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Large magnetocaloric effects over a wide temperature range in $MnCo_{1-x}Zn_xGe$

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The magnetic and structural transitions can be controlled to coincide by partial substitution of Zn for Co in $MnCo_{1-x}Zn_xGe$, leading to a large magnetocaloric effects over a wide temperature range. The magnetostructural transition from paramagnetic to ferromagnetic state results in magnetic entropy changes ($-\Delta S_M$) of 26 J/kg K at 327 K for $\Delta H = 5$ T in the case of $x = 0.045$. Interestingly, a structurally driven first-order phase transition between two high magnetization states as observed for $x = 0.05$ and 0.06 also lead to large values of $-\Delta S_M = 31.4$ and 20.6 J/kg K for $\Delta H = 5$ T at 281 and 209 K, respectively. The observed large magnetocaloric effects with tunable phase transition temperatures make these materials promising for near room-temperature magnetic cooling applications. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4798339]

The research focused on magnetocaloric effects (MCE) is increasing progressively because of its potential applicability in energy-efficient, eco-friendly magnetic cooling technology.[1–8] In this regard, an extensive investigation is going on to find materials with large MCE. In the present study, we report a large MCE in partially Co substituted $MnCo_{1-x}Zn_xGe$, which has been observed over a wide temperature range around room temperature due to drastic shift of the first-order phase transition temperature with small changes in Zn concentration.

Stoichiometric MnCoGe with the orthorhombic TiNiSi-type structure exhibits a second-order ferromagnetic (FM) transition at $T_C \sim 345$ K. In the paramagnetic (PM) state, it undergoes a martensitic structural transformation (T_M) from a low-temperature orthorhombic TiNiSi-type structure to a high-temperature hexagonal Ni_2In-type structure at about 650 K. However, lowering the T_M by changing the stoichiometry,[9,10] chemical composition,[7,8,11] or by applying pressure,[11,12] it is possible to couple the magnetic and structural transitions. Previous studies of MnCoGe based systems indicate that the simultaneous magnetic and structural transitions occur in relative narrow temperature range for particular matching of T_C and T_M.[7] Larger reduction of T_M w.r.t. T_C of Ni_2In-type structure results in decoupling of magnetic and structural phase transitions. However, if T_M is situated just below or at the edge of the T_C as expected for broad magnetic phase transition, the magnetic and structural changes can coincide and the corresponding first-order phase transition is dominated by crystallographic transition.[11] In this paper, we are reporting the experimental observation of a structurally driven first-order phase transition between two high magnetization states in $MnCo_{1-x}Zn_xGe$, and show that the associated MCE is comparable to that observed for a PM-FM (disorder-order) magnetostructural transition (MST).

The polycrystalline samples were prepared by arc-melting the constituent elements of purity better than 99.99% in an argon atmosphere. The arc-melted samples were further annealed in high vacuum ($\approx 10^{-5}$ Torr) for 4 days at 850 °C. To determine the crystal structure of the samples, the X-ray diffraction (XRD) measurements were performed using Cu $K\alpha$ radiation. A superconducting quantum interference device (SQUID) magnetometer was employed to measure the magnetization of $MnCo_{1-x}Zn_xGe$ in the temperature interval (10–380 K), and in applied magnetic fields up to 5 T. The differential scanning calorimetry (DSC) measurements from 123 to 473 K were carried out using a DSC 8000 (with the ramp rate of 20 K/min during heating and cooling). An estimation of the latent heat (L) was made from the measured endothermic peak of the heat flow curve during the heating cycle of the 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, T_s and T_f are, respectively, the starting and finishing temperatures of the first-order transition upon heating.

