Magnetoresistance and magnetocaloric effect in metamagnetic alloys $Ni_{45}Co_5Mn_{36.5}In_{13.5}$

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Magnetoresistance (MR) and magnetocaloric effect around martensitic transformation were investigated in a $Ni_{45}Co_5Mn_{36.5}In_{13.5}$ alloy. The martensitic temperature (T_M) locates at ~260 K. An external magnetic field can drive T_M to a lower temperature at a rate of ~9.2 K/T. Associated with the field-induced metamagnetic behaviors, a large MR takes place. The maximal MR exceeds 80% under a field of 5 T around 235 K. More attractive is that the MR behavior is fully recoverable against magnetic field. We also studied the magnetocaloric effect associated with the martensitic transformation and found a large magnetic entropy change (ΔS) around 252 K. © *2010 American Institute of Physics*. [doi:10.1063/1.3359806]

Magnetoresistance (MR) effect has attracted a lot of interests because of its extensive applications in magnetoresistive read-head technology. Much effort has been focused on artificial structures since the first discovery of the giant magnetoresistance (GMR) effect in Fe/Cr multilayers.[1] GMR effect comes from spin-dependent scattering at the interfaces of multilayer structures, where the scattering being lower for a parallel spin alignment than for an antiparallel one. Additionally, the colossal magnetoresistance (CMR) effect was observed in perovskite manganites.[2] The CMR is commonly related to double exchange between Mn^{3+} and Mn^{4+} ions but strongly influenced by the interplay between spin, charge, and orbital degrees of freedom. Besides the GMR in artificial multilayers and CMR in perovskite manganites, a considerable large MR was also reported in many intermetallic compounds, such as FeRh,[3] GdSiGe,[4] MnAs,[5] and the natural layered $SmMn_2Ge_2$.[6] The mechanism varies depending on the specifics in different systems. In this paper, we report large MR and magnetocaloric effect (MCE) associated with the metamagnetic behaviors in $Ni_{45}Co_5Mn_{36.5}In_{13.5}$ alloys.

The huge ferromagnetic shape memory effect recently discovered in metamagnetic alloys $Ni_{45}Co_5Mn_{50-x}In_x$ (x=13.3, 13.4, and 13.5) (Refs. 7 and 8) warrants further experimental and theoretical studies of these alloys with the exact compositions. In metamagnetic alloys, an excess of Mn makes the martensitic phase show a small magnetization while the austenitic phase exhibits strong ferromagnetic properties. The abrupt change in magnetization between two phases results in a large Zeeman energy $\mu_0 \Delta M \cdot H$, which drives a metamagnetic transition behavior and a structure transformation, hence a huge shape memory effect. The incorporation of Co enhances the Zeeman energy $\mu_0 \Delta M \bullet H$ through enlarging the magnetization difference across the martensitic transformation, thus an extremely large stress can be generated by magnetic field. It has been reported that the stress output for a composition of $Ni_{45}Co_5Mn_{36.6}In_{13.4}$ can be over 100 MPa under a 7 T field,[7] which is approximately 50 times larger than that in conventional Heusler alloys. The simultaneous change in the structure and magnetic properties induced by magnetic field should be accompanied by a large MCE. The concurrent changes in the electronic structure and scattering mechanisms across martensitic transformation would also alter the transport properties. Naturally, large MCE and distinct MR effect can be expected along with the field-induced structural transformation. People have investigated the MR and MCE effect in a few metamagnetic alloys.[9,10] In this paper, we report the MR and MCE in the novel composition $Ni_{45}Co_5Mn_{36.5}In_{13.5}$.

$Ni_{45}Co_5Mn_{36.5}In_{13.5}$ alloys employed in our investigations were prepared by repeatedly arc melting appropriate amounts of starting materials in high-purity argon atmosphere (99.996%) with a base pressure of 10^{-4} Pa. The commercial purities of Ni, Mn, Co, and In are 99.999, 99.9, 99.9, and 99.995 wt %, respectively. The obtained ingots were each wrapped with Ta foil and homogenized in a sealed quartz tube at 1173 K for 24 h, then quenched in ice water. X-ray diffraction analysis confirmed that the samples are with $L2_1$ Heusler-type ordered structure. Magnetic and transport measurements were performed using a superconducting quantum interference device equipped with a probe for four-point electrical resistance measurements.

