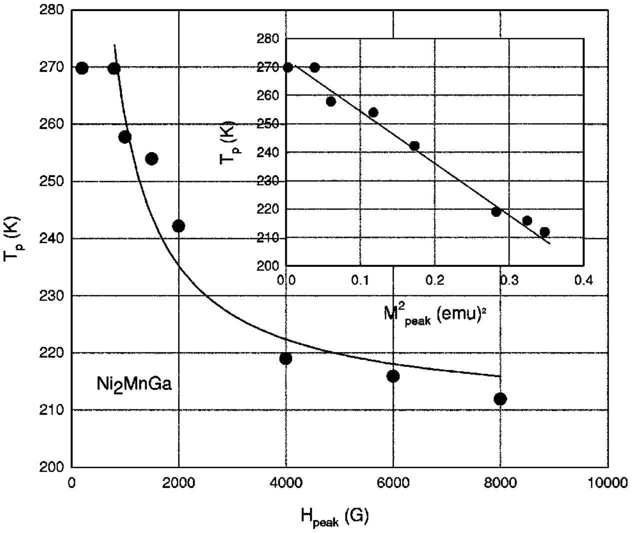

FIG. 5. Peak temperature as a function of peak field with the solid line as a fit. The inset is a plot of peak temperature vs m^2. The line is a linear fit to the data.

To look at the field dependence of the premartensitic transition temperature more carefully, the magnetizations are normalized to the peak magnetic moment, M/M_{peak}, and plotted as a function of temperature, as shown in Fig. 4. The curves are each scaled to a factor to suggest the nature of the increasing M_{peak} with increasing field (not to scale) and to spread out for a better view. Several features are clear: (a) the peak temperature decreases with increasing field; (b) the peak width decreases strongly with increasing field; (c) the peak temperature is hardly distinguishable from the Martensitic transition at $H=1$ T.

If we plot the peak temperature as a function of applied field, T_p is almost inversely proportional to the applied field, as shown in Fig. 5. The circles are extrapolated from the peak positions, and the solid line is a fit to $T_p=T_o(1+H_o/H_{peak})$ with $T_o=210$ K and $H_o=245$ G. For field less than 800 G, the peak temperature is constant and thus cannot be described by the inverse field dependence. The inset shows the peak temperature dependence on the squared magnetic moment. A quasilinear dependence of $T_p \propto m^2$ is clear within the experimental scatters.

The observation of the field-dependent premartensitic transition from direct magnetization measurements has not been reported before. Previous works were limited to high fields and were concentrated only on the Martensitic transition. The large jump at T_m corresponds to the structural transition from a high-temperature phase to a low-temperature tetragonal phase. The reduced moment below T_m arises from the formation of lattice constrained magnetic domains, as observed directly from electron microscopy. Above T_m, the magnetic domains are easily aligned to the field direction.[1]

The observed T_p at small field is consistent with the determination of premartensitic transition temperature from other measurements such as neutron-scattering and ultrasound attenuations. Inelastic neutron scattering and transmission-electron microscopy show that there is significant TA_2 phonon softening at wave vector $q=0.33$ at temperatures well above the Martensitic transition.[6] The studies established the existence of a weakly first-order strucutral transition at $T_1 \sim 265$ K and premartensitic phase for temperature in between T_m and 265 K. The premartensitic phase is approximately fcc with a modulation corresponding to a wave vector $\frac{1}{3}[110]$. Below T_m, the structural 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.[8] The peak temperature of about 270 K in the magnetization in small fields corresponds well to the reported $T_1 \sim 265$ K transition.

