

## Tuning the magnetic entropy change of $\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$ alloys by varying the Mn content

B. Gao, F. X. Hu,<sup>a)</sup> J. Shen, J. Wang, J. R. Sun, and B. G. Shen

State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

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Magnetocaloric effect associated with the first-order martensitic transition ( $T_M$ ) is investigated in polycrystalline  $\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$  alloys with varying Mn content but fixing In content. It is found that when Mn content reaches  $x=3$ , a field-induced metamagnetic transition takes place. An external magnetic field can reduce  $T_M$  to a lower temperature at a rate of 3.5 K/T, thereby yielding a large magnetic entropy change  $\Delta S$  near room temperature. The  $\Delta S$  magnitude attains to 33 J/kg K under a magnetic field of 5 T at 285 K for the sample with  $x=3$ , while the temperature span of the  $\Delta S$  peak can reach 15 K because of the reduction in  $T_M$  by the external magnetic field. The calculated refrigerant capacity reaches 279 J/kg for the sample with  $x=3$ . These values of the magnetocaloric parameters suggest that these alloys are suitable candidates for magnetic refrigerants. © 2009 American Institute of Physics. [DOI: 10.1063/1.3098229]

### I. INTRODUCTION

Many materials with first-order magnetic phase transition have been found to exhibit a giant magnetocaloric effect (MCE).<sup>1–14</sup> These materials indicate that their magnetic entropy changes are negative in general, but a few of them, such as  $\text{CoMnSiGe}$  (Ref. 13) and  $\text{Mn}_3\text{GaC}$ ,<sup>14</sup> exhibit that their magnetic entropy changes are positive and small in magnitude. As one of the typical MCE materials, Mn-based Heusler alloys exhibit many distinctive properties, and they have become a hot point of research recently.<sup>6–12</sup> Ni–Mn–Ga Heusler alloys are well known for their unusual properties: large magnetostriction, superelasticity, and ferromagnetic shape memory effect. These alloys undergo a structural transformation from an  $L1_2$ -type cubic structure to a tetragonal, orthorhombic, monoclinic structure or a modulated variation, crucially depending on their compositions. The structural transformation is of first order in nature and in most cases the magnetic orderings in both parent and product phases are ferromagnetic but different in exchange interaction. The magnetic entropy change  $\Delta S$  associated with the structural transformation can be very large, but the large  $\Delta S$  occurs usually in a very narrow temperature range due to the fact that the structural transformation, which is driven by temperature, can be hardly shifted by an external magnetic field. Both phases in these alloys show ferromagnetic nature across the structural transformation. The difference in saturated magnetization upon phase transition is small and thus the resulting Zeeman energy  $\mu_0\Delta MH$  is not large enough to drive the structural transformation. As is known, a practical magnetic refrigerator requires not only a large MCE but also a wide temperature span of the MCE. Although the  $\Delta S$  in the conventional Heusler alloys can be very large, about 86 J/kg K, for example,<sup>10</sup> the narrow temperature span of the  $\Delta S$ , about 1–2 K, does hinder these alloys from being used practically.

Fortunately, the physical properties of the Mn-based Heusler alloys can be tuned through adjusting valence electron concentrations, chemical surroundings, as well as band structures. Their magnetic properties can be critically changed, depending on their compositions and corresponding ratio. The previous studies indicated that ferromagnetic properties and martensitic transformation had been also observed in Ga-free Ni–Mn–Z Heusler alloys where Z could be a group-III or group-IV element such as In, Sn, or Sb. These alloys exhibit complex phase diagrams, especially those that have excessive Mn content.<sup>15</sup> Several research groups have studied their magnetic properties and observed a large magnetic entropy change ( $\Delta S$ ) in both NiMnSn and NiMnIn alloys.<sup>16–19</sup> A positive value of  $\Delta S$  reaches 18.5 J/kg K at about 300 K under a magnetic field of 5 T in a polycrystalline alloy  $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$ . A detailed investigation on  $\text{Ni}_{50}\text{Mn}_{50-y}\text{In}_y$  alloys<sup>20</sup> indicated that the samples with In content in a range  $16.5 \leq y \leq 25$  showed ferromagnetic properties and retained cubic structure without any structural transition. For the composition with In concentration  $y \leq 16$ , the martensitic structural transformation appears, and both austenitic and martensitic states showed ferromagnetic nature in a range  $15 \leq y \leq 16$ . At a critical composition, i.e.,  $y=16$ , lattice instabilities showed up and magnetic-field-induced structural transition took place.<sup>20</sup> This alloy with  $x=16$  is the only composition with which the alloy can exhibit a field-induced transition in this series of alloys. The alloys with In content  $y=15.5$  and 15 show martensitic transform but no shift in transition temperature with applying a magnetic field, which can give rise to a very narrow temperature span for the MCE. The alloy with  $x=16$  shows a strong shift of martensitic transition ( $T_M$ ) toward lower temperatures with applying a magnetic field. Several research groups investigated its shape memory effect and magnetocaloric effect. The reported positive  $\Delta S$  with a considerable large temperature span reaches 12 J/kg K under a magnetic field of 5 T,<sup>21</sup> which is larger than that of Gd. However, the large  $\Delta S$