Temperature dependent magnetization under different fields was measured in both zero-field-cooled (ZFC) and field-cooled (FC) processes in order to determine the magnetic state, transition temperature, and the nature of the

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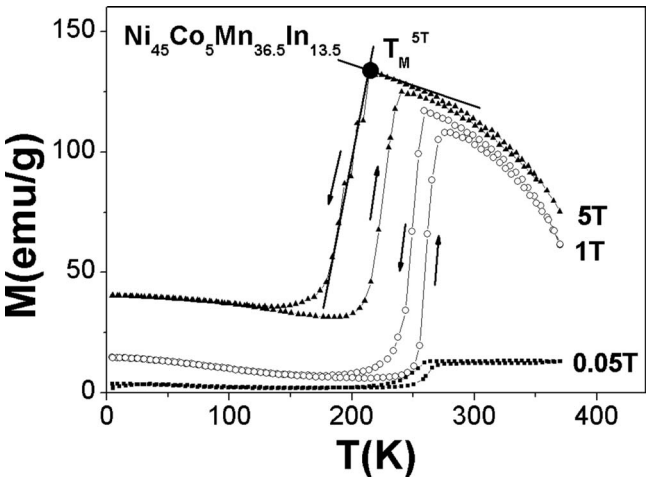

FIG. 1. Temperature dependence of ZFC and FC magnetizations under fields of 0.05, 1, and 5 T for $Ni_{45}Co_5Mn_{36.5}In_{13.5}$. The arrows indicate the heating/cooling path.

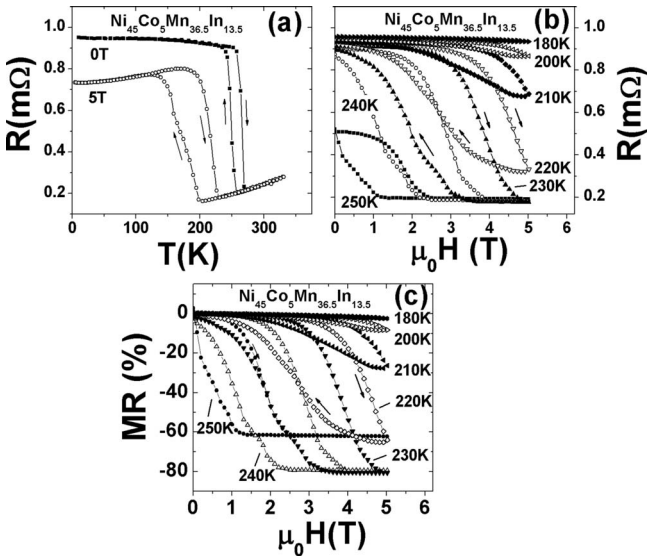

FIG. 2. (a) Temperature dependent resistance under 0 T ($R_{0\ T}$) and 5 T ($R_{5\ T}$), (b) field dependent resistance up to 5 T at different temperatures, and (c) field dependent MR$[(R_{5\ T}-R_{0\ T})/R_{0\ T}]$ at different temperatures for $Ni_{45}Co_5Mn_{36.5}In_{13.5}$. The arrows indicate the heating/cooling path as well as the field ascending/descending path.

transitions.[11] Figure 1 presents the ZFC-FC magnetization measured under 0.05, 1, and 5 T for present $Ni_{45}Co_5Mn_{36.5}In_{13.5}$. One can note that the magnetization curve of 0.05 T drops suddenly at about 260 K on cooling and increases drastically at about 250 K on heating, indicating the martensitic and reverse transformation. Due to the first-order nature of the martensitic transformation, a thermal hysteresis, about 10 K, appears. The thermomagnetization curves under 1 and 5 T are found to be similar to that under 0.05 T, but the martensitic temperature (T_M) notably shifts to low temperature. The magnetization change ΔM across martensitic transformation reaches ~95 emu/g under 5 T. The resulted Zeeman energy $\mu_0 \Delta M \cdot H$ pushes T_M to lower temperatures. T_M locates at 214 and 260 K for the sample under 0.05 and 5 T, respectively. Here, the T_M is defined as shown on the thermomagnetization curve of 5 T. It was found that a decrease of about 46 K was driven by an external magnetic field of 5 T. The equated driving rate of T_M is ~9.2 K/T, one time higher than that of $Ni_{45}Co_5Mn_{36.6}In_{13.4}$ reported in Ref. 7. This means that the martensitic transformation in present case is easier to be driven by magnetic field. From Fig. 1 one can also find that the thermal hysteresis enlarges from ~10 to ~32 K when the magnetic field increases from 0.05 to 5 T. Hysteresis behavior is commonly believed to be related to the nucleation of the new phase and the interfacial interaction at phase boundary in first-order systems. Previous investigations indicated that the hysteresis gap can characterize the friction strength of phase boundary motions during the martensitic transformation in Heusler alloys.[12] The enhancement of hysteresis in present case may imply that the friction to resist the transformation becomes larger with the increasing of magnetic field.

