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Kinetic arrest of martensitic transformation in the NiCoMnIn metamagnetic shape memory alloy

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Magnetic and electrical resistivity changes due to a martensitic transformation in large magnetic fields were investigated in a NiCoMnIn alloy. The transformation is interrupted at about 150 K during field cooling and does not proceed with further cooling. The obtained two-phase condition is frozen at low temperatures and zero field heating releases this condition, inducing a "forward" transformation. These unusual phenomena can be explained by an abnormal behavior in the transformation entropy change and an extremely low mobility of the phase interfaces detected at low temperatures. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2833699]

Since a large magnetic field-induced strain (MFIS) was reported for Ni_2MnGa single-crystalline alloy in 1996,[1,2] ferromagnetic shape memory alloys (FSMAs), especially the Ni_2MnGa alloy, showing an extremely large MFIS of about 9%,[3] have received much attention as high performance actuator materials. To date, several FSMAs besides Ni_2MnGa have also been reported in Ni–Co–Al,[4,5] Ni–Co–Ga,[5,6] Ni–Fe–Ga,[7] and Fe–Pd (Ref. 8) alloy systems. Recently, our group has found an unusual type of FSMAs in the Ni–Mn–X (X=In, Sn, and Sb) based Heusler alloy systems, which show a drastic change of magnetization by martensitic transformation from the ferromagnetic parent phase to the very weak magnetic martensite phase.[9–11] The martensitic transformation temperatures of these alloys are drastically decreased by an applied magnetic field and the magnetic field induced transformation (MFIT), which is a kind of metamagnetic phase transition, has been confirmed in the martensite state near the martensitic transformation starting temperature M_s. Moreover, an almost perfect shape memory effect induced by a magnetic field, i.e., the metamagnetic shape memory effect, was found in the $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ single crystalline and $Ni_{43}Co_7Mn_{39}Sn_{11}$ polycrystalline alloys at room temperature.[10–12] Furthermore, some other interesting properties, such as giant magnetoresistance[13,14] (GMR) and the inverse magnetocaloric effect,[15] have been reported.

In the present study, the magnetic and electrical resistivity (ER) changes induced by martensitic transformation in the $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ alloy were investigated mainly at low temperatures and high magnetic fields.

A $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ (at.%) alloy specimen was prepared by induction melting under an argon atmosphere. The obtained polycrystalline ingot was annealed at 1173 K for 96 h in a vacuum and then quenched in ice water. To make the martensitic transformation temperature decrease and the Curie temperature increase, the specimens were additionally aged at 623 K for 1 h. Some single crystals were cut from the specimens with large grains using a diamond saw. The magnetization was measured by an extraction-type magnetometer in magnetic fields H to 18 T using a superconducting magnet and a superconducting quantum interference device in the magnetic field range from 0 to 5 T at heating and cooling rates of 2 K min^{-1}. The ER and MR were examined by a conventional four-probe method in magnetic fields up to 17 T. The martensitic and magnetic transformation temperatures were confirmed by magnetization and ER measurements. High-field x-ray powder diffraction (XRD) experiments with Cu $K\alpha$ radiation under magnetic fields up to 5 T were conducted in a wide temperature range from 8 to 300 K.

Figure 1(a) shows the thermomagnetization (TM) curves obtained in magnetic fields of H=0.05, 3, 5, and 8 T. The martensitic transformation temperatures (M_f is the transformation finishing temperature and A_s and A_f are the reverse transformation starting and finishing temperatures, respectively) were defined, as demonstrated in the curves in Figs. 1(a) and 1(b). It is seen in Fig. 1(a) that with increasing magnetic field the martensitic transformation temperatures from the ferromagnetic parent to weak magnetic martensite phase decrease and the magnetization of martensite phase increases. It is interesting to note that the M_f temperatures in both the 3 and 5 T specimens are located at about 150 K and that in the 8 T specimen, where an M_s temperature is expected to be at arround 150 K, no martensitic transformation is detected. Similar behaivors are confirmed from the ER curves, as shown in Fig. 1(b). Here, the ER changes under fields of 0 and 3 T are extremely large, i.e., over about 80% {=[ρ(200 K)-ρ(270 K)]/ρ(200 K)}. The same kind of large

