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Magnetostructural phase transitions and magnetocaloric effects in MnNiGe$_{1-x}$Al$_x$

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The thermomagnetic and magnetocaloric properties of the MnNiGe$_{1-x}$Al$_x$ system have been investigated by magnetization and differential scanning calorimetry (DSC) measurements. The presence of first-order magnetostructural transitions (MSTs) from hexagonal ferromagnetic to orthorhombic antiferromagnetic phases has been detected for x = 0.085 and 0.09 at 193 K and 186 K, respectively. The values of latent heat (L = 6.6 J/g) and corresponding total entropy changes (ΔS_T = 35 J/kg K) have been evaluated for the MST (x = 0.09) from DSC measurements. The magnetic entropy change for x = 0.09 (ΔS_M = 17.6 J/kg K for 5 T) was found to be comparable with well-known giant magnetocaloric materials, such as $Gd_5Si_2Ge_2$, $MnFeP_{0.45}As_{0.55}$, and $Ni_{50}Mn_{37}Sn_{13}$. © *2012 American Institute of Physics*. [doi:10.1063/1.3681798]

Materials that undergo magnetostructural phase transitions (MSTs) are the subject of intense research due to their significant magnetoresponsive properties such as magnetocaloric effects (MCE),[1–3] magnetoresistance,[4] magnetostriction,[5] etc. Therefore, from an application point of view, it is highly desirable to discover new materials that exhibit magnetostructural transitions.

MnNiGe orders antiferromagnetically (AFM) with a spiral magnetic structure below $T_N \sim 346$ K. In the paramagnetic (PM) region, a first-order structural transition (FOT) from a low-temperature orthorhombic TiNiSi-type structure to a high-temperature hexagonal Ni_2In-type structure occurs at 470 K.[6] The structural transition of MnNiGe in the paramagnetic state does not lead to a significant change in the magnetization. Recently, it has been observed that the FOT temperature can be lowered below Curie temperature (T_C) of the MnNiGe system by changing the stoichiometry[7,8] as well as the chemical composition.[9,10] However, almost all of the studied systems are related to the constriction of the lattice, which can be considered as the application of external pressure. It has been shown that the structural stability and associated transition temperatures are very sensitive to the Mn-Mn separation.[7,8,11]

In the present work, we expanded the lattice cell volume, i.e., increased the Mn-Mn distance, by substituting the larger size Al for Ge in MnNiGe$_{1-x}$Al$_x$, and investigated the corresponding magnetostructural phase transitions as well as MCE.

The samples were prepared by arc-melting the constituent pure elements of purity better than 99.99% in an argon atmosphere, followed by annealing in high vacuum ($\approx 10^{-5}$ torr) for 4 days at 850 °C. The room temperature x-ray diffraction patterns of the samples have been obtained using Cu $K\alpha$ radiation. Structural refinement was carried out using the Rietveld profile refinement method of the FULLPROF program. A superconducting quantum interference device magnetometer (SQUID) was employed to measure the magnetization of MnNiGe$_{1-x}$Al$_x$ within the temperature interval of 5–400 K and in applied magnetic fields up to 5 T. The differential scanning calorimetry (DSC) measurements were carried out employing a DSC 8000 (with the ramp rate of 20 K/min during heating and cooling) in the temperature range of 103-573 K. The latent heat (L) has been estimated from the measured endothermic peak of the heat flow curve of DSC measurement using

$$L = \int_{T_s}^{T_f} \frac{dQ}{dT} dT,$$

where $\frac{dQ}{dT}$ is the change of heat flow with respect to temperature, and T_s and T_f are the start and finishing temperatures, respectively, of the MST on heating.