The room temperature XRD patterns of $MnCo_{1-x}Zn_xGe$ are shown in Fig. 1. For lower concentration of Zn, $x = 0.045$, the system predominantly crystallizes in the orthorhombic martensitic TiNiSi-type structure with very small traces of the hexagonal phase. With a further increase of Zn concentrations, the hexagonal Ni_2In-type structure starts to stabilize at lower temperature. For $x = 0.06$ and 0.07, the single-phase hexagonal Ni_2In-type structure have been detected at room temperature. It has been found in the literature that smaller Co-Co separation in MnCoGe-based system prefer to be stabilized in the orthorhombic phase, and as a result, the distance between Co atoms is increased by inducing Co vacancies in the system, or substituting Co by a larger element can stabilize the hexagonal phase at relatively lower temperature.[10,13] Therefore, the substitution of Co by

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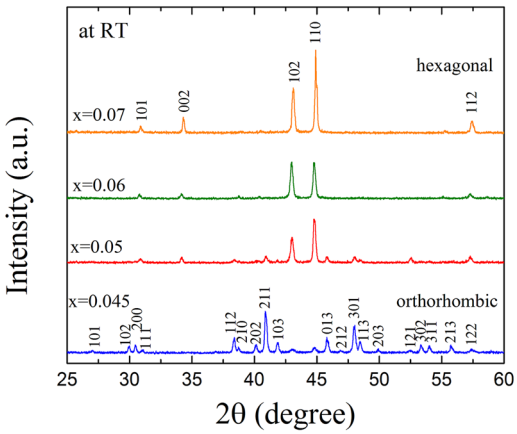

FIG. 1. XRD patterns of $MnCo_{1-x}Zn_xGe$ measured at room temperature.

larger Zn atoms ($R_{Co} \sim 0.1252$ nm and $R_{Zn} \sim 0.1394$ nm)[14] can stabilize the hexagonal Ni_2In-type structure at relatively lower temperature with increasing Zn concentration.

The thermomagnetization curves, M(T), during heating and cooling cycles for $MnCo_{1-x}Zn_xGe$ are plotted in Fig. 2(a), as measured in the presence of 0.1 T magnetic field. For lower Zn concentration, a single step-like magnetic transition with a temperature hysteresis typical for a first-order MST from a PM Ni_2In-type structure to a FM TiNiSi-type structure has been observed for $x = 0.045$. Two-step phase transitions have appeared in the M(T) curves for $x = 0.05$ and 0.06. The

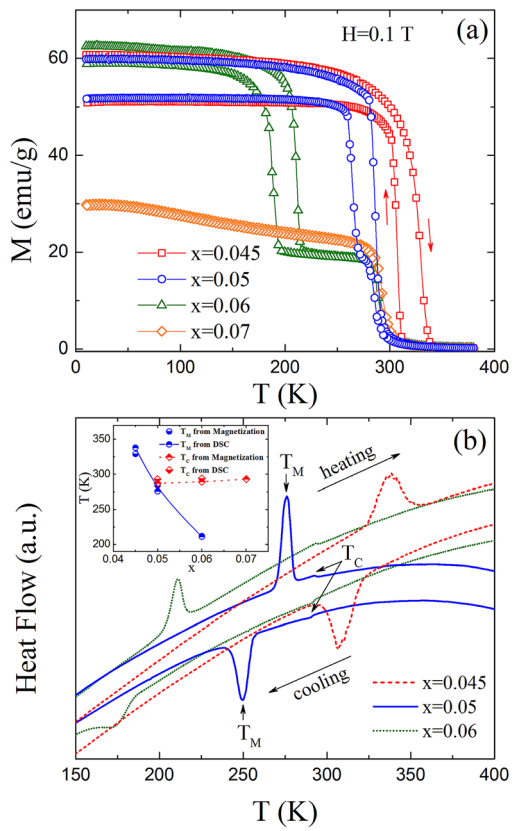

FIG. 2. (a) Temperature dependence of the magnetization [M(T)] measured during heating and cooling under the application of 0.1 T magnetic field. (b) DSC heat flow curves as a function of temperature measured at a rate of 20 K/min. The maxima and minima indicate the endothermic and exothermic behaviors during heating and cooling cycles, respectively. Inset: The transition temperatures as a function of Zn concentration.

