Magnetic properties of $Ni_{2.18}Mn_{0.82}Ga$ Heusler alloys with a coupled magnetostructural transition

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Polycrystalline $Ni_{2.18}Mn_{0.82}Ga$ Heusler alloys with a coupled magnetostructural transition are studied by differential scanning calorimetry, magnetic and resistivity measurements. Coupling of the magnetic and structural subsystems results in unusual magnetic features of the alloy. These uncommon magnetic properties of $Ni_{2.18}Mn_{0.82}Ga$ are attributed to the first-order structural transition from a tetragonal ferromagnetic to a cubic paramagnetic phase.

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In Ni_2MnGa, as in many other Heusler alloys containing manganese, the indirect exchange interaction between magnetic ions results in ferromagnetism, which is usually described in terms of the local magnetic moment at the Mn site.[1,2] This makes it possible to discuss the occurrence of ferromagnetism in terms of the dependence of the exchange interaction on the spatial separations of neighboring manganese atoms. Hydrostatic pressure experiments performed on ferromagnetic Mn-containing Heusler alloys (see Refs. 3 and 4, and references therein) demonstrated that this actually is the case. In contrast with other Mn-containing Heusler alloys, stoichiometric and nonstoichiometric Ni-Mn-Ga alloys have been the subjects of numerous investigations in resent years due to their interesting physical properties.[5–12]

For stoichiometric Ni_2MnGa, a structural phase transition of the martensitic type from the parent cubic to a complex tetragonally based structure takes place at $T_m = 202$ K, whereas ferromagnetic ordering sets at $T_C = 376$ K (Ref. 13). The structural phase transition is driven by a band Jahn-Teller distortion,[14,15] and is accompanied by a reduction in the unit-cell volume. In Ref. 16 it was suggested that in $Ni_{2+x}Mn_{1-x}Ga$ alloys the Martensitic and ferromagnetic phase transitions couple (i.e., the order-disorder magnetic transition occurs simultaneously with the order-order crystallographic phase transition) in the range of compositions $x = 0.18–0.20$.

The phenomenon of coupled magnetic and structural phase transitions is very rare in condensed-matter physics and just a few intermetallic compounds with this specific type of transition have been mentioned in the literature (Refs. 17–19, and references therein). Generally, in this case the strong interrelation of magnetic and structural subsystems leads to an unusual magnetic behavior of the materials.[17,18] Such systems, with a close relation between crystallographic structure and magnetism, are also of a great technological significance, since they demonstrate such attractive properties as giant magnetocaloric effect, magnetostriction, and magnetoresistance.[20,21] Therefore, finding and investigating a system with coupled magnetostructural transition may be of importance. Although $Ni_{2+x}Mn_{1-x}Ga$ alloys were studied by a variety of methods, a systematic study of their magnetic properties in the vicinity of the magnetostructural transition is lacking. In this paper we report an experimental study of the magnetostructural transition in $Ni_{2.18}Mn_{0.82}Ga$.

A polycrystalline $Ni_{2.18}Mn_{0.82}Ga$ ingot was prepared by a conventional arc-melting method in argon atmosphere. The ingot was homogenized at 1050 K for nine days, and quenched in ice water. Determined by x-ray diffraction the crystal structure of the alloy at room temperature has a simple tetragonal modification with lattice parameters $a = b = 0.774$ nm, and $c = 0.6485$ nm. Samples for differential scanning calorimetry (DSC), resistivity, and magnetic measurements were spark cut from the middle part of the ingot. The DSC measurements were done by a Perkin-Elmer thermal analysis equipment with a heating/cooling rate of 5 K/min. Temperature and magnetic field dependencies of magnetization were performed by a superconducting quantum interference device magnetometer. Electrical resistivity was measured by a standard four-probe technique in a zero magnetic field with a heating/cooling rate of 1 K/min.

