Room temperature magnetocaloric effect in Ni–Mn–In

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We have studied the effect of magnetic field on a nonstoichiometric Heusler alloy $Ni_{50}Mn_{35}In_{15}$ that undergoes a martensitic as well as a magnetic transition near room temperature. Temperature dependent magnetization measurements demonstrate the influence of magnetic field on the structural phase transition temperature. From the study of magnetization as a function of applied field, we show the occurrence of inverse-magnetocaloric effect associated with this magneto-structural transition. The magnetic entropy change attains a value as high as 25 J/kg K (at 5 T field) at room temperature as the alloy transforms from the austenitic to martensitic phase with a concomitant magnetic ordering. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2823601]

In recent years, there has been an increasing awareness toward incorporating an alternate technology for refrigeration that would replace the conventional gas compression/expansion technique. In this respect, the promising candidates are the magnetic materials that exhibit an inherent *magnetocaloric effect* (MCE). With its potential impact on energy saving and environment-friendly applicability, these magnetic materials are also looked up as economically viable option for domestic and industrial refrigeration. Fundamentally, MCE is a process in which an isothermal variation in the magnetic entropy takes place with an adiabatic temperature change of the system on the application of magnetic field. In this regard, many rare-earth and transition-metal based alloys have found to show promising results. These include the alloys such as $MnFeP_{1-x}As_x$, $Gd_5(SiGe)_4$, $MnAs_{1-x}Sb$, and $La(Fe_xSi_{1-x})_{13}$.[1–5] The research for the development of such MCE materials is made primarily with two objectives: high MCE around room temperature and low-cost production. Ferromagnetic Heusler alloy, Ni_2MnGa which pertains to the class of shape memory alloy has been attracting much attention in view of the giant MCE effect.[6] The factor responsible for the large entropy change is the first order structural and concomitant magnetic transition taking place in the nonstoichiometric composition of this material, also giving rise to the possibility of a magnetic control of shape memory effect. The latest candidates in the field of such materials have been alloys with composition $Ni_{50}Mn_{50-x}Z_x$ with $Z=Sn,In,Sb$.[7] These materials share a number of features with Ni–Mn–Ga alloys and also display interesting magnetic properties.[8,9] Being rich in Mn content (as compared to the Heusler composition Ni_2MnZ), there are two crystallographic sites occupied by Mn atoms giving rise to competing antiferromagnetic exchange along with the underlying ferromagnetic order.[10] A certain composition of the Ni–Mn–Sn and Ni–Mn–In alloys are shown to exhibit an *inverse* MCE effect in the vicinity of martensitic to austenitic structural transition.[11,12] However, the temperatures where such a phenomenon is observed are much below the room temperature. In this paper, we present one such composition of Ni–Mn–In alloy that undergoes a martensitic as well as a magnetic transition, both occurring in a narrow temperature interval very close to the room temperature. Owing to this fact, an appreciable change in the magnetic entropy is observed at the transformation temperature. The alloy has been thoroughly investigated for its magnetic properties and the order of the sequential phase transitions has been clearly determined.

Polycrystalline ingot of Ni–Mn–In was prepared by arc-melting the starting elements (99.99% purity) under argon atmosphere. To attain a good compositional homogeneity, the ingots were remelted four to five times with a weight loss of $\leqslant 0.5\%$ and annealed at the temperature of 900 K for 48 h in an evacuated quartz ampoule followed by quenching in cold water. The precise composition of the alloy was determined from energy dispersive x-ray analysis to be Ni=50.4 at. %, Mn=34.5 at. %, and In=15.1 at. %. Magnetization (M) measurements were performed on a superconducting quantum interference device magnetometer (Quantum Design, MPMS-5S) in the temperature range of 5–330 K and magnetic field $H=0.01$ and 5 T. $M(H)$ up to 5 T was measured at various temperatures near the region of both martensitic and magnetic transformations with an interval of 2 K between each temperature value.