<sup>a)</sup>Electronic mail: hufx@g203.iphy.ac.cn.

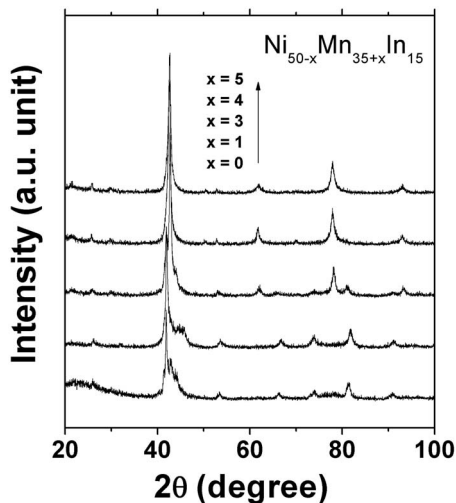


FIG. 1. XRD patterns obtained at room temperature for  $\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$  ( $x=0-5$ ) alloys.

occurs around 180 K, still far from room temperature. In the present paper, we present magnetic properties and MCE in Heusler alloys  $\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$  ( $x=0-5$ ). By changing Mn content but fixing In content, a field-induced structural transition is realized in a modified composition with  $T_M$  at 285 K. Associated with the field-induced metamagnetic behavior, a huge  $\Delta S$  with a wide temperature span is observed near room temperature.

## II. EXPERIMENT

$\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$  ( $x=0-5$ ) alloys employed in the present study were prepared by repeatedly arc melting appropriate quantities of starting materials in high-purity argon atmosphere (99.996%) with a base pressure of  $10^{-4}$  Pa. The commercial purities of Ni, Mn, and In are 99.999, 99.9, and 99.995 wt %, respectively. The obtained ingots were wrapped each with a Ta foil and subsequently homogenized in a sealed quartz tube with a high vacuum of  $10^{-4}$  Pa at 1173 K for 24 h, and then quenched in ice water. Samples for measurements were cut from the central parts of each ingot. Magnetic measurements were performed by using a superconducting quantum interference device magnetometer and physics property measurement system.

## III. RESULTS AND DISCUSSION

Powder x-ray diffraction (XRD) analysis was carried out by using  $\text{Cu K}\alpha$  radiation to identify the crystal structure. Figure 1 shows the XRD patterns obtained at room temperature. As expected,<sup>20</sup> the sample with  $x=0$  shows a martensitic structure at room temperature. With Mn concentration increasing, the alloys gradually become of the austenitic cubic structure. At the critical composition  $x=3$ , martensitic and austenitic structures coexist because the structural transition temperature  $T_M$  is near room temperature. Such structural characteristics accord with the magnetic measurements which will be shown below.