The large field dependence demonstrates a large magnetoelastic effect in the intermediate phase, contrary to some previous assumptions that there is no magnetoelastic effects based on the existence of phonon anomaly at temperatures above the Curie temperature.[6] Although the magnetoelastic effect was suggested earlier in a thermal ac susceptibility measurement on some stress-induced nonstoichiometric alloys.[2]

The exact origin of the magnetic field and temperature dependence for the intermediate phase is not clear. Qualitatively, the free energy of the ferromagnetic Martensite can be expressed as a sum of three contributions $F=F_e+F_m+F_{em}$, where F_e is the elastic energy, F_m is the magnetic energy, and F_{em} is the magnetic-elastic energy. The presence of large soft phonon modes above T_p suggest that elastic energy favors the intermediate phase. The magnetic energy contribution, $F_m=K(m_z^2m_y^2+m_z^2m_x^2+m_x^2m_y^2)-M\cdot H$ will be dependent on the anisotropy constant K. In general, the applied magnetic field will increase the magnetic transition temperature. The fact that T_p decreases with increasing H suggests that either the F_m term is not important here or that the first term in F_m dominates. The presence of an applied field will increase the alignment of the magnetic domains in the direction of the field, thus will increase the magneticelastic energy contribution. It is plausible that the increased magnetoelastic interaction will result in a reduced T_p. The quasilinear m^2 dependence of the peak temperature suggests that the magnetoelastic energy is quasilinear with m^2, i.e., $F_{em} \sim m^2$. Careful theoretical modeling is necessary to quantitatively understand the temperature and field dependence of the intermediate state. It is worth pointing out that T_m is barely affected in the field range, which suggests that the magnetoelastic effect is absent or negligible at temperatures near the Martensitic transition temperature.

In summary, magnetization as a function of temperature displays a field-dependent peak effect at a temperature above the Martensitic transition temperature. At small field, the peak effect is consistent with the observation of micromodulated structure transition from neutron scattering, electron microscopy, and ultrasound studies. At high field, the peak effect is drastically suppressed. This is direct magnetic evidence for the premartensitic phase or intermediate phase. The strong field dependence of the peak temperature suggests a large magnetoelastic effect in the premartensitic phase.

One of us (F.Z.) acknowledges partial support by a general research grant from the University of Miami.

---

[1] P. J. Webster, K. R. A. Ziebeck, S. L. Town, and M. S. Peak, Philos. Mag. B **49**, 295 (1984).

[2] V. A. Chernenko, A. Amengual, E. Cesari, V. V. Kokorin, and I. K. Zasimchuk, J. Phys. IV **5**, C2-95 (1995).

[3] A. D. Bozhko, A. N. Vasil'ev, V. V. Khovailo, V. D. Buchel'nikov, I. E. Dikshtein, S. M. Seletskii, and V. G. Shavrov, Pis'ma Zh. Éksp. Teor. Fiz. **67**, 212 (1998) [JETP Lett. **67**, 227 (1998)].

[4] V. A. L'vov, E. V. Gomonaj, and V. A. Chernenko, J. Phys.: Condens. Matter **10**, 4587 (1998).

[5] G. Fritsch, V. V. Kokorin, and A. Kempf, J. Phys.: Condens. Matter **6**, L107 (1994).

[6] A. Zheludev, S. M. Shapiro, P. Wochner, A. Schwartz, M. Wall, and L. E. Tanner, Phys. Rev. B **51**, 11 310 (1995).

[7] V. A. Chernenko, C. Segui, E. Cesari, J. Pons, and V. V. Kokorin, Phys. Rev. B **57**, 2659 (1998).

[8] T. E. Stenger and J. Trivisonno, Phys. Rev. B **57**, 2735 (1998).

[9] J. Worgull, E. Petti, and J. Trivisonno, Phys. Rev. B **54**, 15 695 (1996).

[10] L. Manosa, A. Gonza‘lez-Comas, E. Obrado, A. Planes, V. A. Chernenko, V. V. Kokorin, and E. Cesari, Phys. Rev. B **55**, 11 068 (1997).

[11] E. Cesari, V. A. Chernenko, V. V. Kokorin, J. Pons, and C. Segui, Acta Mater. **45**, 999 (1997).

[12] C. Kittel, *Introduction to Solid State Physics*, 6th ed. (Wiley, New York, 1992).