



Magnetocaloric properties and universal behavior in electron-doped manganite $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$



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ABSTRACT

The magnetocaloric properties of an electron-doped manganite $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ have been studied in detail. A reversible magnetocaloric effect has been observed at the Curie temperature T_C of 100 K, which is related to a second order magnetic transition from paramagnetic to ferromagnetic state. The values of maximum magnetic entropy change can reach 0.82 and $1.92 \text{ J kg}^{-1} \text{ K}^{-1}$ for a field change of 2 and 5 T, respectively, with no obvious hysteresis loss in the vicinity of the Curie temperature. The magnetic entropy change can be well described by the recently proposed phenomenological universal behavior. This result can shed light on the design of magnetic refrigerators in engineering.

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1. Introduction

The mixed-valent manganites of $\text{AE}_{1-x}\text{RE}_x\text{MnO}_3$ (AE = Ca, Sr, Ba, Pb, etc. and RE = La to Tb) have been extensively investigated on the account of their diverse phase diagrams [1,2]. Earlier works mostly focused on the phenomena such as colossal magnetoresistance (CMR) and charge ordering state [3,4]. Recently these CMR manganites compounds have also been found to exhibit the magnetocaloric effect (MCE) [5] under a moderate applied magnetic field, revealing that the CMR manganites are possible candidate materials for the magnetic refrigeration applications. For the magnetic materials, the MCE is intrinsic and is induced via the coupling of magnetic sublattice with the external magnetic field, which alters the magnetic part of the total entropy due to a corresponding variance of the magnetic field. The MCE can be measured and/or calculated as the isothermal magnetic entropy change $\Delta S_M(T, \Delta H)$.

The magnetocaloric properties of the rare earth manganites were studied from 1996 [6]. But to date, the reported MCE values of the rare earth manganites are moderate, and not as outstanding as

those magnetic materials, such as $\text{Gd}_5(\text{Si}_{1-x}\text{Ge}_x)_4$, $\text{Mn}(\text{As}_{1-x}\text{Sb}_x)_4$, and $\text{La}(\text{Fe}_{13-x}\text{Si}_x)$ [7]. As a matter of fact, several manganites have magnetic entropy change ΔS_M values to be comparable with Gd [8], but most are smaller. The hole-doped manganites have been widely studied so far, such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [9], and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [10], which has not very large magnetocaloric properties. However, the magnetocaloric properties in electron-doped manganites are investigated in detail relatively few [11].

In this paper, we have studied the magnetic entropy change and analyzed the relative cooling power (RCP) of electron-doped manganite $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ from 20 K up to 200 K, where the magnetic phase exhibits a second order magnetic transition. Furthermore, the universal behavior [12] is fulfilled for the magnetic entropy change $\Delta S_M(T)$ curves measured for various field changes, which is useful for the design of a magnetic refrigerant.

2. Experimental methods

Polycrystalline sample with a composition $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ was prepared by the conventional solid-state reaction method. Stoichiometric amounts of high purity CaCO_3 , Dy_2O_3 , MnO_2 were mixed, ground, and subsequently sintered in air at 1000 °C for 12 h. The obtained powders were reground, palletized, and sintered at 1200 °C for 12 h, and then 1300 °C for 24 h with intermediate

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grinding, and finally cooled to room temperature in the furnace. The crystal structure and the lattice constant were determined by powder X-ray diffraction (XRD) using Cu K_α radiation at room temperature. The dc magnetization (M) measurements were carried out by means of the commercial Quantum Design physical property measurement system (PPMS). The magnetization versus temperature curves were recorded in field-cooled cooling (FCC) and warming (FCW) cycles using the standard procedure. The field dependence of magnetization, at various temperatures, was carried out after zero field cooling (ZFC) to the measurement temperature. Due to the highly nonlinear response at the low temperatures, and in order to obtain the “virgin” curves, the sample was heated to $T = 200$ K after each magnetic cycle at low temperatures.

