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Large magnetocaloric effects over a wide temperature range in MnCo$_{1-x}$Zn$_x$Ge

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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$_x$Ge, leading to a large magnetocaloric effects over a wide temperature range. The magnetostuctural 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. 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$_x$Ge, 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$_2$In-type structure at about 650 K. However, lowering the $T_M$ by changing the stoichiometry, or by applying pressure, 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 $T_M$. Larger reduction of $T_M$ w.r.t. $T_C$ of Ni$_2$In-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. 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$_x$Ge, 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 Kz radiation. A superconducting quantum interference device (SQUID) magnetometer was employed to measure the magnetization of MnCo$_{1-x}$Zn$_x$Ge 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

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

where $\frac{dQ}{dT}$ is the change of heat flow with respect to temperature, $T_i$ 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$_x$Ge 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$_2$In-type structure starts to stabilize at lower temperature. For $x = 0.06$ and 0.07, the single-phase hexagonal Ni$_2$In-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. Therefore, the substitution of Co by

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larger Zn atoms \( \text{RCo}_{0.1252} \text{C}_{24} \text{Zn}_{0.1394} \text{nm} \) can stabilize the hexagonal Ni\(_2\)In-type structure at relatively lower temperature with increasing Zn concentration.

The thermomagnetization curves, \( M(T) \), during heating and cooling cycles for \( \text{MnCo}_{1-x} \text{Zn}_x \text{Ge} \) 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\(_2\)In-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 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 \( x = 0.05 \) 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\(_2\)In-type structure has been detected without signature of first-order transition. The variation of transition temperatures with Zn concentration is shown in inset of Fig. 2(b).

The isothermal magnetic entropy change \( -\Delta S_M \) as a function of temperature for \( \text{MnCo}_{1-x} \text{Zn}_x \text{Ge} \) is plotted in Fig. 3(a). Employing a Maxwell relation, \( \Delta S_M = \int_0^H \frac{\Delta M}{\Delta T} dH \), the value of \( -\Delta S_M \) was estimated taking the isothermal magnetization curves as measured at different constant.

FIG. 1. XRD patterns of \( \text{MnCo}_{1-x} \text{Zn}_x \text{Ge} \) measured at room temperature.

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.

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.
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 −ΔS_M have been observed for MnCo_{1-x}Zn_{x}Ge in the vicinity of T_M. The estimated −ΔS_M under a magnetic field change of ΔH = 5 T reaches a value of 26 J/kg K in the vicinity of T_M ~ 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 −ΔS_M = 31.4 and 20.6 J/kg K for ΔH = 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 −ΔS_M = 28.1 J/kg K as observed at 266 K for x = 0.05. The values of −ΔS_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 ΔH = 5 T during heating and cooling cycles, respectively [where, AM = 36.1, 34.2 emu/g and ΔT = 5, 5 K during heating and cooling, respectively], which were calculated from magnetocaloric 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. However, the observed values of −ΔS_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 including well-known giant MCE materials, such as Gd_{5}Si_{2}Ge_{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, −ΔS_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 −ΔS_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_{5}Mn_{30}Ga_{25} (−ΔS_T = 24 J/kg K as estimated from latent heat). Therefore, the exhibition of large, composition-dependent −ΔS_M over a wide temperature range makes the MnCo_{1-x}Zn_{x}Ge 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_{x}Ge, which make these materials promising for magnetic refrigeration.

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<tr>
<th>Material</th>
<th>Type of phase transitions</th>
<th>T_C (K)</th>
<th>T_M (K)</th>
<th>−ΔS_M (J/kg K)</th>
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<td>MnCo_{1-x}Zn_{x}Ge</td>
<td>MST PM-FM</td>
<td>329</td>
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<td>MnFeP_{0.45}As_{0.55}</td>
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References