Magnetization as a function of temperature measured in low magnetic field of 0.01 T is presented in Fig. 1(a). The sample was initially cooled in the absence of field and data were collected on warming from 5 to 330 K [Zero field cooled (ZFC)], followed by cooling [field cooled (FC)] back to 5 K and again during warming in the presence of field [field warmed (FW)]. The ferromagnetic transition is marked by the sharp rise in magnetization at $T_C=305$ K. Below the magnetic ordering temperature, a sudden drop in magnetization takes place at 302 K with value almost close to zero. This signature marks the formation of the new structural phase. The drop in magnetization can be conjectured to be due to the variants of the new crystallographic phase being formed that temporarily disturbs the local ferromagnetic ori-

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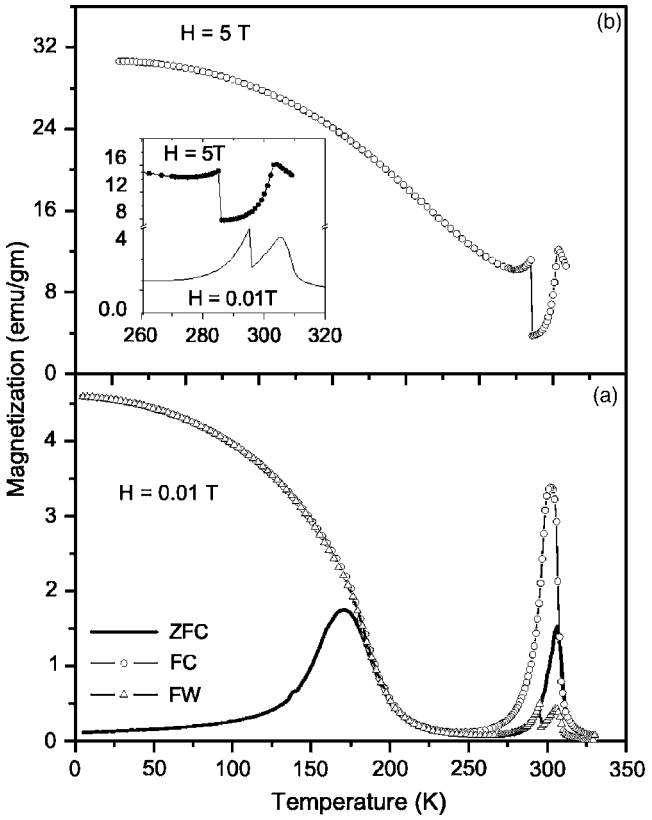

FIG. 1. Thermal variation in magnetization of $Ni_{50}Mn_{35}In_{15}$ measured in an applied field of (a) 0.01 T and (b) 5 T. Hysteresis between the FC, FW, and sudden rise in ZFC, FC, FW near 300 K are signatures of structural and magnetic transitions, respectively. The influence of magnetic field on the structural transition is evident through the shift observed in T_M (shown in the inset).

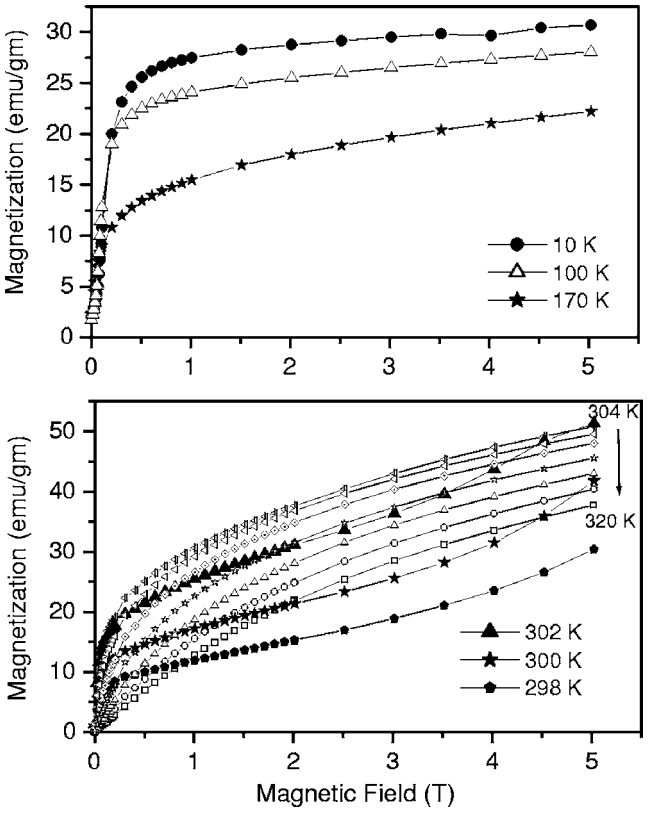

FIG. 2. Magnetization isotherms measured above and below the magnetic and structural phase transitions in $Ni_{50}Mn_{35}In_{15}$. Some of the low temperature isotherms are shown separately in the upper panel of the figure.