3. Results and discussion

The powder XRD pattern of the sample can be indexed using an orthorhombic perovskite-type space group $Pnma$ as shown in Fig. 1. The Rietveld refinement for the compound was carried out with the GSAS package [13], confirming the single-phase nature of the compound. The goodness of the fit, refined lattice parameter, and atomic positions were given in Table 1, where the structure parameters are closed to those in the literature [14]. The temperature dependence of magnetization, $M(T)$, measured at applied field of 0.01 T is shown in Fig. 2. A paramagnetic to antiferromagnetic (PM-AFM) transition is observed for the compound $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$, leading to a moderate magnetic entropy change in this compound. The Curie temperature T_C (defined as the one corresponding to the peak of dM/dT in the M vs T curve is shown in the inset of Fig. 2) is about 100 K. The temperature dependence of inverse molar susceptibility, $\chi_m^{-1}(T)$, is plotted and is also show in Fig. 2. For a magnet in the PM region, the relation between inverse molar susceptibility χ_m and temperature T should obey the Curie–Weiss law, i.e., $\chi_m = C/(T-\theta_p)$, where C is the Curie constant and θ_p is the paramagnetic Curie temperature. The solid line is calculated curve deduced from the Curie–Weiss equation. It can be seen that the experimental curve in the whole PM temperature range is well described by the Curie–Weiss law.

Isothermal magnetization measurements were done between 20 and 100 K and a set of isothermal magnetization (M) curves for a few selected temperatures are shown in Fig. 3(a). In order to estimate the reversibility of the magnetic transition, the M versus the magnetic field (H) loops were measured at different temperatures (Fig. 3(d)). Obviously, there is no magnetic hysteresis in each loop,

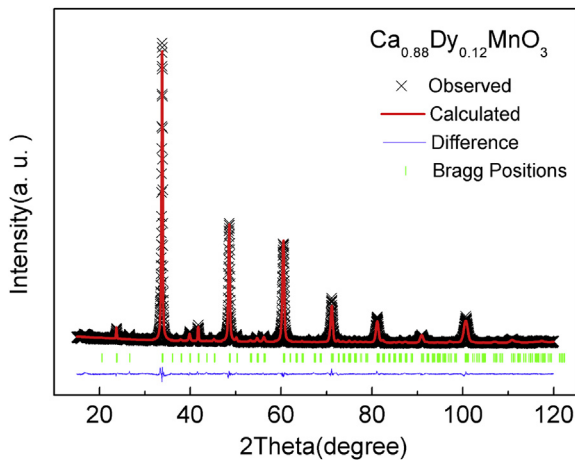


Fig. 1. The powder X-ray diffraction pattern at room temperature and the result of the Rietveld analysis for $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ compound.

Table 1
Crystal data for structure refinement for $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ compound.

Crystal system, space group	Orthorhombic, $Pnma$			
Unit cell dimensions (Å)	$a = 5.2878(5)$, $b = 7.4761(9)$, $c = 5.3034(6)$			
Volume (Å ³)	209.66(6)			
2θ range for data collections	$10^\circ - 120^\circ$			
R_{wp}	7.27%			
R_p	5.94%			
Atom	Site	x	y	z
Ca/Dy	4c	0.0265(5)	0.25	-0.0042(6)
Mn	4b	0	0	0.5
O(1)	4c	0.457(3)	0.25	0.360(3)
O(2)	8d	0.266(2)	0.044(1)	-0.2791(8)

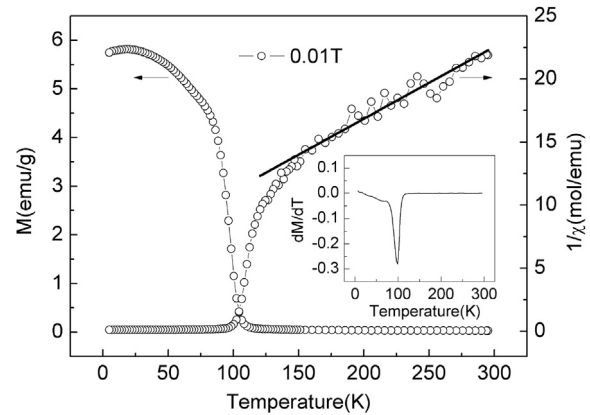


Fig. 2. Temperature dependence of magnetization and inverse of magnetic susceptibility, measured at $H = 0.01$ T in the field cooled mode for $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$. The inset shows the dM/dT as a function of temperature.