The x-ray diffraction (XRD) patterns confirm that MnNiGe$_{1-x}$Al$_x$ with x = 0.085 and 0.09 both crystallize in a hexagonal Ni_2In-type structure at room temperature (shown in Fig. 1). However, parent MnNiGe shows an orthorhombic martensite TiNiSi-type structure at room temperature and

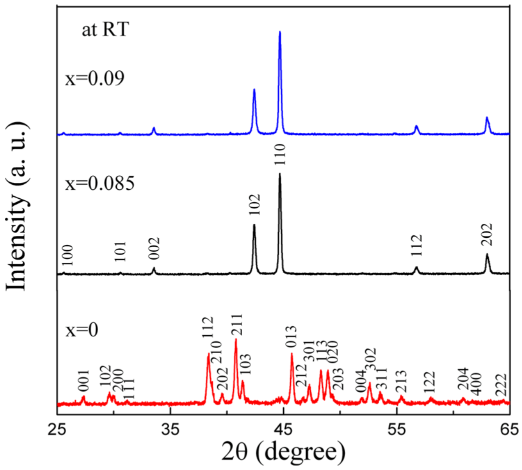

FIG. 1. (Color online) Room temperature XRD patterns for MnNiGe$_{1-x}$Al$_x$ with x = 0, 0.085, and 0.09.

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transforms into the hexagonal Ni_2In-type structure at 470 K. The structural refinement was carried out using the rietveld profile refinement method. It was found that the hexagonal lattice parameters increased with the increasing Al doping concentration (a = 4.099, 4.101 Å and c = 5.424, 5.425 Å for x = 0.085, 0.09, respectively). The increase in cell volume by the substitution of Al for Ge is qualitatively analogous to increasing of Mn-Mn separation in $MnNiGe_{1-x}Al_x$, which stabilizes the hexagonal Ni_2In-type structure at a lower temperature relative to that of the parent MnNiGe.

The temperature dependence of the magnetization (M) for $MnNiGe_{1-x}Al_x$ (x = 0.085, 0.09) measured during heating and cooling in the presence of 1 kOe magnetic field is shown in Fig. 2. Two magnetic phase transitions have been observed in M(T) curves for both of the samples. The small value of magnetization in the low-temperature region is similar to that of the parent MnNiGe and indicates that the low-temperature phase of $MnNiGe_{1-x}Al_x$ is AFM with an orthorhombic TiNiSi-type structure. Typical for a MST from an AF to FM state, a sharp jumps in the M(T) of the $MnNiGe_{1-x}Al_x$ system have been observed with increasing temperature (see Figure 2). The calculated values of magnetostructural transition temperatures (T_M) were 193 K and 186 K for x = 0.085 and 0.09, respectively. The observed temperature hysteresis of about 15 K in heating and cooling M(T) curves in the vicinity of T_M signifies the first-order nature of magnetostructural transition. On further heating, both the samples undergo the FM-paramagnetic (PM) transition similar of that observed for Ni_2In-type structure at T_C. The T_C (∼213 K) remains unchanged in both samples.

The first-order magnetostructural transition and second-order FM-PM transition were also detected in DSC measurements, which are shown in Fig. 3. The observed large endothermic/exothermic peaks during heating/cooling cycles are associated with the latent heat of the first-order magnetostructural transition from the AFM TiNiSi-type structure to the FM Ni_2In-type structure. The thermal hysteresis of about 22 K between heating and cooling cycles signifies the first-order nature of magnetostructural transition. On the other hand, a small anomaly has been observed for the second-order FM-PM phase transition (SOT) with negligible thermal hysteresis. Because of the narrowly spaced transitions upon heating, the T_M and T_C are not distinctly visible in the case of x = 0.085 [shown in Fig. 3(b)].

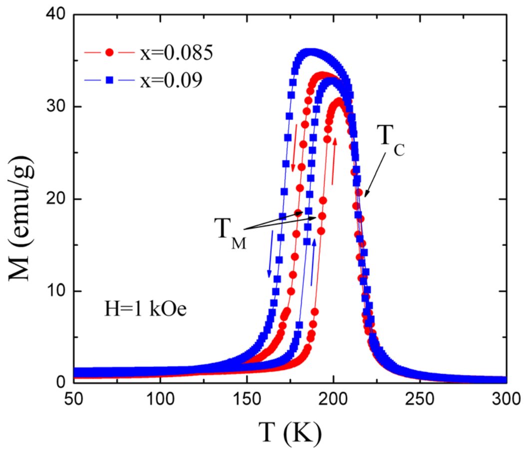

FIG. 2. (Color online) Temperature dependence of the magnetization in the presence of 1 kOe magnetic field during heating and cooling for $MnNiGe_{1-x}Al_x$ with x = 0.085 and 0.09.