Temperature dependent magnetizations under different fields have been measured in zero-field-cooled (ZFC) and field-cooled (FC) conditions in order to determine the mag-

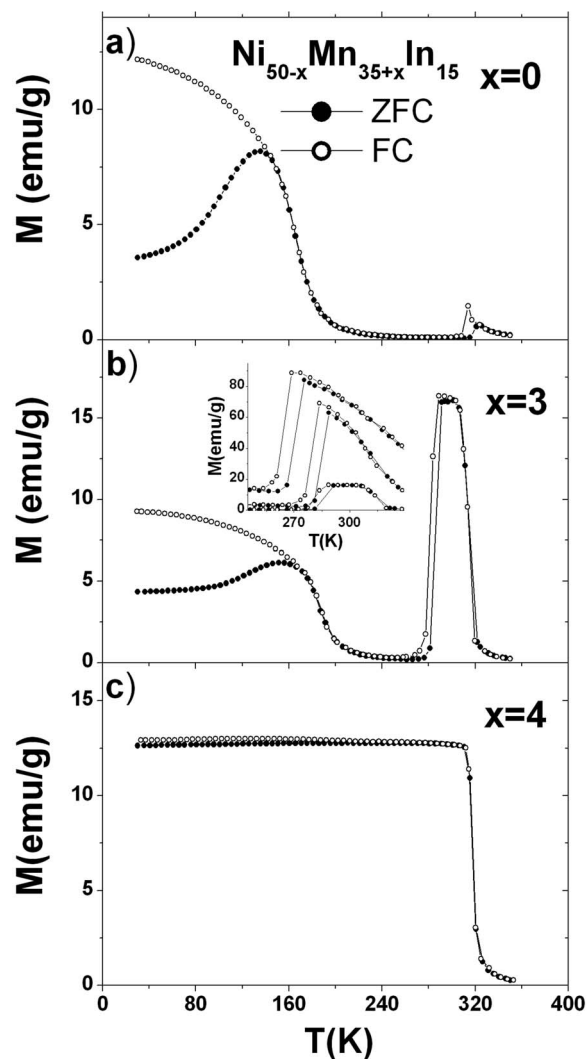


FIG. 2. Temperature dependent ZFC and FC magnetizations measured under a 0.05 T magnetic field for the typical samples  $\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$  with: (a)  $x=0$ , (b)  $x=3$ , (c)  $x=4$ , where the inset of (b) shows the ZFC—ZC magnetizations measured under different fields of 0.05, 1, and 5 T for the sample with  $x=3$ .

netic state, the transition temperature, and the nature of the transitions. The samples were first cooled down to 5 K in a zero field, then a magnetic field was applied to the samples and their magnetizations were measured with heating the samples with the field fixed; thus the ZFC magnetization curves were obtained. The FC magnetizations were measured with cooling the samples down to 5 K in the same field. Figure 2 displays the temperature dependent ZFC and FC magnetizations under 0.05 T for the typical samples. For the sample with  $x=0$ , the magnetization gradually increases with the sample cooling. The small cusp indicates the appearance of ferromagnetic order of austenitic phase. However, before the ferromagnetic transition in austenitic phase is completed, martensitic transformation has already taken place at 314 K, higher than the austenitic Curie temperature  $T_C^A$ , with a hysteresis of 8 K. Continuously reducing the temperature leads to magnetic ordering of the martensitic phase with a Curie temperature  $T_C^M$  of 170 K, the temperature at which  $dM/dT$  reaches a maximum value. At temperatures lower than 135 K, a large separation between ZFC and FC magnetizations is

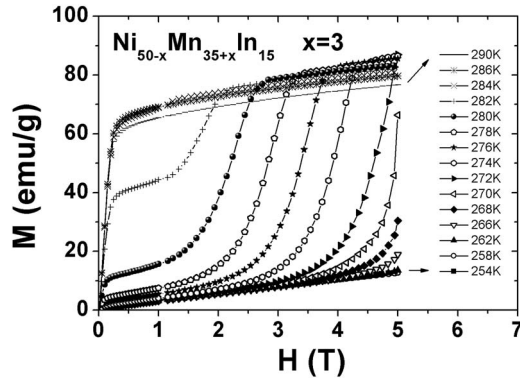


FIG. 3. Curves for magnetization isotherm  $M$ - $H$  for  $\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$  ( $x=3$ ) alloy measured during field increasing near the martensite-to-austenite transition temperature.