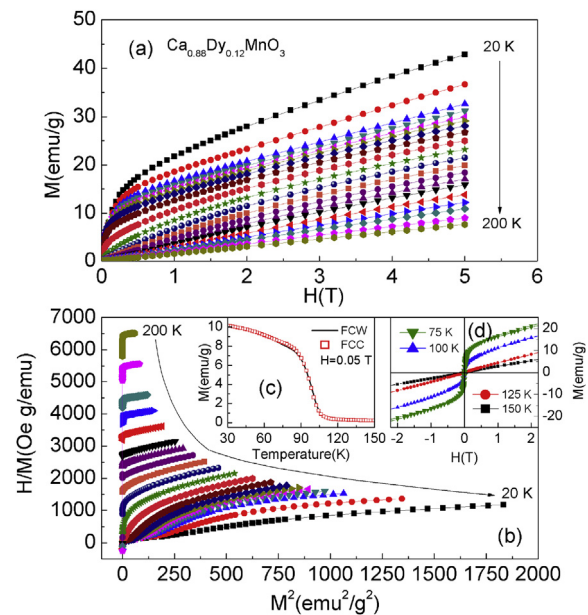


Fig. 3. (a) Isothermal magnetization curves measured at different temperatures between 20 and 200 K for $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$. (b) Arrott plots of $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ from 20 to 200 K. Inset: (c) M vs T curves in the field cooled cooling and warming cycles under a magnetic field of 0.05 T. (d) The M vs H curves recorded at various temperatures.

indicating the perfect magnetic reversibility of the magnetic transitions in $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ sample. In addition, it can be seen that the field cooled cooling (FCC) and field cooled warming (FCW)

curves (Fig. 3(c)) follow the same path at the transition temperature, i.e., no thermal hysteresis, exhibiting the characterization of a second order transition with good thermal reversibility [15]. A MCE is expected around the transition temperature where the magnetization rapidly changes with varying temperature. Because the temperature and magnetic field change dependence of MCE have a strong correlation with the order of the corresponding magnetic phase transition, it is very important to determine the nature of the magnetic phase transition in $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$. According to Banerjee's criterion [16], if the H/M versus M^2 curves, i.e., Arrott plot, show negative slope at some point, the magnetic transition is of a first-order. On the other hand, the magnetic transition is of the second-order if all the H/M versus M^2 curves have positive slope. To further understand the nature of the magnetic transition in $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ the Arrott plots H/M versus M^2 at some selected temperatures for $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ were shown in Fig. 3(b). The positive slopes of all the plots suggest that this magnetic transition at about 100 K is of second order in accordance with the case mentioned above where the thermal hysteresis is absent. The good thermal and magnetic reversibility around magnetic transition temperature indicate that the $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ compound exhibits perfect reversibility of the MCE.

Based on the thermodynamical theory [17], the isothermal magnetic entropy changes (ΔS_M) associated with a magnetic field variation is given by

$$\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0) = \int_0^H \left(\frac{\partial S}{\partial H} \right)_T dH. \quad (1)$$

From the Maxwell's thermodynamic relation:

$$\left(\frac{\partial S}{\partial H} \right)_T = \left(\frac{\partial M}{\partial T} \right)_H \quad (2)$$

One can obtain the following expression:

$$\Delta S_M(T, \Delta H) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH \quad (3)$$

where S , M , H , and T are the magnetic entropy, magnetization of the material, applied magnetic field, and the temperature of the system, respectively. In the case of magnetization measurements at small discrete field and temperature intervals, ΔS_M can be approximately calculated by the following expression:

$$\Delta S_M = \sum \left[\frac{(M_i - M_{i+1})H_i}{T_{i+1} - T_i} \right] \Delta H_i \quad (4)$$

where M_i and M_{i+1} are the experimental data of the magnetization at T_i and T_{i+1} , respectively, under a magnetic field H_i . According to the method described by Pecharsky and Gschneidner [17], the accuracy of the ΔS_M calculated from the magnetization data for the materials studied here is better than 10%. The ΔS_M was calculated using Equation (4) in the vicinity of its ordering temperature based on the results of magnetization isotherms. The resulting changes of magnetic entropy $-\Delta S_M$ as a function of temperature at different magnetic field variations up to 5 T are given in Fig. 4. It is easy to see that $-\Delta S_M$ is proportional to the derivative of the magnetization with respect to temperature at constant magnetic field from Equation (3). Therefore, it is expected that any material should have the largest magnetic entropy change when its magnetization is changing rapidly with temperature, that is to say, in the vicinity of a spontaneous magnetic ordering temperature. The magnetic