As evident from the DSC measurements (Fig. 1), both direct and reverse Martensitic transitions are accompanied by a well-defined peak on the heat flow due to the latent heat of

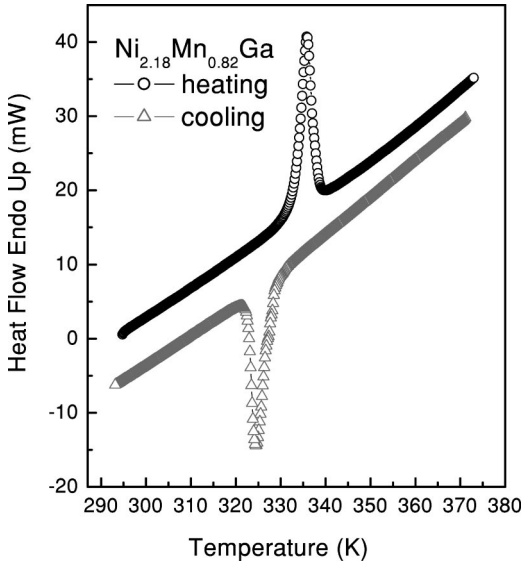

FIG. 1. Heat flow measured during heating and cooling for $Ni_{2.18}Mn_{0.82}Ga$.

the transition. Critical temperatures of the Martensitic transition, Austenite finish (A_f), and Martensite start (M_s), determined from DSC curves are equal to $A_f = 338$ K and $M_s = 330$ K. A temperature hysteresis of the Martensitic transformation estimated as $\delta T = A_f - M_s$ was found to be 8 K. The calculated value of the latent heat of transition, $Q = 9.6$ J/g, is in agreement with values obtained for nonstoichiometric alloys by Chernenko *et al.*[22]

The temperature dependencies of electrical resistivity of $Ni_{2.18}Mn_{0.82}Ga$, during heating and cooling, are shown in Fig. 2. Generally, the resistivity has a normal metallic character, and upon heating continuously increases due to the increase in both electron-phonon and electron-magnon scat-

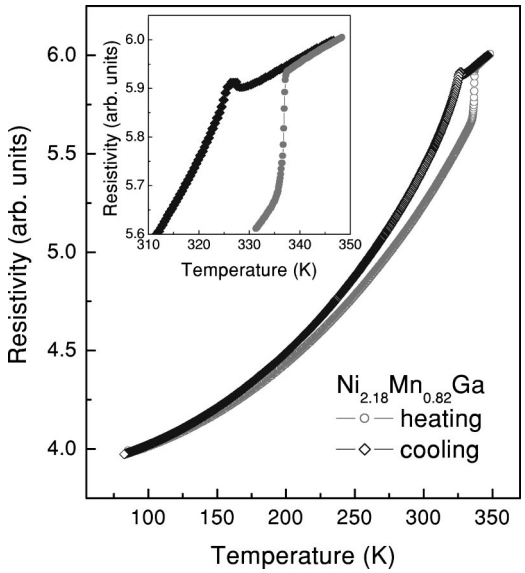

FIG. 2. Temperature dependencies of the electrical resistivity for $Ni_{2.18}Mn_{0.82}Ga$ measured during heating and cooling. The inset shows the behavior of the resistivity in the vicinity of the magnetostructural transition in more detail.