Figures 2(a) and 2(b) display the temperature dependent resistance under 0 T ($R_{0\ T}$) and 5 T ($R_{5\ T}$) and the field dependent resistance up to 5 T at different temperatures for the present sample. One can find that an abrupt increase in resistance appears as the sample undergoes martensitic transformation. An enlarged thermal hysteresis with increasing field can also be identified from the R-T curves, consistent with the results of thermomagnetization measurements. With T_M shifting to a lower temperature under an external field, a negative MR was observed. Figure 2(c) plots the deduced field dependent MR $[(R_{5\ T}-R_{0\ T})/R_{0\ T}]$ at various temperatures around T_M. One can note that the maximal MR under 5 T exceeds 80% around 235 K. At temperatures near T_M, a low field can induce a metamagnetic transition, thus generate a considerable large MR. For example, at 250 K a field of 2.5 T can produce a MR as large as 60%. Importantly, the transport resistance is fully recoverable against magnetic field. It can return to its original value after a field cycle up to 5 T. Usually, the electrical resistivity of an intermetallic compound originates primarily from four parts, i.e., electron-phonon, electron-spin, electron-electron, and electron-defect scatterings. In the region of the magnetic and structural transitions, the two most important contributions to the resistance are electron-phonon and electron-spin scatterings. As the sample experiences martensitic transformation in present $Ni_{45}Co_5Mn_{36.5}In_{13.5}$, the increased interfacial scattering at the twin boundaries and the change in lattice symmetry may result in an enhanced resistivity due to the electron-phonon scattering. Moreover, the concurrent alteration of magnetic properties may also contribute to a change in resistivity due to the electron-spin scattering. In metamagnetic Heusler alloys, the austenitic state usually exhibits strong ferromagnetic properties while the martensitic state shows a small magnetization. The nature of the low magnetization in martensitic state remains controversial and unsettled up to now.[13–15] Some people believe that it is of paramagnetic phase,[13] while others think of it as being of a mixture of ferro- and antiferromagnetic phases.[14,15] A recent neutron-polarization-analysis experiment[16] has observed antiferromagnetic correlations at temperatures lower than T_M for some Mn-rich alloys with metamagnetic properties. Similar to the materials that undergo antiferromagnetic transition,[17] the formation of superzone boundary gaps may alter the den-

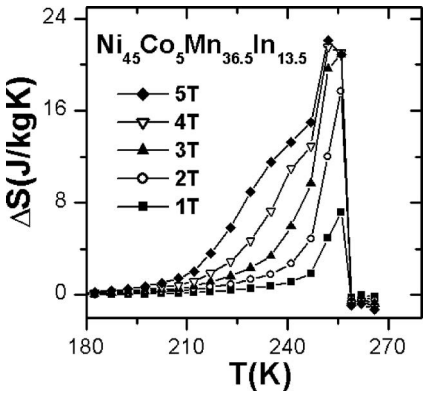

FIG. 3. Magnetic entropy change ΔS as a function of temperature under different magnetic fields for $Ni_{45}Co_5Mn_{36.5}In_{13.5}$.

sity of the electronic states near the Fermi surface, leading to an enhancement of transport resistance due to electron-spin scattering.

The MCE associated with the field induced metamagnetic transition around T_M is also investigated for the present sample. We carried out magnetization measurements as a function of temperature and magnetic field, and calculated magnetic entropy change (ΔS) using the Maxwell relation,[18] $\Delta S(T,H)=S(T,H)-S(T,0)=\int_0^H(\partial M/\partial T)_H dH$. Figure 3 displays the obtained ΔS as a function of temperature under different fields. One can note that a positive ΔS peaks around T_M and gradually broadens to low temperature, which is a result of the field-induced metamagnetic transition[19] from martensitic to austenitic state at temperatures below T_m. Because the critical field, under which the metamagnetic transition takes place, increases with decreasing temperature, the ΔS peak asymmetrically broadens to low temperature. The maximal ΔS reaches ~22 J/kg K at ~252 K under a field change of 0–5 T. In recent years an increasing attention has been attracted to MCE in first-order systems. However, the ways to evaluate the magnetic entropy change in first-order system remain in controversy. It was argued that Clausius–Clapeyron relation is more rational than using Maxwell relation.[20] Recent investigations indicated that both hysteresis effect[21] and phase coexistence[22] during phase transition may lead to an overestimation of magnetic entropy change when using Maxwell relation. Considering the visible hysteresis in our $Ni_{45}Co_5Mn_{36.5}In_{13.5}$, the calculated ΔS may be somewhat overestimated. However, we noticed that the entropy change ΔS in a close composition $Ni_{45}Co_5Mn_{36.6}In_{13.4}$, obtained by using Clausius–Clapeyron relation and DSC measurements, is ~27 J/kg K under 7 T.[7] This value roughly agrees with our results (~22 J/kg K, 5 T) in $Ni_{45}Co_5Mn_{36.5}In_{13.5}$. Detailed experiments are still required for fully understanding the intrinsic MCE in present system.