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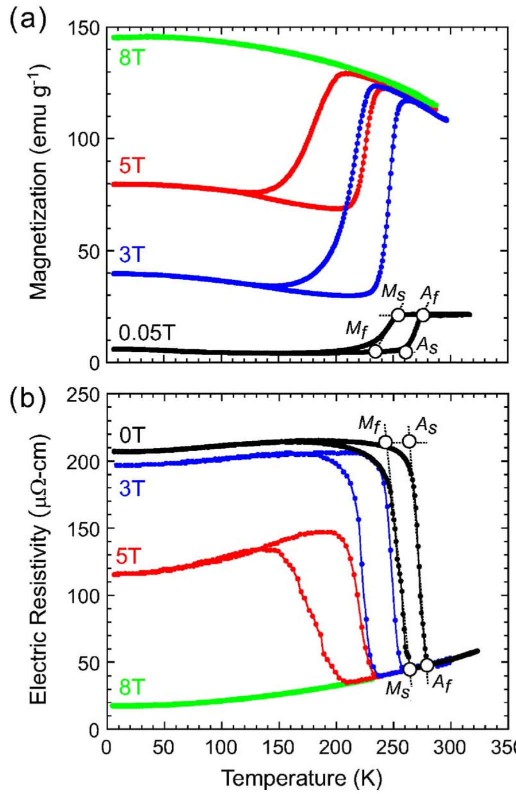

FIG. 1. (Color online) (a) Thermomagnetization (TM) and (b) electric resistance (ER) curves under magnetic fields of $H=0$ (or 0.05), 3, 5, and 8 T.

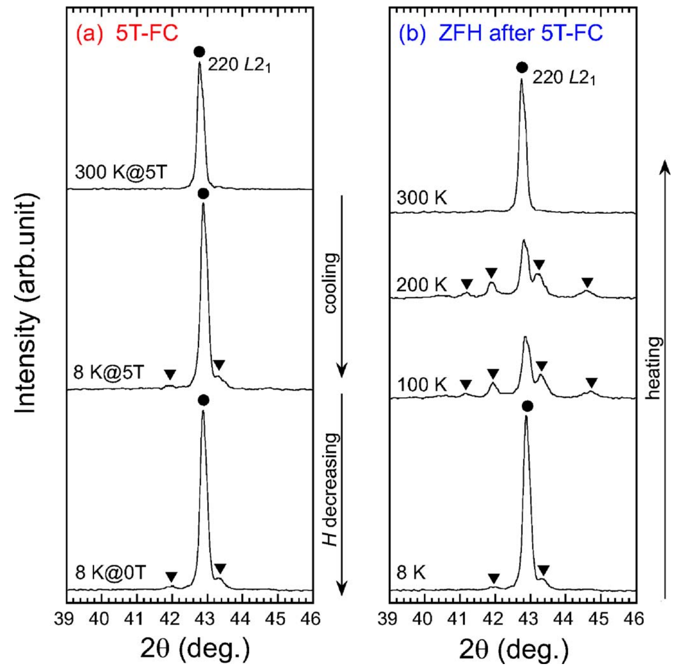

FIG. 3. (Color online) X-ray powder diffraction profiles in (a) 5 T FC and (b) ZFH after the 5 T FC. The arrow-head symbols indicate reflections from the martensite phase.