part of transition is second-order character and the remaining lower temperature part is associated with a structurally driven first-order phase transition between two high magnetization states due to the coincidence of martensitic transformation with magnetic changes below the second-order magnetic phase transition. The nature of M(T) curve during heating for $x = 0.05$ apparently appears as single first-order FM-PM MST. However, careful observation of M(T) curve during cooling as well as the observed two narrowly spaced peaks in DSC heat flow curve (as shown in Fig. 2(b)) clearly indicate that the part of the transition is second-order character followed by a first-order transition at lower temperature for $x = 0.05$. For $x = 0.07$, a second-order magnetic transition similar to that observed for the PM-FM transition with the hexagonal Ni_2In-type structure has been detected with no signature of first-order transition. The variation of transition temperatures with Zn concentration is shown in inset of Fig. 2(b). It has been found that a small variation in the Zn concentration from $x = 0.045$ to $x = 0.060$ results in a large shift of T_M from ~329 to 212 K, as determined from the maximum change of the temperature dependent dM/dT curves and considering the peak position of DSC heat flow curve (as shown in Fig. 2(b)). The observed large endothermic/exothermic peaks during heating/cooling cycles in DSC heat flow curves, accompanied by the latent heat, as well as the clearly visible thermal hysteresis between heating and cooling cycles, indicate the first-order nature of the phase transition.

The isothermal magnetic entropy change ($-\Delta S_M$) as a function of temperature for $MnCo_{1-x}Zn_xGe$ is plotted in Fig. 3(a). Employing a Maxwell relation, $\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$, the value of $-\Delta S_M$ was estimated taking the isothermal magnetization curves as measured at different constant

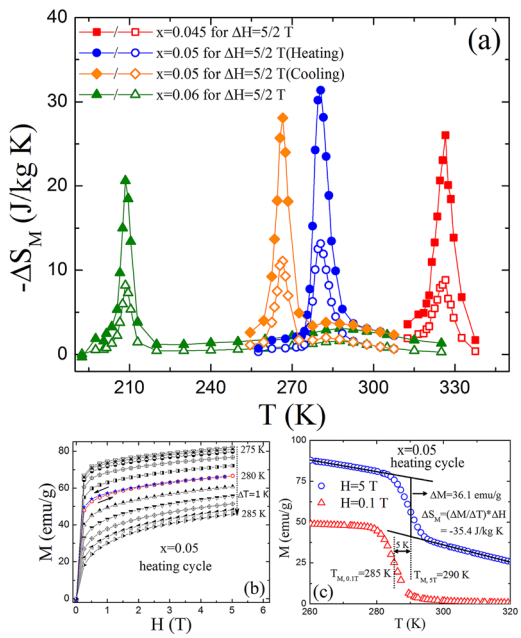

FIG. 3. (a) Plot of the magnetic entropy changes ($-\Delta S_M$) as a function of temperature for different magnetic field changes of $\Delta H = 5$ (solid symbols) and 2 T (open symbols), respectively. (b) The isothermal magnetization measured during heating in the vicinity of T_M for $x = 0.05$. (c) Heating thermomagnetization curves for applied fields $H = 0.1$ and 5 T, respectively, to estimate the value of $-\Delta S_M$ for $x = 0.05$ using Clausius-Clapeyron equation.

TABLE I. Type of phase transitions, Curie temperatures (T_C), and maximum $-\Delta S_M$ for different materials including $MnCo_{1-x}Zn_xGe$ (present work) for a field change of 5 T.

Material	Type of phase transitions	T_C (K)	T_M (K)	$-\Delta S_M$ (J/kg K)	References
$MnCo_{1-x}Zn_xGe$					Present work
$x = 0.045$	MST PM-FM	329		26	
$x = 0.05$	Structurally driven first-order	293	285	31.4, heating	
		293	265	28.1, cooling	
$x = 0.06$	Structurally driven first-order	294	211	20.6	
$MnCoGeB_x$					7
$x = 0.01$	MST PM-FM	304		14.6	
$x = 0.02$	MST PM-FM	287		47.3	
$x = 0.03$	MST PM-FM	275		37.7	
$x = 0.05$	Second-order PM-FM	260		3.4	
$Mn_{1-x}Cr_xCoGe$					8
$x = 0.04$	MST PM-FM	322		28.5	
$x = 0.11$	MST PM-FM	292		27.7	
$x = 0.18$	MST PM-FM	274		15.6	
$x = 0.25$	MST PM-FM	237		12.3	
$Gd_5Si_2Ge_2$	MST PM-FM	277		18	15
$MnFeP_{0.45}As_{0.55}$	MST PM-FM	305		18	3