In summary, we investigated transport properties and MCE in metamagnetic alloys with the novel composition $Ni_{45}Co_5Mn_{36.5}In_{13.5}$. An abrupt increase in resistance appears as the sample undergoes martensitic transformation. The origin of the drastic increase in resistance can be ascribed to the combined effect of electron-phonon and electron-spin scatterings upon martensitic transformation. With T_M shifting to lower temperature under an external field, a negative MR was observed. The maximal MR exceeds 80% under a field of 5 T. Associated with the field-induced metamagnetic behavior, a large ΔS was also observed. The extremely large MR and its full reversibility against magnetic field, as well as the large ΔS, provide this novel alloy more innovative applications.

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[1]M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).
[2]*Colossal Magnetoresistive Manganites*, edited by T. Chatterji (Kluwer, Dordrecht, 2004).
[3]P. A. Algarabel, M. R. Ibarra, C. Marquina, A. del Moral, J. Galibert, M. Iqbal, and S. Askenazy, Appl. Phys. Lett. **66**, 3061 (1995).
[4]E. M. Levin, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **60**, 7993 (1999).
[5]J. Mira, F. Rivadulla, J. Rivas, A. Fondado, T. Guidi, R. Caciuffo, F. Carsughi, P. G. Radaelli, and J. B. Goodenough, Phys. Rev. Lett. **90**, 097203 (2003).
[6]E. V. Sampathkumaran, P. L. Paulose, and R. Mallik, Phys. Rev. B **54**, R3710 (1996).
[7]R. Kainuma, Y. Imano, W. Ito, Y. Sutou, H. Morito, S. Okamoto, O. Kitakami, K. Oikawa, A. Fujita, T. Kanomata, and K. Ishida, Nature (London) **439**, 957 (2006).
[8]H. E. Karaca, I. Karaman, B. Basaran, Y. Ren, Y. I. Chumlyakov, and H. J. Maier, Adv. Funct. Mater. **19**, 983 (2009).
[9]V. K. Sharma, M. K. Chattopadhyay, K. H. B. Shaeb, A. Chouhan, and S. B. Roy, Appl. Phys. Lett. **89**, 222509 (2006).
[10]T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, and A. Planes, Nature Mater. **4**, 450 (2005).
[11]F. X. Hu, X. L. Qian, G. J. Wang, J. Wang, J. R. Sun, X. X. Zhang, Z. H. Cheng, and B. G. Shen, J. Phys.: Condens. Matter **15**, 3299 (2003).
[12]W. H. Wang, J. L. Chen, Z. H. Liu, G. H. Wu, and W. S. Zhan, Phys. Rev. B **65**, 012416 (2001).
[13]D. L. Schlagel, W. M. Yuhasz, K. W. Dennis, R. W. McCallum, and T. A. Lograsso, Scr. Mater. **59**, 1083 (2008).
[14]T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, A. Planes, E. Suard, and B. Ouladdiaf, Phys. Rev. B **75**, 104414 (2007).
[15]V. K. Sharma, M. K. Chattopadhyay, R. Kumar, T. Ganguli, P. Tiwari, and S. B. Roy, J. Phys.: Condens. Matter **19**, 496207 (2007).
[16]S. Aksoy, M. Acet, P. P. Deen, L. Mañosa, and A. Planes, Phys. Rev. B **79**, 212401 (2009).
[17]Y. Q. Zhang, Z. D. Zhang, and J. Aarts, Phys. Rev. B **70**, 132407 (2004).
[18]A. M. Tishin and I. Spichkin, *The Magnetocaloric Effect and Its Applications* (Institute of Physics, University of Reading, Berkshire, 2003).
[19]F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Cheng, G. H. Rao, and X. X. Zhang, Appl. Phys. Lett. **78**, 3675 (2001).
[20]A. Giguère, M. Foldeaki, B. Ravi Gopal, R. Chahine, T. K. Bose, A. Frydman, and J. A. Barclay, Phys. Rev. Lett. **83**, 2262 (1999).
[21]J. S. Amaral and V. S. Amaral, Appl. Phys. Lett. **94**, 042506 (2009).
[22]G. J. Liu, J. R. Sun, J. Shen, B. Gao, H. W. Zhang, F. X. Hu, and B. G. Shen, Appl. Phys. Lett. **90**, 032507 (2007).