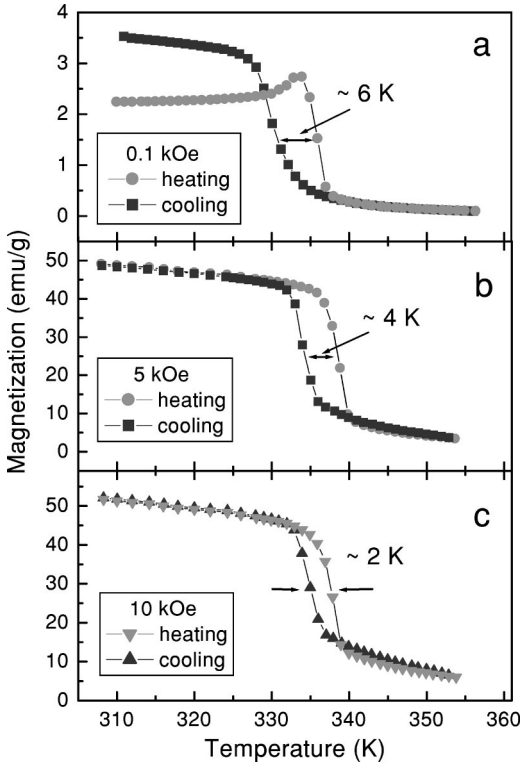

FIG. 3. The temperature dependencies of magnetization of $Ni_{2.18}Mn_{0.82}Ga$ during continuous heating and cooling in various magnetic fields.

terings. A distinguishing feature of the resistivity is a very large temperature hysteresis between heating and cooling processes, extending up to several hundred degrees. The behavior of the resistivity in the neighborhood of the magnetostructural transition (inset in Fig. 2) gives rise to the conclusion that the transition has a temperature hysteresis. Indeed, in ferromagnetic materials $\rho(T)$ can be presented as $\rho(T) = \rho_0 + \rho_{ph} + \rho_{mag}$, where ρ_0 represents the residual resistivity, and ρ_{ph} and ρ_{mag} are contributions due to the lattice vibration and spin-disorder scattering, respectively. In a paramagnetic state ρ_{mag} becomes temperature independent, and the resistivity increases due to the contribution from electron-phonon scattering, which can be approximated as $\rho_{ph} = AT$, with A a constant. As seen from Fig. 2, for the alloy studied the linear part of the resistivity starts at 337 K upon heating, but extends down to 329 K upon subsequent cooling. These critical temperatures, 337 and 329 K, are in good consistent with A_f and M_s temperatures determined from the DSC measurements (Fig. 1).

The temperature dependencies of the magnetization M of $Ni_{2.18}Mn_{0.82}Ga$, for continuous heating and cooling, confirm the hysteretic feature of the magnetostructural transition (Fig. 3). The temperature hysteresis of magnetization in a 0.1-kOe magnetic field [Fig. 3(a)] is estimated as $\delta T \simeq 6$ K, in good accordance with the results of DSC and resistivity measurements. A notable feature of the magnetization measured in this field is that during heating M increases up to a temperature at which the transformation into a paramagnetic state occurs. We suggest that this behavior is caused by the formation of ferromagnetic Austenite, which possesses a

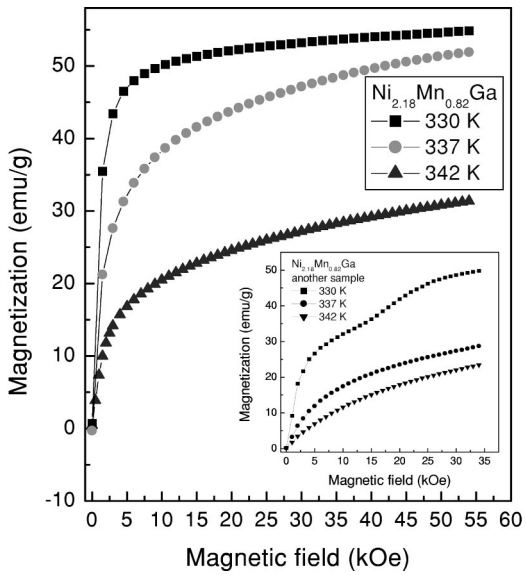

FIG. 4. Magnetic-field dependence of the magnetization M of $Ni_{2.18}Mn_{0.82}Ga$ measured in the vicinity of the phase transition. The inset shows the results of $M(H)$ measured for another $Ni_{2.18}Mn_{0.82}Ga$ sample.

higher magnetization in low magnetic fields.[13] Measurements of the magnetization in higher magnetic fields [Figs. 3(b) and 3(c)] point to a shift of the characteristic temperatures of the magnetostructural transition, which is accompanied by a narrowing of the temperature hysteresis of magnetization. The critical temperatures of the direct and reverse Martensitic transitions A_f and M_s, determined as a minimum on the $(\partial M/\partial T)_H$ derivative, were found to increase from 336 to 338 K for A_f temperature and from 330 to 335 K for M_s temperature as the magnetic field increases from 0.1 to 10 kOe.

