Magnetic and structural properties of nonstoichiometric Ni_2MnGa alloys with Ni and Ga excess

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The influence of nickel and gallium excess on local structure and magnetic properties of Ni–Mn–Ga alloys has been studied. Nuclear magnetic resonance experiments showed that excessive Ni occupies Mn and Ga positions. This leads to the appearance of low-frequency line from the nearest Mn^{55} nuclei and generation of fractional nuclear echo signals due to the increase of electrical field gradients on these nuclei. Magnetic measurements revealed the difference of Curie temperature determined from ac susceptibility and extrapolated from high-temperature magnetization behavior. The most probable explanation of this fact is the reduction of manganese–manganese indirect exchange via the faults in Mn–Ga layers interchange caused by excessive Ga. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1555978]

INTRODUCTION

In recent years considerable attention has been devoted to the Ni–Mn–Ga alloy system as a material for actuating devices.[1–3] The magnetic field-induced reorientation of martensite in these alloys can cause up to 10% length variation.[4] This effect strongly depends on alloy composition and structure. Because optimum magnetic shape memory effect was observed for nonstoichiometric Ni_2MnGa alloys, the relation between the composition and magnetic and structural properties of these materials is of great interest now.

Our nuclear magnetic resonance experiments[5,6] on Mn^{55} and Ga^{70} nuclei showed that ordering in Ni–Mn–Ga systems leads to appearance of stoichiometric Ni_2MnGa while excessive Mn (Ga) form faults in the Mn/Ga atomic layers interchange. Taking into consideration that ferromagnetism in this system is mainly determined by indirect exchange between manganese atoms,[7] strong correlation between magnetic properties and local structure should be expected.

The present work is devoted to the investigation of the correlation between magnetic properties and local structure in Ni–Mn–Ga systems of nonstoichiometric compositions with Ni and Ga excess.

EXPERIMENTAL PROCEDURE

Polycrystalline $Ni_{2.08}Mn_{0.81}Ga_{1.01}$ alloy was used as a main object for the investigation in this work. The results were compared with data obtained on another systems with different compositions. The composition of the alloys was determined by wave-length dispersive spectroscopy. Back-reflection Laue technique was used for the structure characterization. The martensitic transformation (T_m) and Curie (T_C) temperatures were determined from ac magnetic susceptibility, magnetization, and resistivity measurements. The powders of the materials, used in nuclear magnetic resonance (NMR) and magnetic measurement experiments, were prepared by milling of bulk materials. Then the powders were annealed in argon atmosphere 24 h at 800 °C with subsequent slow cooling. X-ray diffraction and composition investigations reveal no differences between parent single crystals and the powders.

Magnetic measurements were performed using superconducting quantum interference device magnetometer in 2–350 K temperature range and vibrating sample magnetometer in the 300–800 K temperature range. NMR spectra were recorded at 4.2, 77, and 293 K using nuclear spin-echo spectrometer of 50–400 MHz frequency range.

RESULTS AND DISCUSSION

It has been shown[6] that in $Ni_2Mn_{1-x}Ga_{1+x}$ alloys ($-0.2<x<0.2$) ordering leads to formation of stoichiometric Ni_2MnGa while excessive Mn or Ga atoms form faults in atomic layers interchange such as: $\cdots$–(GaNi)–(MnNi)–(**GaNi**)–(**GaNi**)–(MnNi)–$\cdots$ (in the case of Ga excess) or $\cdots$–(MnNi)–(GaNi)–(**MnNi**)–(**MnNi**)–(GaNi)–$\cdots$ (for Mn excess) instead of $\cdots$–(MnNi)–(GaNi)–(MnNi)–(GaNi)–(MnNi)–$\cdots$ in

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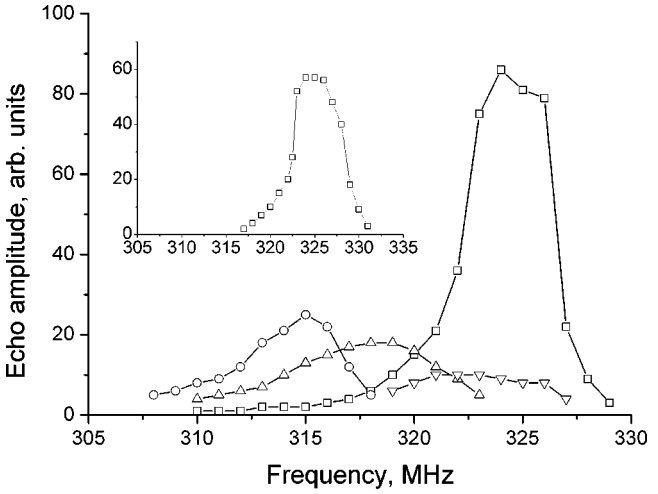

FIG. 1. Mn^{55} NMR spectra in $Ni_{54}Mn_{21}Ga_{25}$ alloy at 4.2 K for "usual" nuclear spin echo $t=\tau$ (□) and additional multiple spin echoes $t=1/2\tau$ (○), $t=2\tau$ (△), and $t=3\tau$ (▽). The intensities of the additional signals are substantially increased. The spectrum of the stoichiometric Ni_2MnGa alloy is represented in the inset.