entation. This argument is further supported by the large hysteresis in the temperature range of 265–310 K observed in ZFC, FC, and FW magnetization curves. Though the difference in ZFC and FC curves can also be interpreted to be due to the nonzero coercivity of the ferromagnetic material, the hysteresis between FC and subsequent FW curves strongly suggests the presence of a first order structural transition within this temperature interval. Thus, the initial rise and the subsequent fall in magnetization with decreasing temperature are signatures of the magnetic (T_C=305 K) and concomitant martensitic ($T_M \approx 302$ K) phase transformations that the present Ni–Mn–In system undergoes. Below 150 K, an irreversible behavior between the ZFC and FC curves is observed with ZFC response lying below the FC. Such irreversibility is an indication of some degree of frustrated spin alignment. The frustration of spins may result from the competition between the underlying ferromagnetic coupling and an incipient antiferromagnetic coupling between Mn atoms present at two different crystallographic positions.[10] The subsequent FW curve is seen to retrace the FC curve over this temperature range.

Another striking feature in the magnetization curves is the decrease in intensity of the peaklike signature in the vicinity of T_M and T_C for the FW curve. This curve also shows a considerable splitting in the narrow temperature interval. Such a signature dictates the influence of magnetic field on the martensitic transformation. Prior to the FW measurement, the sample undergoes a cooling in some magnetic field (0.01 T in the present case) that causes the T_M to shift to a lower temperature value (295 K) whereas the T_C remains unchanged. This gives rise to the observed splitting of the peaklike feature associated with martensitic and magnetic transitions in the $M(T)$ curve. Figure 1(b) that represents the FW $M(T)$ measurement in magnetic field of 5 T, further supports this observation. It is seen that the splitting of peak observed at 295 K in the FW curve, shifts to a lower value of 285 K in the magnetic field of 5 T. Thus, an overall shift in T_M of about −17 K is observed from the initial value of 302 K upon the application of 5 T magnetic field. The lowering of T_M in Ni–Mn–In system implies that the magnetic field favors the formation of the austenitic phase.

To further investigate the magnetic properties of this alloy, magnetization isotherms were measured for different temperatures with an interval of 2 K, both above and below the two transition temperatures. The measurements were carried out by cooling the sample from 330 K down to the required temperature of interest and then varying the field from 0 to 5 T. At the second order magnetic transition, the magnetization isotherms presented in the Fig. 2 show Brillouin-like dependence, with a slope that decreases monotonically with increasing field. While the $M(H)$ in the temperature interval between 302 and 296 K show prominent metamagneticlike characteristics that implies the first order austenite to martensite structural phase transition. The $M(H)$ recorded at very low temperatures show a typical ferromagnetic nature. In order to further assess the occurrence of first order martensitic and second order magnetic transition in this sample, the Arrott plots were plotted in the temperature range of 280⩽320 K, as shown in Fig. 3. For temperatures around T_C=305 K; the slopes are positive throughout, confirming the second order continuous nature of the transition

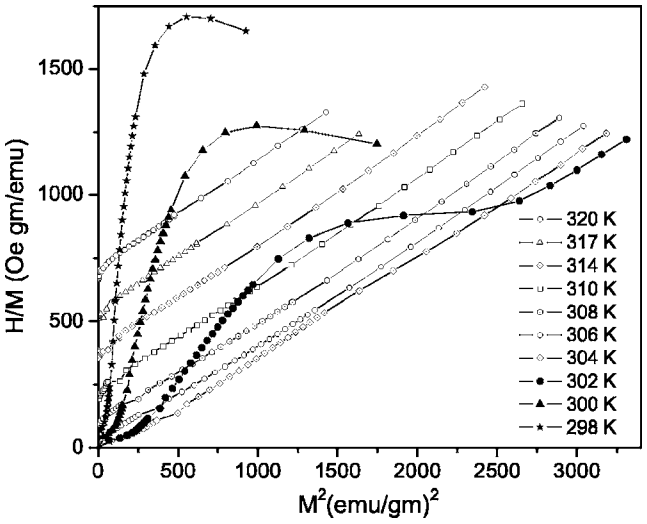

FIG. 3. Arrott plots indicating the second order magnetic and first order structural transition in $Ni_{50}Mn_{35}In_{15}$.