Since representatives of intermetallic compounds with coupled magnetostructural transitions usually show pronounced anomalies on isothermal magnetization curves,[17] a similar behavior could be expected for $Ni_{2.18}Mn_{0.82}Ga$. With this aim we undertook measurements of isothermal magnetization in the vicinity of the magnetostructural transition. Contrary to the expectation, the measurements revealed field dependencies of the magnetization, typical of a ferromagnet (Fig. 4). At $T=330$ K, the magnetization saturates in a magnetic field of 5 kOe. The value of the magnetization saturation, $M_s \simeq 54$ emu/g, is in good correspondence with the results of $M(T)$ measurements [Fig. 3(b)]. However, the $M(H)$ dependencies measured for another $Ni_{2.18}Mn_{0.82}Ga$ sample at the same temperatures revealed that the isothermal magnetization process is essentially sample dependent. As is seen from the inset in Fig. 4, a well-defined anomaly appears at the $M(H)$ curve taken at 330 K when the magnetic field reaches a critical value of 15 kOe. The $M(H)$ dependencies, measured at higher temperatures, show a monotonic increase of M; thus no anomaly is seen up to the maximum magnetic field used in the measurements. Since $Ni_{2.18}Mn_{0.82}Ga$ is on the edge of the compositional interval of alloys with coupled magnetostructural transitions, this drastic difference in the magnetization process between two samples could be due to a slight compositional inhomogeneity which is intrinsic for intermetallic compounds.

The spatial dependence of the Mn-Mn exchange interaction in Mn-containing Heusler alloys was demonstrated by hydrostatic pressure experiments.[3,4] The authors found that the Curie temperature T_C of Ni_2MnZ (Z=Al, Ga, In, Sn, and Sb) increases with increasing pressure. Based on these and previously published results, Kanomata *et al.*[3] defined an interaction curve where T_C was plotted as a function of the interatomic distance of Mn-Mn atoms. This curve also supports the idea that ferromagnetic ordering in Heusler alloys containing manganese depends strongly and definitely on the Mn-Mn distance.

This strong dependence of T_C on Mn-Mn distance is presumably responsible for the surprising temperature hysteresis in the ferromagnetic ordering of $Ni_{2.18}Mn_{0.82}Ga$ observed by the resistivity (Fig. 2), and confirmed by the magnetization measurements (Fig. 3). Since previous magnetic studies of Ni-Mn-Ga did not report on a hysteretic feature of magnetization,[23,24] it can be assumed that the coupling of magnetic and structural transitions plays the sole role in the hysteretic behavior of the magnetization in $Ni_{2.18}Mn_{0.82}Ga$. Taking into account the crucial role of the nearest Mn-Mn distance in the formation of long-range ferromagnetic ordering, a first-order Martensitic transition from a low-temperature low-volume tetragonal phase to a high-temperature high-volume cubic phase provokes a temperature hysteresis of the magnetization due to the fact that the temperature at which the high-volume cubic phase nucleates upon warming up is higher than the temperature at which it transforms to the low-volume tetragonal phase upon subsequent cooling down. Comparison of the results of the DSC and resistivity measurements (Figs. 1 and 2) reflects this strong sensitivity of the long-range ferromagnetic order to the unit-cell volume. As is evident from Fig. 2, during warming up the sample transforms to the paramagnetic state at 337 K, which matches with the Austenite finish temperature $A_f=338$ K determined from the DSC measurements. Upon subsequent cooling down the linear temperature dependence of the resistivity, suggesting that the sample is in paramagnetic state, extends down to 329 K, which agrees well with the onset of formation of the low-volume Martensitic phase: $M_s=330$ K. Therefore, from these results it can be deduced that the ferromagnetic ordering sets in (or disappears) not by means of a classical mechanism but due to the structural transformation.