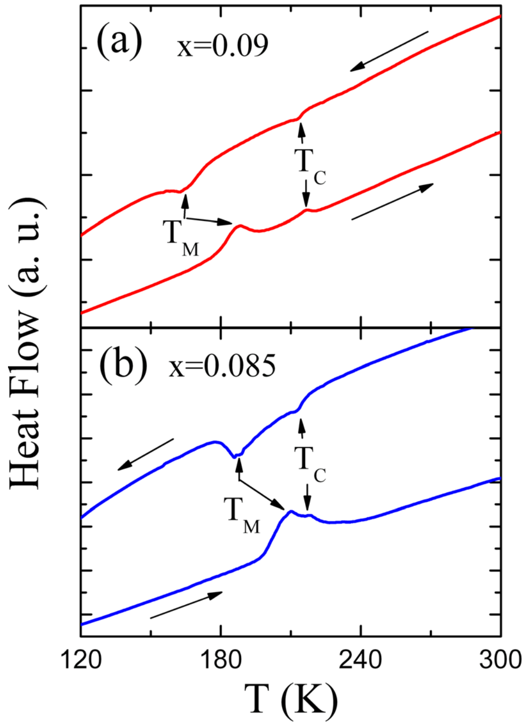

FIG. 3. (Color online) DSC heat flow curves as a function of temperature. The heating and cooling rates were 20 K/min (for $MnNiGe_{1-x}Al_x$ with x = 0.085 and 0.09).

Thus, it has been found that T_M decreases with increasing Al concentration in $MnNiGe_{1-x}Al_x$. Based on the above results, it can be concluded that the increase in the lattice parameters by substituting the larger Al atoms for Ge (can be realized as negative chemical pressure effect) stabilizes the FM hexagonal Ni_2In-type structure in $MnNiGe_{1-x}Al_x$ compounds. However, previous reports suggest that the constriction of lattice by applying hydrostatic pressure/positive chemical pressure (due to substitution of smaller atomic species in MnNiGe) results in a decrease in T_M and, therefore, also results in the stabilizing of the Ni_2In−type structure.[7–10,12] The abovementioned contrasting behavior can be explained by considering the changes of the valence electron (e) concentration per atom (a), e/a, in $MnNiGe_{1-x}Al_x$. It has been reported the T_M decreases with the decrease in e/a for NiMn-based Heusler alloys.[13] A similar type of decrease in T_M has been observed in $MnNiGe_{1-x}Al_x$ alloys by decreasing e/a ratio with the substitution of fewer valence electrons (i.e., Al for Ge). Therefore, not only the Mn-Mn separation but also the e/a ratio plays a crucial role in determining the relative stability of the TiNiSi-type and Ni_2In-type structures in $MnNiGe_{1-x}Al_x$ alloys.

The magnetic entropy changes (ΔS_M) were estimated from magnetization isotherms measured at different temperatures using the Maxwell relation, $(\partial S/\partial H)_T = (\partial M/\partial T)_H$. For ideal FOT, the Maxwell relation is not applicable for the analysis of ΔS_M, because of discontinuous transition [$(\partial M/\partial T)_H$ is infinite].[14] However, the majority of materials in practice as our samples do not show ideal discontinuous FOT [$(\partial M/\partial T)_H$ is finite, i.e., not perfectly discontinuous].