observed, which is understandable when the magnetic anisotropy in the martensitic state is considered.<sup>20,22</sup> Reducing the structural symmetry can enhance the magnetic anisotropy. An external cooling field can govern the magnetic domain configuration, resulting in the splitting between FC and ZFC magnetizations. In the sample with  $x=0$ ,  $T_M$  can be hardly fluctuated by magnetic field, which is consistent with the previous observation for the same composition.<sup>20</sup>

With the increase in Mn content,  $T_M$  decreases but  $T_C^M$  increases. When Mn content reaches  $x=3$ ,  $T_M$  appears at 285 K and  $T_C^M$  at 190 K. The temperature hysteresis around  $T_M$  is 5.5 K for the sample of  $x=3$ , and, importantly, the increase in magnetic field does not enlarge the hysteresis [insert of Fig. 2(b)]. Further increasing the Mn content results in the disappearance of martensitic transition, while the samples each retain a cubic structure in the whole measured temperature range, which is also indicated in the XRD spectra in Fig. 1. Valence electron concentration  $e/a$  is a critical factor that influences the characteristics of Heusler alloys. The previous studies<sup>16</sup> indicated that in Ni-Mn-based Heusler alloys, both  $T_C^M$  and  $T_M$  were strongly dependent on  $e/a$ .  $T_M$  decreases rapidly but  $T_C^M$  increases with  $e/a$  decreasing. For the present alloys with changing Mn content but fixing In content,  $e/a$  decreases monotonically from 7.9 ( $x=0$ ) to 7.75 ( $x=5$ ). Here,  $e/a$  is calculated as the concentration weighted sum of the numbers of  $3d$  and  $4s$  electrons for Ni and Mn and the numbers of  $5s$  and  $5p$  electrons for In.  $T_M$  decreases from 314 to 285 K while  $T_C^M$  increases from 170 to 190 K when Mn content increases from  $x=0$  to  $x=3$ , which accord with the general rule in Ni-Mn-based alloys. As  $e/a$  reaches 7.78 ( $x=4$ ), the martensitic transition disappears, which is also roughly consistent with the general rule in the NiMnIn systems.

The inset of Fig. 2(b) shows the ZFC and FC magnetizations measured under different fields of 0.05, 1, and 5 T for the sample with  $x=3$ . In contrast to the case with  $x=0$ ,  $T_M$  can be reduced to a lower temperature at a rate of 3.5 K/T. More attractively, a field-induced metamagnetic transition takes place in this sample, similar to the case in  $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$  alloy. Figure 3 displays the curves for magnetization isotherm ( $M$ - $H$ ) measured during field increasing at temperatures around  $T_M$ . The upturn in the curves below but near  $T_M$  is associated with the field-induced metamagnetic behavior,

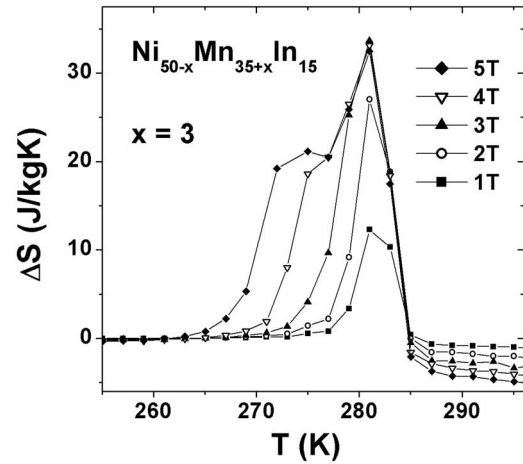


FIG. 4. Curves for magnetic entropy change  $\Delta S$  as a function of temperature at several different magnetic fields for  $\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$  ( $x=3$ ) alloy.

accompanied by a structural transition from martensitic to austenitic state. Such a metamagnetic behavior is related to the fundamental change in magnetism across martensitic transition. Austenitic state of the sample with  $x=3$  shows strong ferromagnetic behavior with  $T_C^A=313$  K, but martensitic state displays a small magnetization at temperatures where martensitic transition is just completed. The nature of the low magnetization in martensitic state is still controversial for this kind of material. Some people believe that the martensitic state is of paramagnetic phase,<sup>23</sup> while the others think of it as being of a mixture of ferro- and antiferromagnetic phases.<sup>19,21</sup> To understand the exact origin, a knowledge of site occupancy of atoms and band structure giving the details of the  $p$  and  $d$  states, as well as neutron diffraction studies on the origin of magnetic properties, is required. Anyway, a large change in magnetization across  $T_M$  produces a large Zeeman energy  $\mu_0\Delta MH$ , which leads to the occurrence of metamagnetic behavior. Such a field-induced structural transition predicts a large magnetocaloric effect.