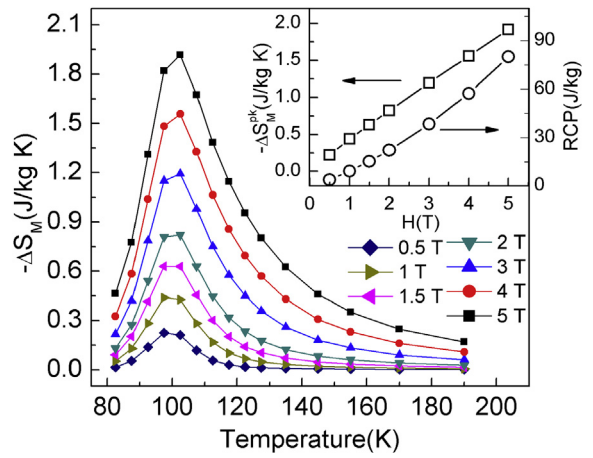


Fig. 4. Temperature dependences of magnetic entropy change. Inset: The maximum magnetic entropy change and the relative cooling power (RCP) as a function of magnetic field respectively.

entropy change $-\Delta S_M$ gradually decreases both below and above the magnetic ordering temperature. Therefore, the conventional ferromagnets typically display a "caretlike" behavior in $-\Delta S_M$ versus T curves [6]. As shown in Fig. 4, a moderate magnetocaloric effect can be observed around 100 K. The maximum values of magnetic entropy change ($-\Delta S_M^{\max}$) reach 0.82 and 1.92 $\text{J kg}^{-1} \text{K}^{-1}$ for a field change of 2 and 5 T, respectively. The field dependence of the maximum magnetic entropy change and the relative cooling power (RCP, evaluated by $\text{RCP} = \Delta S_M^{\max} \times \delta T_{\text{FWHM}}$) [18] were also shown in the inset of Fig. 4. This MCE is related to a second order magnetic phase transition.

The magnetocaloric properties was discussed for the amorphous alloys, such as $\text{Fe}_{83}\text{Zr}_6\text{B}_{10}\text{Cu}_1$, Gd, $\text{LaFe}_{10.8}\text{Si}_{2.2}$, $\text{Mn}_5\text{Ge}_{2.7}\text{Ga}_{0.3}$, and TbCo_2 , and a universal behavior was proposed to describe the magnetic entropy change with temperature and magnetic field [19–21]. However, up until now, few exact analytical form of this universal curve has been given in the oxides [15], especially in the manganites. With respect to the intermetallics, a universal behavior is found to describe the variation in magnetic entropy change ΔS_M with temperature T for the electron-doped $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ perovskite. As a consequence, the $\Delta S_M(T)$ curve for $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ can be determined by knowing its magnetic transition temperature T_C , peak entropy change ΔS_M^{pk} , and two additional reference temperatures. The phenomenological universal curve can be constructed from the following method [19]. First, normalizing all the magnetic entropy change $\Delta S_M(T)$ curves with their respective peak magnetic entropy change ΔS_M^{pk} , that is to say, $\Delta S'(T) = \Delta S_M(T) / \Delta S_M^{\text{pk}}$; Second, rescaling the temperature axis in a different way below and above T_C , which is defined in Equation (5). Using this temperature rescaling way, there is an imposing constraint that the position of two additional reference points in the curve corresponds to $\theta = \pm 1$,

$$\theta = \begin{cases} -(T - T_C) / (T_{\text{cold}} - T_C), & T \leq T_C, \\ (T - T_C) / (T_{\text{hot}} - T_C), & T > T_C, \end{cases} \quad (5)$$

where T_{cold} and T_{hot} are the temperatures of the two reference points that, for the present work, have been selected as those corresponding to $\Delta S_M(T_{\text{cold,hot}}) = \Delta S_M^{\text{pk}}/2$. The rescaled temperature θ dependence of the transformed $\Delta S'(\theta)$ curves for typical applied field changes from 0.5 T to 5 T for the studied sample is shown in Fig. 5(a). One can clearly find that all the experimental points distribute on one universal curve. Interestingly, the universal