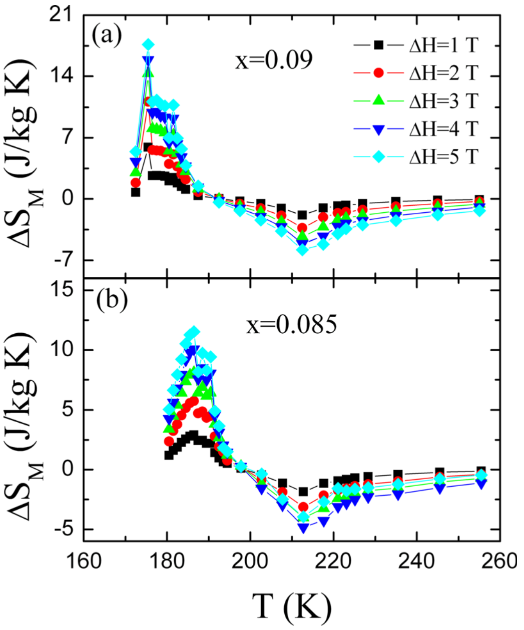

FIG. 4. (Color online) The temperature dependence of the magnetic entropy change (ΔS_M) of $MnNiGe_{1-x}Al_x$ with $x = 0.085$ and 0.09, for magnetic field changes up to 5 T.

Therefore, it is possible to use the Maxwell relation for estimating ΔS_M.[15] The temperature dependences of ΔS_M for different changes in magnetic field (ΔH) are shown in Fig. 4. Large inverse MCE has been observed in vicinity of T_M (see Fig. 4), which is associated with the abrupt change of magnetization (see Figure 2) due to the AF-FM first-order MST. The maximum change of ΔS_M in the vicinity of T_M for $x = 0.09$ (17.6 J/kg K for $\Delta H = 5$ T) is comparable with the well-known giant MCE materials exhibiting first-order transitions near room temperature, such as $Gd_5Si_2Ge_2$ (−18 J/kg K for $\Delta H = 5$ T),[16] $MnFeP_{0.45}As_{0.55}$ (−18 J/kg K for $\Delta H = 5$ T),[2] and $Ni_{50}Mn_{37}Sn_{13}$ (18 J/kg K for $\Delta H = 5$ T).[3] The value of ΔS_M ($x = 0.09$) due to the first-order MST as estimated from Clausius-Clapeyron equation was found out to be 16.6 J/kg K for $\Delta H = 5$ T [where, $\Delta M = 18.2$ emu/g and $\Delta T = 5.48$ K], which was calculated from thermomagnetization curves measured at different constant magnetic fields following the procedure as mention in Ref. 5. Another striking aspect of our study is that the latent heat (L) due to the first-order magnetostructural transition for $x = 0.09$ as estimated from DSC heating curve reaches the value of 6.6 J/g, corresponding to a total entropy change of $\Delta S_T = 35$ J/kg K. The estimated value of ΔS_T of the magnetostructural transition is larger than some giant MCE materials, such as single crystalline $Ni_{55}Mn_{20}Ga_{25}$ ($\Delta S_T = -24$ J/kg K as estimated from latent heat).[17] Large negative values of ΔS_M of −5.8 and −4.8 J/kg K for $\Delta H = 5$ T in the vicinity of T_C were obtained for $x = 0.09$ and 0.085, respectively. These entropy changes in the vicinity of the SOT are comparable to that observed at the FOT for $Ni_{50}Mn_{36}Sb_{14}$ (5.2 J/kg K for $\Delta H = 5$ T).[18] Therefore, considering the proposed refrigeration technique,[19] it is possible to enhance the efficiency of a magnetic refrigerator by utilizing large inverse and conventional (negative ΔS_M) MCE of $MnNiGe_{1-x}Al_x$, which suggests that $MnNiGe_{1-x}Al_x$ alloys could be potential candidates for magnetic refrigeration.

In summary, owing to the large latent heat associated with magnetostructural transition, a large MCE has been observed in $MnNiGe_{1-x}Al_x$. The decrease of the e/a ratio by the partial substitution an atom (Al) with fewer valence electrons than Ge results in a decrease in T_M. Therefore, the increase in e/a by incorporating more valence electron in the system could shift the T_M towards room temperature, and possibly achieve large MCE in Mn-Ni-Ge systems.

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