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Field dependence of magnetic entropy change and estimation of spontaneous magnetization in Cd substituted MnCoGe

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ABSTRACT

MnCoGe-based alloys have recently attracted much attention due to their possible large magnetocaloric effect related to the magnetostructural coupling. In this paper, we report a comprehensive study of the spontaneous magnetization and magnetic entropy change of $MnCo_{1-x}Cd_xGe$ ($x = 0.04$ and $x = 0.06$) alloys for magnetization and demagnetization modes. Landau theory and the dispersion width of the vertical spread of normalized magnetic entropy curves are performed to confirm the second-order transition in this series, consistent with the Banerjee criterion. The maximum isothermal entropy change is presented to depend on magnetic field as follows: $|\Delta S_{Max}| = A\ (H + H_0)^{2/3} - AH_0^{2/3} + BH^{4/3}$. Here A and B are the intrinsic parameters, and H_0 is a measure of homogeneity. Moreover, we verify the validity and usefulness of magnetic entropy change to estimate the spontaneous magnetization in this system. Finally, these new findings and related discussions with negligible hysteretic losses contribute to the research on the magnetic properties and magnetocaloric potentials in thermomagnetic applications.

1. Introduction

Magnetocaloric materials around room temperature have attracted considerable attention for some time due to their great potential applications as energy efficient and environmentally friendly magnetic refrigerators [1,2]. In the past two decades, great efforts have been made to investigate the materials undergoing first-order magnetic transition because of their possible giant magnetocaloric effect (MCE) and potential applications near the room temperature [3–5]. However, for practical applications, large MCE and negligible hysteresis losses are expected.

Previous studies have revealed that the stoichiometric MnCoGe compound exhibits a martensitic structural transition (T_{stru}~650 K) from a high-temperature Ni_2In-type hexagonal structure to a low-temperature TiNiSi-type orthorhombic structure in the paramagnetic (PM) state. A second-order magnetic transition from the paramagnetic state to ferromagnetic state occurs at the Curie temperature (T_C) about 345 K [6]. Generally, magnetic and crystallographic transitions are sensitive to both chemical and physical conditions. Thus, changing the stoichiometry [7–9], introducing atomic substitutions [10–12], and introducing physical hydrostatic pressure [13,14] can effectively tune the magnetic and structural transitions to coincide, leading to the appropriate Curie temperature and a giant MCE with less hysteresis losses. Recent investigations have revealed that the structural stability, magnetic transition and magnetocaloric effect of MnCoGe-based alloys are strongly influenced by Co concentrations [15,16]. Zhang et al. [12] showed two successive first-order magnetic transitions, a ferromagnetic (FM) to antiferromagnetic (AFM)-like transition and an AFM to FM-like transition in the $MnCo_{1-x}Cu_xGe$ alloys. Choudhury et al. [17] revealed that an increase in Zn doping in the $MnCo_{1-x}ZnxGe$ system rapidly reduces the martensitic structural transition temperature while keeping the ferromagnetic transition, leading to large magnetocaloric effect around room temperature. Ren et al. [18] reported that the substitution of Fe for Co in the MnCoGe shows the occurrence of a magneto-structural transition around the room temperature from the ferromagnetic orthorhombic structure to the paramagnetic hexagonal structure. In addition, to investigate the nature of the magnetic transition, experimental data with different theoretical models, such as the critical behavior, magnetic entropy change, and universal curve in the MnCoGe-based alloys also have been reported [19–21]. Although different

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properties of the member of MnMX family have been extensively studied, a systematic comparison of experimental data with different theoretical models is still insufficient and more experimental evidences of those mechanisms still need to be verified.

In our previous papers [22–24], the phase transition, magnetocaloric effect, critical behavior, and universal curve have been investigated in $Mn_{1-x}Al_xCoGe$, $MnCo_{1-x}Nb_xGe$ and $MnCoGe_{1-x}Cu_x$ around room temperature, and some interesting results have been obtained. The aim of this study is the investigation of magnetic and magnetocaloric properties in $MnCo_{1-x}Cd_xGe$ alloys. The nature of the second-order magnetic transition is confirmed using Arrott plots, Landau coefficients, and the universal curve. In addition, magnetic field and spontaneous magnetization dependence of magnetic entropy change have been analyzed in detail for magnetizing and demagnetizing modes. Large magnetocaloric effect with negligible hysteresis losses makes this series suitable for potential thermomagnetic power generation applications.

2. Experimental details

Nominal composition $MnCo_{1-x}Cd_xGe$ ($x = 0.04$ and 0.06) were synthesized by arc-melting constituent metals with high-purity elements Mn: 99.99%, Co: 99.9%, Cd: 99.99%, Ge: 99.99% in an argon atmosphere. To ensure a good homogeneous composition, the ingots were re-melted four times. The ingots were then annealed at 1173 K for seven days in evacuated quartz tubes and subsequently quenched into cool water. The structure of this system was characterized by the room-temperature powder X-ray diffraction (XRD, BRUKER D8 ADVANCE) using Cu Kα radiation. Magnetic measurements were performed by Physical Properties Measurement System (PPMS-9 T) with the temperature interval (5–385 K) and the applied magnetic field varying from 0 to 7 T.

