Large magnetoresistance in single-crystalline Ni$_{50}$Mn$_{50-x}$In$_x$ alloys ($x=14–16$) upon martensitic transformation

S. Y. Yu,$^{a,b}$ Z. H. Liu, G. D. Liu, J. L. Chen, Z. X. Cao, and G. H. Wu$^{b)}$

Beijing National Laboratory for Condensed Matters Physics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, China

B. Zhang and X. X. Zhang
Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China and Institute of Nanoscience and Technology, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

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Variation of electrical resistance in single-crystalline Ni$_{50}$Mn$_{50-x}$In$_x$ alloys ($x=14–16$) upon martensitic transformation was investigated. In Ni$_{50}$Mn$_{35}$In$_{15}$ with $T_m \sim 295$ K, a negative magnetoresistance (MR) over 60% is attainable at moderate field strengths; in Ni$_{50}$Mn$_{34}$In$_{16}$ with $T_m \sim 190$ K, the MR can exceed 70% over a temperature of approximately 100 K. The significant change in electric resistance upon martensitic transformation originates primarily from the altered electronic structure, while the large effect of a magnetic field follows its ability to manipulate the transformation in materials of low $T_m$ and large $\Delta M/\Delta S$. The extremely large MR promises more innovative applications for these important alloys. © 2006 American Institute of Physics. [DOI: 10.1063/1.2362581]

Giant magnetoresistance effect is a significant material’s property that promises extensive applications in magnetoresistive reading heads and similar devices; therefore it has attracted much interest in recent years. This effect, usually attributed to the spin-dependent scattering of conduction electrons, has been realized in magnetic multilayers and granular systems. It is noticeable that large magnetoresistance (MR) effect also occurs in bulk intermetallic compounds, particularly in those alloys that undergo first-order phase transformations, such as FeRh, GdSiGe, and MnAs. Ferromagnetic shape memory alloys (FSMAs) are a class of materials that, upon cooling, will undergo a first-order phase transition to a martensitic phase of low symmetry. The magnetic field-induced strains of these alloys have been extensively scrutinized to explore their potential usage as actuators. Also MR has been measured in a few such alloys recently. Oikawa and coworkers reported that in NiMn-based FSMAs, a reversible martensitic transformation following a magnetic transition from the ferromagnetic parent phase to the antiferromagnetic-like martensitic phase can be induced by the magnetic field. In this letter we report the observation of very large MR in Ni$_{50}$Mn$_{50-x}$In$_x$ alloys ($x=14–16$) in different temperature regions. It can peak at $\sim 80\%$ and assume a value above 70% over a temperature of approximately 100 K. Moreover, a value over 60% was attained near room temperature by modifying the alloy composition. The underlying mechanism related to the field-induced transformation will be discussed.

Single-crystalline Ni$_{50}$Mn$_{50-x}$In$_x$ ($x=14–16$) alloys were grown by the Czochralski method. The starting materials are elemental Ni, Mn, and In of 99.95% purity, and the pull rate is 15 mm/h. For the subsequent characterizations and measurements, the crystals were cut into rods of $1 \times 10$ mm$^3$ in dimension along the (100) directions. The magnetization was investigated by using a Superconducting quantum interference device magnetometer (Quantum Design, MPMS-7) and the MR was measured in a physical properties measurement system (Quantum Design, PPMS-9) by using the four-point probe method.

Figure 1 illustrates the electrical resistance measured in the Ni$_{50}$Mn$_{50-x}$In$_x$ alloys as a function of temperature. The abrupt changes in resistance result from the martensitic and reverse martensitic transformations accompanying a ferromagnetic–partial antiferromagnetic transition, as will be justified later. A rapid dropping of the transition temperature $T_m$ with increasing In content can be clearly verified, as in previous studies. In addition, the samples with given compositions, except for the one with $x=14$, demonstrate a composition-insensitive Curie temperature $T_C$ at $\sim 310$ K. The martensitic transformation in our NiMnIn alloys provokes an enormously large resistance increase. The resistance for the parent phase exhibits a typical metallic behavior, whereas it is semimetal-like for the martensite. The sharp rise of the electrical resistance upon the martensitic transformation may be attributed to the formation of superzone boundary gaps, which alters the density of the electronic states.

FIG. 1. Variation of electrical resistance in a thermal excursion measured on Ni$_{50}$Mn$_{50-x}$In$_x$ alloys. The arrows indicate the direction of temperature regulation.

$^{a}$Electronic mail: syyu@aphy.iphy.ac.cn
$^{b)}$Author to whom correspondence should be addressed; electronic mail: userm201@aphy.iphy.ac.cn
states near the Fermi surface, as usually occurs in materials that undergo antiferromagnetic transitions. By shifting the \( T_m \) from 350 to 200 K, the absolute value of \( \Delta R/R_m \), \( R_m \) denotes the resistance of the martensitic phase, is readily raised from 50% up to 70% (Fig. 1), which mainly comes from the reduced \( R \) value at lower temperature for the metallic parent phase.

The temperature dependence of the electrical resistance can be effectively modified by a magnetic field in our NiMnIn alloys. To illustrate this, in Fig. 2 the \( R-T \) curves measured for Ni\(_{50}\)Mn\(_{34}\)In\(_{16}\) and Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\) are plotted. The martensitic transformation, again recognized from the abrupt resistance change, is significantly shifted towards lower temperatures, which occurs only when the field is competitive with temperature in shaping the transition. For Ni\(_{50}\)Mn\(_{34}\)In\(_{16}\) which has a \( T_m \sim 190 \) K, the transition temperature shifts down at a rate of about 12 K/T, more rapidly than that obtained in similar materials such as Ni\(_{45}\)Co\(_{5}\)Mn\(_{36.6}\)In\(_{13.4}\) (4 K/T) and Ni\(_{50}\)Mn\(_{42}\)In\(_{13}\) (7 K/T). From the Clausius-Clapeyron equation,

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dT/dH = -\Delta M/\Delta S,
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where \( \Delta M \) and \( \Delta S \) denote the differences in magnetization and entropy upon transformation, respectively, it is clear that the large \( dT/dH \) comes from a large \( \Delta M/\Delta S \). For conventional FSMAs such as NiMnGa or NiFeGa, \( dT/dH \) is generally not more than 1 K/T because the \( \Delta M \) therein is small. In Ni\(_{50}\)Mn\(_{34}\)In\(_{16}\), \( \Delta M \) amounts to 70 emu/g (Fig. 3). Though this is somewhat smaller than the record 100 emu/g in Ni\(_{46}\)Mn\(_{41}\)In\(_{13}\) with \( T_m \sim 223 \) K, a very large \( dT/dH \) was obtained since here \( \Delta S \) was rather small. The same argument suggests a relatively larger \( \Delta S \) in Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\) for which \( dT/dH \) amounts to only 2 K/T. As a matter of fact, the \( \Delta S \) values for these two samples are 5.5 and 25.0 J/K kg, respectively, as determined by differential scanning calorimetry, demonstrating that the entropy change in the NiMnIn alloys can be effectively reduced by composition adjustment.

Magnetization behaviors at various temperatures reveal more about the change in magnetic orderings following the transformation. Figure 3 displays, for example, the magnetization curves of Ni\(_{50}\)Mn\(_{42}\)In\(_{16}\) measured at various temperatures. The curves for 205 and 100 K exhibit correspondingly the typical magnetization behavior for the ferromagnetic parent phase and the partial antiferromagnetic martensite, from which a \( \Delta M \) of \( \sim 70 \) emu/g across the transformation was read. At temperatures just below \( T_m \), here 170 and 180 K, the hysteresis of rich fine structures evidences the reverse martensitic transformation induced by fields. That the critical field decreases as the temperature approaches the reverse transformation temperature indicates the interplay between temperature and magnetic field in shaping the martensitic transformation.

Since a magnetic field can induce the martensitic transformation in NiMnIn alloys involving significant changes in the electrical resistance, a large MR effect is expected in these materials. Figure 4(a) displays the MR, defined as \( (R_H-R_0)/R_0 \), versus field strength for Ni\(_{50}\)Mn\(_{42}\)In\(_{16}\) measured below the transition temperature, thus showing that the sample is in the martensitic structure. The values for 100 and 150 K peak at over 80%, and in a wide range from 100 to 180 K the MR can exceed 70%. Remarkably, such a high MR is available with a rather low field, say, 3.0 T at 180 K. At 190 K the MR recovered only a value of 30% because in the proximity of the transition temperature the sample cannot fully revert back to the martensitic phase at vanishing field. The smallness of the MR at 70 K is, however, due to the fact that a field up to 9.0 T is still insufficient to fully reverse the transformation. In Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\) with

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\text{FIG. 2. Variation of electrical resistance in a thermal excursion measured under different fields on } \text{Ni}_{50}\text{Mn}_{34}\text{In}_{16} \text{ (left) and Ni}_{50}\text{Mn}_{35}\text{In}_{15} \text{ (right).}
\]
a completely recoverable saturated value of ~60% was already attained at only about 3.5 T, even though the temperature, 289 K, is very close to the reverse transformation temperature (303 K) and the Curie temperature for this sample. The saturated MR is depicted in Fig. 4c. Noticeably, in Ni$_{50}$Mn$_{34}$In$_{16}$, the saturated MR displays a marked increase when the temperature falls from 200 to 100 K; it becomes smaller below 100 K because under such circumstances the largest field available to us can only induce an incomplete transformation. In view of practical applications, it would be favorable to adjust the composition for materials of this category towards an even smaller entropy change by martensitic transformation so that a large MR can be obtained with a low field. The sample Ni$_{50}$Mn$_{35}$In$_{15}$ is also of potential importance though it only has a MR above 50% over a temperature of approximately 12 K, bearing in mind the full reversibility of its MR near room temperature and the low field required.

In summary, large MR effect has been realized in single-crystalline Ni$_{50-\chi}$Mn$_{\chi}$In$_{\chi}$ (\(\chi = 14-16\)) alloys by exploiting the large resistance difference across the martensitic transformation induced by a magnetic field. In the sample of a small entropy change, a large MR can be obtained over wide temperature ranges. In Ni$_{50}$Mn$_{34}$In$_{16}$, the MR can exceed 70% over a temperature of approximately 100 K, and in Ni$_{50}$Mn$_{35}$In$_{15}$ an equally large MR is attainable near room temperature at moderate field strengths. In order to obtain a large MR with even lower field strengths, the material composition should be optimized to reduce the entropy change. These NiMnIn alloys with the aforementioned properties promise various innovative applications as magnetic refrigerants, magnetic actuators, and so forth.

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