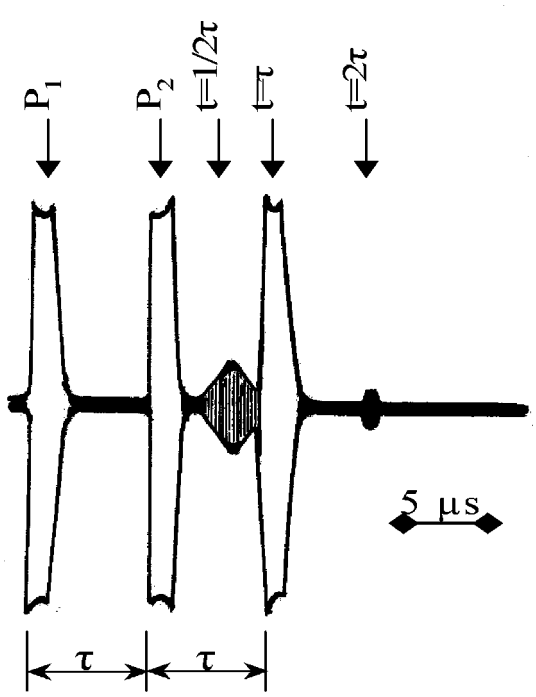

FIG. 2. Oscillogram of multiple echo signals in $Ni_{54}Mn_{21}Ga_{25}$ alloy at 4.2 K. The intensities of exciting pulses and "usual" spin echo are substantially decreased.

stoichiometric alloy. As a result in stoichiometric and Ga excess ordered alloys all Mn atoms have the same surrounding in and the first, second, and third second-coordinating spheres and single resonance line is observed on NMR spectra. In the case of Mn excess, Mn atoms near the faults has additional Mn atom instead of Ga in the second coordinative sphere. That leads to appearance of the additional low frequency line on Mn^{55} NMR spectra. In disordered alloys the substitution of Ni atoms in the first coordinative sphere as well as Ga and Mn atoms in the second and third ones is possible. As a result a broad multipeak spectra in a frequency range below the frequency of ordered Ni_2MnGa alloy are observed.[6]

The deviation of nickel content from the stoichiometry leads to appearance of weak low-frequency satellite even in the ordered alloy where gallium content exceeds manganese (see Fig. 1). This fact can be explained if one supposes the random substitutions of Mn and Ga atoms by Ni. As a result some Mn atoms have Ni atom in the second and third coordinative spheres and that leads to appearance of the low frequency satellite in the NMR spectrum.

The second characteristic feature is the possibility to observe fractional echo signals in multiple echo series (Fig. 2), i.e., signals arisen in fractional time moments ($t=1/2\tau$, $3/2\tau$, etc., where τ is the time interval between exciting pulses and t is the time after the second exciting pulse). These signals are caused by the multiquantum transition between quadrupole split nuclear levels.[8,9] It should be noted that fractional echoes excitation conditions are defined by the quadrupole interaction only. These echo signals arise if $\omega_0 > \omega_q > \Delta\omega_q > \Delta\omega_0$,[8] where ω_0 and $\Delta\omega_0$ are the Zeeman frequency and its inhomogenety, ω_q and $\Delta\omega_q$ are the qudrupole splitting and its inhomigeneity. Up to now fractional echo-signals were observed only in diamagnetic crystals and in magnetic semiconductors.

Fractional echo signals were not observed in alloys with stoichiometric Ni content. Spectra of fractional signals coincide with low frequency satellite of "usual" ($t=\tau$) echo. Spectra of signals arising at $t=2\tau$, 3τ associated with multiquantum transitions also shift to low frequency area. The appearance of Ni atoms in the second coordinative sphere discussed above leads to appearance of large electric field gradients on nearest Mn^{55} nuclei. This results in formation of the fractional echo signal from these nuclei. The NMR spectrum for such nuclei is shifted towards low-frequency area. Thus the spectra of fractional signals also should be observed in lower frequency range.

Temperature dependences of magnetization at different applied magnetic fields are presented in Fig. 3. The low-temperature part corresponded to martensite phase that has higher coercivity and saturation magnetization. Martensite–austenite transformation is observed around 290 K. Austenite has lower coercivity and saturation magnetization. In the area of the transformation where both martensite and austenite phases coexist the material has highest coercivity, due to fixation of domain walls on the phases boundaries, and intermediate saturation magnetization. This transformation is accompanied with characteristic peak on temperature dependence of resistance (see Fig. 4). Narrow temperature range of martensite–austenite transformation indicates high phase homogeneity of the material while the week temperature dependence of resistance is typical for disordered systems. This well correlates with our previous conclusion about formation of stack faults in atom layers interchange rather than phase separation in such systems.[6]

It is interesting to note that Curie temperature determined from ac susceptibility measurements (~330 K) and from extrapolation of high temperature behavior of reverse dc susceptibility (~350 K) do not coincide (see Fig. 5). The