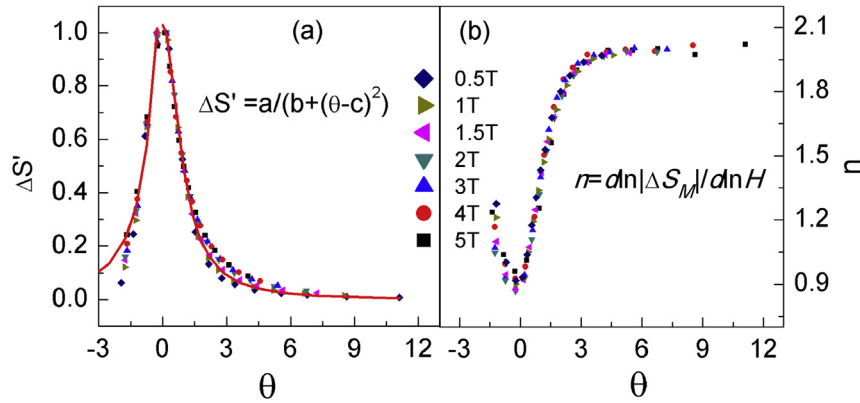


Fig. 5. (a) θ dependence of $\Delta S'$ for the studied sample for typical field changes; the solid line is the fitted curve. (b) θ dependence of the local exponent n for the studied sample for typical field changes.

curve can be well fitted by a Lorentz function [21].

$$\Delta S'(\theta) = \frac{a}{b + (\theta - c)^2}, \quad (6)$$

where a , b , c are the adjustable parameters. Considering the asymmetry nature of the curve, two different sets of parameters have to be used: $a = 1.336 \pm 0.005$, $b = 0.751 \pm 0.002$, $c = 0.500 \pm 0.001$, for $T \leq T_C$; and $a = 0.911 \pm 0.003$, $b = 0.884 \pm 0.002$, $c = 0.010 \pm 0.002$, for $T > T_C$. In the present conditions, a , b and c are common for the sample of difference variation of magnetic field.

With respect to Equation (6), only the three points, which are the position and magnitude of the peak, namely, $(T_C, \Delta S_M^{\text{pk}})$, and the two reference temperatures T_{cold} and T_{hot} (where $T_{\text{cold}} < T_C$ and $T_{\text{hot}} > T_C$), are needed to characterize the entropy change. Among the three points, the point $(T_C, \Delta S_M^{\text{pk}})$ is the most important. So, it is necessary to analyze the field dependence of ΔS_M in detail. To further study the field dependence of the experimental ΔS_M of the sample, a local exponent n is defined as follows [22]: $n = d \ln |\Delta S_M| / d \ln H$. The value of n depends on the values of applied field and temperature. Fig. 5(b) depicts the rescaled temperature θ dependence of the local exponent n for the $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ compound in typical field changes. In a general condition, n is related to the critical exponents of the materials [22], which requires further investigations in this compound. In Fig. 5(b) it is obvious that the local exponent $n = 2$ at the high temperature region, which is a well known consequence of the Curie–Weiss law [23], which is consistent with the magnetic data (see Fig. 2).

From the above discussion mentioned, the point $(T_C, \Delta S_M^{\text{pk}})$ and two reference temperatures T_{cold} and T_{hot} are sufficient to describe the temperature and magnetic field dependence of the magnetic entropy change. That is to say, we can translate $\Delta S'(\theta)$ into the 'real' $\Delta S_M(T)$ in the condition of needing only the three values that are determined by the physical properties of the material. In this way, the incomplete magnetic entropy change $\Delta S_M(T)$ curves, which are experimentally calculated from a small temperature span in the vicinity of T_C for the isothermal magnetization measurements, can be easily transformed into the complete curves. This is a very useful tool for the evaluation of material properties such as the refrigerant capacity, which is particularly helpful for investigating families of similar materials, such as manganites that are electron- and hole-doped. Furthermore, engineers can use this function to analyze the influence of material parameters on the design of a magnetic refrigerator.

4. Conclusions

As a summary, the magnetocaloric effect of electron-doped manganite $\text{Ca}_{0.88}\text{Dy}_{0.12}\text{MnO}_3$ has been studied. The obtained results show a magnetic entropy change at the magnetic phase transition. The moderate values of the magnetic entropy change and the relative cooling power with negligible thermal and magnetic field hysteresis make this low cost material suitable for magnetic refrigeration around its magnetic transition temperature. Furthermore, the magnetic entropy change can be described well by the universal behavior for all the investigated fields. The phenomenological curve can be well fitted by a Lorentz function. Using this function, we only need the point $(T_C, \Delta S_M^{\text{pk}})$ and two reference temperatures T_{cold} and T_{hot} to describe the temperature and magnetic field dependence of the magnetic entropy change. The results can shed light on the design of magnetic refrigerators in engineering.

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