According to the thermodynamical theory, magnetic entropy change  $\Delta S(T, H)$  can be obtained from the Maxwell relation,<sup>1-7</sup>  $\Delta S(T, H) = S(T, H) - S(T, 0) = \int_0^H (\partial M / \partial T)_H dH$ . Shown in Fig. 4 are the curves for the obtained magnetic entropy change  $\Delta S$  for the sample with  $x=3$  versus temperature  $T$  at several different magnetic fields. One can find that the value of  $\Delta S$  is positive and located in an interested refrigeration temperature range. With magnetic field increasing,  $\Delta S$  peak gradually expands toward lower temperatures because of the field-induced metamagnetic transition behavior and a wide span of  $\Delta S$  appears. The maximum of  $\Delta S$  reaches 33 J/kg K, and the temperature span of  $\Delta S$  attains to 15 K under a 5 T magnetic field. As is known, refrigerant capacity (RC) is another key parameter in the estimation of MCE. RC is defined as<sup>24</sup>

$$\text{RC} = \int_{T_1}^{T_2} \Delta S(T)_H dT,$$

where  $T_1$  and  $T_2$  are the temperatures of cold and hot reservoirs of the refrigeration cycle, respectively. According to the method available from the literature,<sup>23</sup> the value of RC can

be obtained by performing the integration over the full width at half maximum in a  $\Delta S$ - $T$  curve. The obtained RC value under 5 T for the present sample with  $x=3$  is 279 J/kg, which is slightly lower than 305 J/kg reported for  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  alloy under the same magnetic field. Several other first-order systems were historically found to have a large  $\Delta S$  with a wide temperature span. The typical and well-known materials are the FeRh alloys.<sup>25</sup> However, the irreversibility of the MCE with respect to alternating magnetic field in FeRh alloy (i.e., it disappears after 1 cycle) makes such an alloy useless for real applications. The wide temperature span in the present alloys is attractive compared with that in conventional Heusler alloys, in which  $\Delta S$  can be extremely large but usually concentrates in a very narrow temperature range, for example, 1–2 K.  $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$  is the only material with such a composition that it can show metamagnetic behavior in the series of  $\text{Ni}_{50}\text{Mn}_{50-y}\text{In}_y$  alloys. Its  $\Delta S$  is large (12 J/kg K under 5 T) but appears at a temperature (180 K) far below room temperature. In the present study, by fixing the In content and modifying the valence electron concentration in  $\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$  alloys, a field-induced metamagnetic transition is realized in a composition ( $x=3$ ) with  $T_M$  at 285 K. As a result, a high and broad peak of magnetic entropy change is observed near room temperature.

#### IV. CONCLUSION

We have investigated the effect of tuning the Mn content on magnetic properties and magnetic entropy change in  $\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$  alloys. It is found that martensitic transition behavior and magnetic properties are sensitive to the Mn content. When  $x$  is increased from 0 to 3, the martensitic transition temperature  $T_M$  decreases from 314 to 285 K while the Curie temperature  $T_C^M$  of martensitic state increases from 170 to 190 K. As  $x$  reaches 4, i.e.,  $x=4$ , the martensitic transition disappears. Such behaviors are consistent with the dependence of transition temperature on  $e/a$ . More importantly, a field-induced metamagnetic transition is realized in a composition ( $x=3$ ) with  $T_M$  (285 K) around room temperature. An applied magnetic field can reduce  $T_M$  to a lower temperature at a rate of 3.5 K/T. Associated with the metamagnetic behavior, a high and broad  $\Delta S$  is observed. The value of  $\Delta S$  can reach 33 J/kg K under a 5 T magnetic field. Such a value considerably exceeds that of  $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ .

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