temperatures. A representative figure of M(H) curves as measured during heating for $x = 0.05$ is shown in Fig. 2(b). Almost negligible magnetic hysteresis has been detected in the vicinity of T_M ($T = 280$ K). Large positive values of $-\Delta S_M$ have been observed for $MnCo_{1-x}Zn_xGe$ in the vicinity of T_M. The estimated $-\Delta S_M$ under a magnetic field change of $\Delta H = 5$ T reaches a value of 26 J/kg K in the vicinity of $T_M \sim 327$ K for $x = 0.045$, due to a single PM-FM (disorder-order) MST. Interestingly, a structurally driven first-order phase transition between two high magnetization states as observed for $x = 0.05$ and 0.06 also lead to large values of $-\Delta S_M = 31.4$ and 20.6 J/kg K for $\Delta H = 5$ T at 281 and 209 K, respectively. The measured M(H) curves during cooling cycle results in a relatively lower but large enough value of $-\Delta S_M = 28.1$ J/kg K as observed at 266 K for $x = 0.05$. The values of $-\Delta S_M$ for $x = 0.05$ as estimated from Clausius-Clapeyron equation were found out to be 35.4 and 33.5 J/kg K for $\Delta H = 5$ T during heating and cooling cycles, respectively [where, $\Delta M = 36.1$, 34.2 emu/g and $\Delta T = 5$, 5 K during heating and cooling, respectively], which were calculated from thermomagnetization curves measured at different constant magnetic fields (see Fig. 3(c)). Previous studies on MnCoGe-based systems indicate that a structurally driven first-order phase transition due to coincidence of magnetic and crystallographic changes can result in a relatively lower value of MCE.[11] However, the observed values of $-\Delta S_M$ due to structurally driven first-order phase transition between two high magnetization states for $x = 0.05$ and 0.06 are comparable with other reported MnCoGe-based systems[7,8,11] including well-known giant MCE materials, such as $Gd_5Si_2Ge_2$ (Ref. 15) and $MnFeP_{0.45}As_{0.55}$ (Ref. 3) exhibiting single PM-FM MST, which is summarized in Table I. Moreover, the total entropy changes, $-\Delta S_T$, as estimated from DSC heating curves, were found out to be 33.1, 39, and 22.8 J/kg K, corresponding to the associated latent heat, $L = -11.2$, -10.66, and -4.81 J/g for $x = 0.045$, 0.050, and 0.060, respectively. Interestingly, the values of $-\Delta S_T$ associated with a structurally driven first-order phase transition between two high magnetization states for $x = 0.05$ and 0.06, respectively, are even larger and comparable than some giant MCE materials exhibiting PM-FM MST's, such as single crystalline $Ni_{55}Mn_{20}Ga_{25}$ ($-\Delta S_T = 24$ J/kg K as estimated from latent heat).[16] Therefore, the exhibition of large, composition-dependent $-\Delta S_M$ over a wide temperature range makes the $MnCo_{1-x}Zn_xGe$ system a promising magnetic refrigerant for magnetic cooling technology that can be effective from well above room temperature down to approximately 209 K.

In summary, it has been found from our experimental study that not only the paramagnetic-ferromagnetic (disorder-order) magnetostructural transition but also the structurally driven first-order phase transition between two high magnetization states can lead to a large MCE. As a result, large composition dependent magnetocaloric effects have been observed over a wide temperature range near room temperature in $MnCo_{1-x}Zn_xGe$, which make these materials promising for magnetic refrigeration.

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