The shift of transition temperature in a magnetic field can be estimated using the Clapeyron-Clausius equation. For a transformation from ferromagnetic Martensite to paramagnetic Austenite, the temperature shift has the form $\Delta T = M_M H T_m / Q$ (Ref. 16), where M_M, H, T_m, and Q are magnetizations of the Martensite, the magnetic field, the Martensitic transition temperature, and the latent heat of transition, respectively. From our experimental results $M_s \simeq 50$ emu/g, $Q=9.6$ J/g, and $T_m=(A_f+M_s)/2=333$ K, and the calculation yields $d\Delta T/dH \simeq 0.18$ K/kOe. This estimation is less than half the experimental value determined from the magnetization data, ~ 0.35 K/kOe. This experimental value as well as the observed narrowing of the hys-

teresis interval is in contradiction with the experimental results obtained by an optical method[25] for $Ni_{2.19}Mn_{0.81}Ga$ in magnetic fields up to 10 kOe, which suggest that the temperatures of the direct and reverse Martensitic transformations as functions of the applied magnetic field, have a linear field dependence with a slope of $\simeq 0.15$ K/kOe. These differences between $Ni_{2.18}Mn_{0.82}Ga$ and $Ni_{2.19}Mn_{0.81}Ga$ can comprise evidence that in the interaction of magnetic and structural subsystems in $Ni_{2+x}Mn_{1-x}Ga$ ($x=0.18$–0.20), chemical composition is the crucial factor.

Theoretical calculations[12] for $Ni_{2+x}Mn_{1-x}Ga$ with $x \leqslant 0.16$ indicate that generally the temperature of the direct Martensitic transformation is more sensitive to the application of a magnetic field than that of the reverse Martensitic transformation. When compared to the theoretical results,[12] the field dependencies of the transition temperatures determined from our experiment have anomalously high rates. This can be accounted for by the fact that, contrary to the $x \leqslant 0.16$ alloys, where a Martensitic transformation occurs in the ferromagnetic matrix, in the alloy studied the structural transformation also results in a switch of the magnetic state of the material.

It was verified experimentally for $Ni_{2+x}Mn_{1-x}Ga$ alloys[12,25,26] that high magnetic fields favor a Martensitic phase. This suggests that if, at some temperature fixed within an interval from A_s to A_f, there is a fraction of paramagnetic Austenite, it will be transformed to a highly magnetized state at some critical value of the applied magnetic field. Therefore, it is likely that the anomaly observed at the magnetization isotherm taken at 330 K (the inset in Fig. 4) is due to a magnetic-field-induced transformation of a fraction of Austenite which is paramagnetic at the given temperature to the ferromagnetic Martensite. Since such a transformation results in marked anomalies on isothermal magnetization of $Gd_5(Si_xGe_{4-x})$ alloys,[17] more pronounced anomalies can be observed at $M(H)$ for $Ni_{2+x}Mn_{1-x}Ga$ ($x=0.18$–0.20) at higher temperatures and in stronger magnetic fields.

In summary, in this paper we have reported on unusual magnetic behavior (first-order character of the ferromagnetic-paramagnetic transition) in $Ni_{2.18}Mn_{0.82}Ga$ Heusler alloy. The obtained experimental results imply that the uncommon magnetic properties of the alloy originate from a first-order structural transition from a tetragonal ferromagnetic structure to a cubic paramagnetic structure. The observed narrowing of the temperature hysteresis of magnetization at high magnetic fields is attributed to differences in the magnetic-field dependencies of the temperatures of the direct and reverse Martensitic transformations. Since magneto-structural transitions frequently lead to physical properties of technological significance, our finding may also make the $Ni_{2+x}Mn_{1-x}Ga$ ($x=0.18$–0.20) alloys attractive from the point of view of their potential application for magnetic refrigeration or magnetostrictive transducers.

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