ER change has been reported in the NiMnIn and NiMnSn alloys.[13,14]

It is worth noting that the degree of change in both the TM and ER due to the martensitic transformation is reduced with increasing magnetic field. Figure 2 shows the ER curve in the field cooling (FC) under 5 T followed by the zero field heating (ZFH) where the broken lines indicate the ER curves under 0 and 5 T as shown in Fig. 1(b). The 5 T FC and ZFH curve basically coincide with the cooling curve under 5 T and the heating curve under 0 T in the ordinary cyclic measurements, except the temperature region from 4.2 to 150 K in the ZFH curve. It is very strange that the release of the magnetic field at 4.2 K does not induce recovery to the ER condition of 0 T and that the recovery gradually occurs during heating from 4.2 to 150 K. A similar behavior was confirmed in the MT curve obtained under the same condition. Figure 3 shows the XRD profiles from $2\theta=39$ to 46° (a) in the 5 T FC and (b) in the ZFH after 5 T FC under the same condition as that in Fig. 2, in which the $\{220\}_{L2_1}$ peak from the $L2_1$ parent phase and several peaks from the martensite phase with the 10 and 14 M modulations are expected.[16] It is seen that during cooling to 8 K in 5 T, some additional peaks from the martensite phase appear besides the $\{220\}_{L2_1}$ reflection, as indicated by the arrow-head symbols in Fig. 3(a). This means that in the 5 T FC condition the martensitic transformation only partially occurs and is not completed even at the temperatures below the M_f' of about 150 K, as indicated in Fig. 2. This coexisting condition of the parent and martensite phases is inherited after the release of the magnetic field. It is very interesting to note that the peak intensity from the martensite phase increases with increasing temperature, while that from the parent phase decreases, as shown in Fig. 3(b). Finally, the martensite peaks disappear due to the "normal" reverse transformation existing in the temperature range between 250 and 300 K. The result observed in the heating stage confirms that forward martensitic transformation occurs during heating. All these results are well consistent with the strange behaviors shown in Figs. 1 and 2. That is, the high TM and the low ER conditions observed in the martensite phase region under the higher magnetic fields result from the mixture of the martensite and parent phases, which is brought about by the interruption for the transformation occurring at about 150 K on cooling. Since this condition is "frozen" at very low temperatures even if the magnetic field is removed, the forward transformation occurs during the ZFH and the values of the TM and ER gradually recover from the frozen to the normal condition in the heating process as shown in Fig. 3.

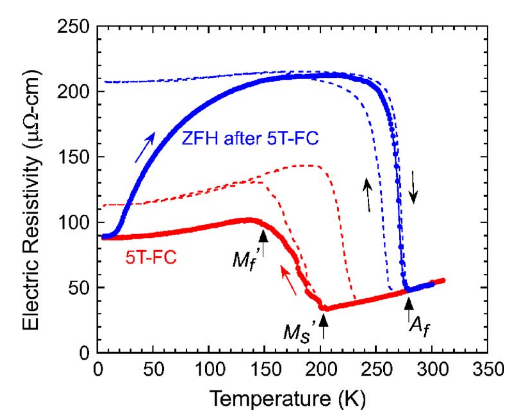

FIG. 2. (Color online) ER curve in field cooling (FC) under 5 T followed by zero-field heating (ZFH). The broken lines indicate the ER curves in the normal cycle under 0 and 5 T.

Figures 4(a) and 4(b) show the magnetization and ER curves in relation to the magnetic field at several temperatures below the M_f temperature. All the curves show a metamagnetic phase transition due to a MFIT from the weak magnetic martensite to ferromagnetic parent phase, and a GMR effect, whose rate, defined with $R=-[\rho(H)-\rho(0)]/\rho(0)$, is