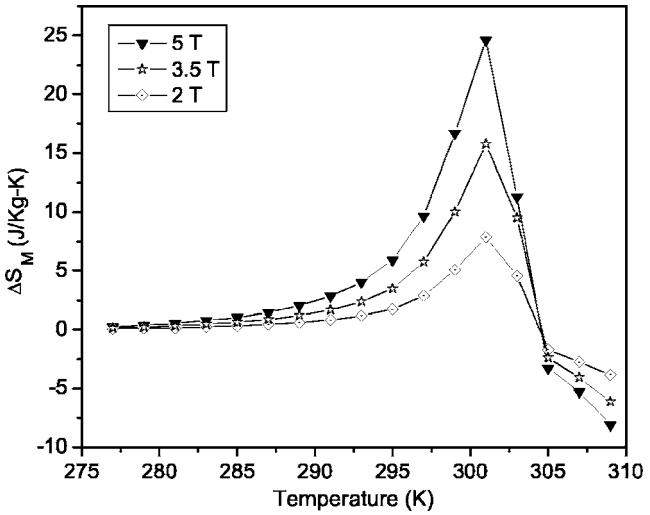

FIG. 4. Magnetic entropy change associated with the structural and magnetic transition for $Ni_{50}Mn_{35}In_{15}$. A large value of 25 J/kg K is observed at 301 K for magnetic field up to 5 T.

in this sample. As the T_M is approached, the corresponding Arrott plots exhibit negative slopes. This criterion has been perviously employed to determine the order of sequential transitions in Ni–Mn–Ga alloys[13] and confirms the first order nature of the martensitic transition at 302 K in the present Ni–Mn–In sample.

Finally, the magnetic entropy change ΔS_M has been evaluated from the magnetization isotherms using the Maxwell equation:

$$\Delta S_M(T,\Delta H) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH. \quad (1)$$

The value of the magnetic entropy changes corresponding to the average temperature between two consecutive $M(H)$ isotherms, calculated by numerical integration using the above expression over the field span of 1–5 T are shown in Fig. 4. A sharp peak, with a ΔS_M value of 25 J/kg K is found at the temperature of ~301 K for the magnetic field variation from 1 to 5 T. The obtained value of the maximum in ΔS_M is an excellent feature particularly because it has been observed at room temperature. This makes the $Ni_{50}Mn_{35}In_{15}$ alloy a potential candidate for practical applications. This property emerges as a consequence of spontaneous magnetization at room temperature followed by the clear martensitic transition in the narrow temperature interval.

In conclusion, we have observed a large magnetic entropy change taking place at room temperature in $Ni_{50}Mn_{35}In_{15}$ alloy. A complete characterization of the magnetic properties of this important material aids to the understanding required for the technological exploitation of such materials. Especially, the narrow difference (~2 K) between the structural and magnetic transition temperature and alteration of T_M by magnetic field are remarkable properties that the present alloy exhibits.

[1] O. Tegus, E. Brück, K. H. Buschow, and F. R. de Boer, Nature (London) **415**, 150 (2002).
[2] H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
[3] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[4] X. X. Zhang, G. H. Wen, F. W. Wang, W. H. Wang, C. H. Yu, and G. H. Wu, Appl. Phys. Lett. **77**, 3072 (2000).
[5] S. Fujieda, A. Fujita, and K. Fukamichi, Appl. Phys. Lett. **81**, 1276 (2002).
[6] L. Pareti, M. Solzi, F. Albertini, and A. Paoluzi, Eur. Phys. J. B **32**, 303 (2003).
[7] Y. Sutou, Y. Imano, N. Koeda, T. Omori, R. Kainuma, K. Ishida, and K. Oikawa, Appl. Phys. Lett. **85**, 4358 (2004).
[8] T. Krenke, M. Acet, E. F. Wassermann, X. Moya, L. Manosa, and A. Planes, Phys. Rev. B **72**, 014412 (2005).
[9] T. Krenke, M. Acet, E. F. Wassermann, X. Moya, L. Manosa, and A. Planes, Phys. Rev. B **73**, 174413 (2006).
[10] P. J. Brown, A. P. Grandy, K. Ishida, R. Kainuma, T. Kanomata, K.-U. Neumann, K. Oikawa, B. Ouladdiaf, and K. R. A. Ziebeck, J. Phys.: Condens. Matter **18**, 2249 (2005).
[11] T. Krenke, E. Duman, M. Acet, E. Wassermann, X. Moya, L. Manosa, and A. Planes, Nat. Mater. **4**, 450 (2005).
[12] A. K. Pathak, M. Khan, I. Dubenko, S. Stadler, and N. Ali, Appl. Phys. Lett. **90**, 262504 (2007).
[13] X. Zhou, W. Li, H. P. Kunkel, and G. Williams, Phys. Rev. B **73**, 012412 (2006).