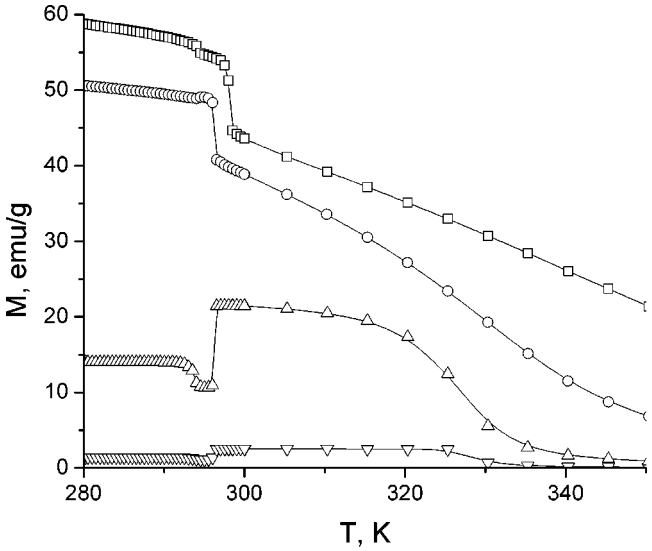

FIG. 3. Dependences of magnetization vs. temperature for $Ni_{54}Mn_{21}Ga_{25}$ at different applied magnetic fields: $H=100$ Oe (▽), $H=1000$ Oe (△), $H=10000$ Oe (○), and $H=50000$ Oe (□).

credible explanation of this fact is the reduction of manganese–manganese indirect exchange via the faults in Mn–Ga layers interchange caused by excessive Ga. Really, if the reduction of exchange takes place the system can be considered as small Ni_2MnGa clusters surrounded by the faults. The exchange interaction inside these clusters is larger than the intercluster interaction. The increase of the temperature leads first to the disruption of the interaction between the clusters. The situation becames similar to that was observed in superparamagnetic granular systems.[10] The transition from ferromagnetically coupled to superparamagnetic-like system should be accompanied by rapid decrease of the magnetic susceptibility and can be easily observed experimentally. Subsequent increase of the temperature will lead to the disruption of interaction inside the clusters and system became paramagnetic. The high-temperature behavior of magnetic susceptibility reflects both the exchange interaction inside and between the clusters. As a result the transformation temperature extrapolated from high-temperature susceptibility measurements will be higher than the temperature of abrupt decrease of magnetic susceptibility for such system.

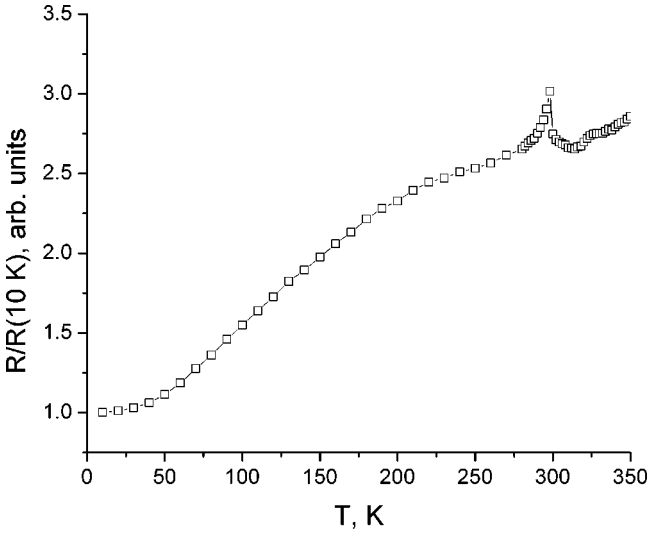

FIG. 4. Temperature dependence of resistance for $Ni_{54}Mn_{21}Ga_{25}$ alloy.

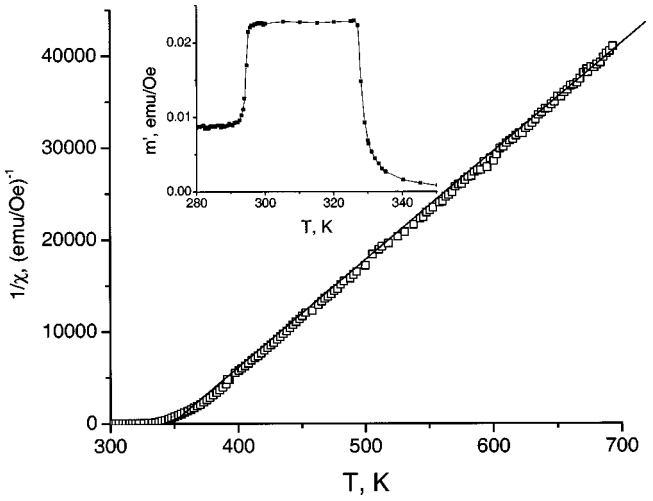

FIG. 5. Temperature dependences of reverse susceptibility dc $1/\chi$ and ac susceptibility m' (inset).

AKNOWLEDGMENT

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