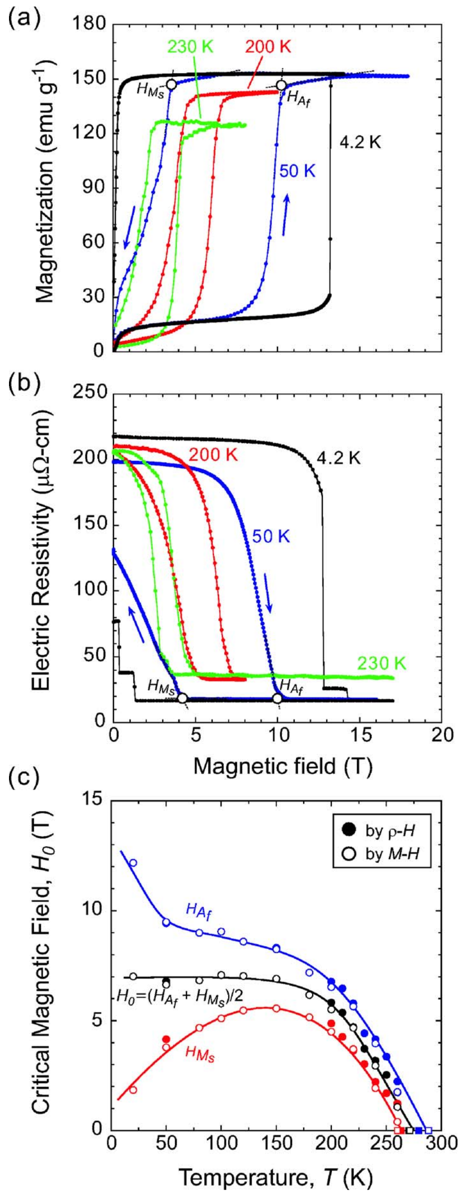

FIG. 4. (Color online) (a) Magnetization and (b) ER curves to magnetic field at several temperatures below M_f temperature and (c) magnetic field-temperature phase diagram, where the H_{Ms}, H_{Af}, and H_0 were evaluated from the (a) *M-H* and (b) *ρ-H* curves.

confirmed to be $R=-93\%$ and -82% at 4.2 and 230 K in the *ρ-H* curves in Fig. 4(b), respectively. It is apparent that the field hysteresis H_{hys} which is about 2–3 T at 200 and 230 K, drastically increases with decreasing temperature, being over 10 T at 4 K, and that the transformation behavior is discontinuous and burstlike similar to nonthermoelastic transformation. Here, the martensitic transformation starting field H_{Ms}, the reverse transformation finishing field H_{Af}, and the equilibrium magnetic field, H_0 $[=(H_{Ms}+H_{Af})/2]$, which are as demonstrated in Figs. 4(a) and 4(b), are plotted in Fig. 4(c). It can be seen that while all the H_{Ms}, H_{Af}, H_0, and the magnetic hysteresis, $H_h=H_{Af}-H_{Ms}$, gradually increase with decreasing temperature in the region from 260 to 150 K, the H_0 becomes almost constant and the H_h drastically increases with decreasing temperature in the region below 150 K. Here, the H_0 is the magnetic field at which the Gibbs energy of parent phase is equal to that of the martensite phase, corresponding to the $T_0 \equiv (A_f+M_s)/2$ in the thermal transformation. Therefore, the following relation is given by the Clausius-Clapeyron relation in the magnetic phase diagram,

$$\frac{dH_0}{dT} = \frac{\Delta S}{\Delta M}, \qquad (1)$$

where ΔM and ΔS are the differences in magnetization and entropy between the parent and martensite phases, respectively. In the present case, since the ΔM is almost constant in the range from 120 to 130 emu g^{-1}, the ΔS is actually in proportion to the dH_0/dT. It is very important to note that the H_0 is almost constant, i.e., $dH_0/dT=0$, below 150 K, which from Eq. (1) means that the ΔS is almost zero. The driving force for thermal martensitic transformation is given with the supercooling ΔT by $\Delta G \approx \Delta S \Delta T$. Therefore, since the driving force for the transformation stored during cooling completely disappears below 150 K, the transformation does not proceed anymore at temperatures below 150 K. Such an abnormal behavior on the ΔS may be caused by a contribution of the magnetic term in the Gibbs energy for the parent phase, as mentioned in our previous paper.[16]

On the other hand, the freezing behavior observed in the very low temperature region is clearly due to the decrease of the mobility of the habit plane between the parent and martensite phases. The discontinuous change of the magnetization and electric resistance at 4.2 K in Fig. 4 supports this deduction. From this view point, the forward transformation during heating up to 150 K can be explained as an unfreezing process due to the recovery of mobility of the habit plane. The reason for the extremely low mobility of the habit planes, however, is not clear at present.

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