3. Results and discussions

3.1. The XRD structural analysis

As shown in Fig. 1, the room temperature X-ray powder diffraction measurement of $MnCo_{1-x}Cd_xGe$ shows that our samples exist in hexagonal Ni_2In-type crystal structure (space group $D_{6h} = P6_3/mmc$). For MnCoGe-based alloys, it has been proved that smaller Co-Co separation in MnCoGe-based systems can stabilize in the orthorhombic phase [25]. In this work, the distance between Co atoms is increased by substituting Co by larger Cd atoms, resulting in a stabilized hexagonal phase. This is consistent with the $MnCo_{1-x}Zn_xGe$ system [17]. Lattice parameters are $a = 4.1168$ Å and $c = 5.5623$ Å for $x = 0.04$, and $a = 4.1312$ Å and $c = 5.5749$ Å for $x = 0.06$, respectively. Moreover, with increasing Cd doping, the main reflections (102 and 110) shift to smaller angle. This is because the radius of Cd (1.57 Å) is larger than that of Co (1.25 Å). Similar results have been reported in $MnCo_{1-x}V_xGe$ system [26].

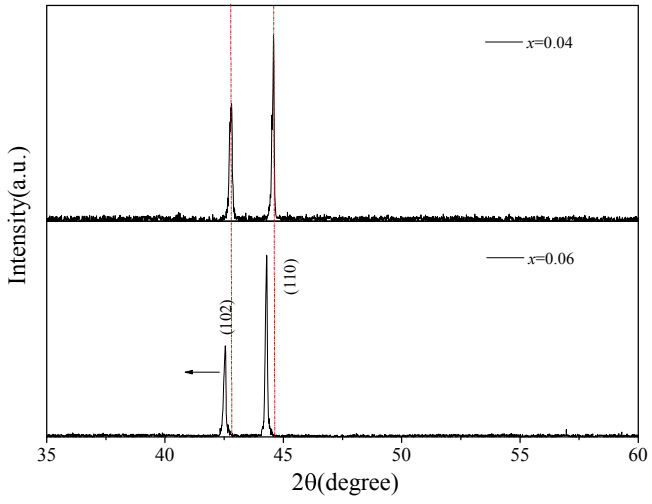

Fig. 1. The room-temperature powder XRD patterns of $MnCo_{1-x}Cd_xGe$ ($x = 0.04$ and 0.06) alloys in $35° \leq 2\theta \leq 60°$ with a step size of 0.02° (Cu-Kα radiation).

3.2. Magnetic properties

Fig. 2 shows temperature dependence of magnetization using zero-field cooling (ZFC) and field cooling (FC) modes and the reciprocal susceptibility at an applied field of 0.02 T. One can observe that a separation between the ZFC and FC curves at low temperature, resulting from the presence of an isotropic field generated from ferromagnetic clusters [27]. The evaluated values of T_C are 330 K and 320 K for $x = 0.04$ and $x = 0.06$, respectively. Generally, susceptibility follows the Curie-Weiss law in the paramagnetic region. The positive values of Curie-Weiss temperature are 341 K ($x = 0.04$) and 330 K ($x = 0.06$), revealing the ferromagnetic (FM) magnetic ground states [28]. The effective magnetic moment values calculated by the Curie constant are $6.684\mu_B$ and $7.198\mu_B$ with the increase of Cd content, which are higher than that of $MnCo_{1-x}Ge$ from ab initio calculations [15]. This is commonly presented in manganites and has a closely relation with Cd substitution and the existence of short-range ferromagnetic interactions above T_C.

To investigate the nature of the magnetic transition, selected magnetization isotherms curves and corresponding Arrott plots with increasing and decreasing magnetic field up to 7 T are shown in Fig. 3. It should be noted that the magnetizing and demagnetizing $M(H)$ curves exhibit a negligible magnetic hysteresis, which is helpful for magnetic refrigeration. Experimentally, the order of magnetic phase transitions can be evidenced by the slope in Arrott plots. Generally, the positive slope corresponds to the second-order magnetic transition while the negative slope corresponds to the first-order magnetic transition. In this work, all the Arrott plots present positive slopes around the Curie temperature, revealing the characterization of the second-order magnetic transition (SOMT) based on the Banerjee criterion [29].

The estimation of hysteretic losses (HL) in the vicinity of magnetic transition temperature is a key point for proper evaluation of the magnetocaloric effect [30,31]. For better understanding in Fig. 3, we presented hysteretic losses around magnetic transition, which was extracted from the enclosed area between the magnetizing and demagnetizing $M(H)$ curves in Fig. 4. As expected, this system presents a negligible hysteresis (less than 1.1 J/kg) around the Curie temperature, increasing the efficiency of magnetic refrigeration. It is clear that the magnetic hysteresis is inherent to the magnetostructural transformation materials. However, our system only possesses a second-order magnetic transition, and thus, the $MnCo_{1-x}Cd_xGe$ system has small hysteretic losses between the magnetizing and demagnetizing curves.

Additionally, with the help of the magnetic free energy, we also can identify the magnetic transition by analyzing Landau coefficients $C_1(T)$, $C_2(T)$ and $C_3(T)$ obtained from the following relationship [32]:

$$\Phi(M,H,T) = \Phi_0(T) + \frac{1}{2}C_1(T)M^2 + \frac{1}{4}C_2(T)M^4 + \frac{1}{6}C_3(T)M^6 + \cdots\cdots - MH \quad (1)$$

with $\frac{\partial\Phi}{\partial M} = 0$, Eq. (1) is given as: