Anisotropic and large low-field magnetic entropy change in a La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal

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Abstract

We have studied the magnetocaloric effect (MCE) in a bilayered La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal with applied field along both $ab$-plane and $c$-direction. Due to the quasi-two-dimensional structure, the crystal exhibits a strong anisotropy in the MCE. The difference of magnetic entropy change between two crystallographic directions depends on external magnetic fields and has a maximum of 2 J/kg K. A large low-field magnetic entropy change, reaching 3.2 J/kg K for a magnetic field change of 15 kOe, is observed when the applied field is along $ab$-plane. This large low-field magnetic entropy change is attributed to the rapid change of magnetization in response to external magnetic fields in the easy magnetizing plane.

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1. Introduction

The magnetocaloric effect (MCE) is a basic characteristic of magnetic materials and is due to the coupling of magnetic sublattice with the external magnetic field. When varying the magnetic field, the magnetic part of the total entropy is altered simultaneously. Since the discovery of the giant MCE in Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ in 1997 [1], a large variety of magnetic materials with the giant MCE have been found, including Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$, MnAs$_{1-x}$Sb$_x$, MnFe(P$_{1-x}$As)$_x$, La(Fe$_{13-x}$Si$_x$), RM$_2$ (where R = rare earth, M = Al, Co, Ni), Gd and its hydrides [1–7]. These materials have been regarded as good candidates for magnetic refrigeration. More recently, lots of work on giant MCE were also focused on the mix-valenced manganites MO($R_{1-x}$M$_x$MnO$_3$)$_n$ (where R = lanthanide, M = Ca, Sr, Ba) [8–10]. Since their magnetic phase transition can be controlled by doping level and crystal structure, these manganites are among the most interesting domains for giant MCE. While there have been many reports on the MCE in manganites with three-dimensional perovskite structure so far [8–12], investigations of MCE in manganites with quasi-two-dimensional bilayered structure are relatively scarce, especially on the single crystal samples. In addition, it has been well known that the anisotropic or dimensional effect plays a crucial role in the colossal magnetoresistance behavior for the bilayered manganites [13–15], but it is still unclear how the anisotropy and dimensionality affect the MCE in these manganites.

In this work, we have investigated the MCE in a bilayered manganite. Our study is performed on a La$_{2-x}$Sr$_{x}$Mn$_2$O$_7$ single crystal with $x = 1/3$, which has double Mn–O layers and a single Sr–O layer. This sample is chosen because ferromagnetic coupling in the crystal should be optimal in this hole-doping level (1/3) according to the Zener’s model [16]. The abrupt change of magnetization in the crystal near Curie temperature ($T_C$) could result in a large magnetic entropy change. In addition, because the magnetic easy axis of the crystal is parallel to $ab$-plane and the magnetic moments of electron
are more willing to lie in the MnO$_2$ layer [14,15], a strong anisotropic magnetic entropy change could be expected.

2. Experiment

A high-quality single crystal of La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ is grown in an optical floating-zone furnace with four reflected mirrors. The starting ceramic rods were synthesized by the standard methods of solid-state reaction of a stoichiometric mixture of La$_2$O$_3$ (99.9%), SrCO$_3$ (99.9+%) and MnCO$_3$ (99.9+%). X-ray diffraction measurement on powders taken from the single crystal shows no traces of any secondary phase. Back-reflection Laue X-ray diffraction method is used to determine the crystallographic direction. The initial magnetization isotherms are measured by using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum design, MPMS-7).

3. Results and discussion

Fig. 1 shows the temperature dependence of the magnetization ($M-T$ curves) in a 1 kOe field with the direction of magnetic field along both $ab$-plane and $c$-direction of the La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal. The Curie temperature $T_C$ can be determined from the $M-T$ curve as 110 K. The magnetization in $ab$-plane is much bigger than that of the $c$-direction, suggesting that the magnetic easy axis lies in the $ab$-plane of the crystal. A steep change of magnetization occurs at $T_C$, implying a first-order phase transition.

A first-order magnetic transition from a paramagnetic to a ferromagnetic state is of particular importance for giant MCE, since the rapid change in magnetization at the critical temperature usually causes a significant change in the magnetic entropy. The first-order nature of phase transition in the La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ crystal can be confirmed by the Banerjee criterion [17,18]. We have measured the initial magnetization isotherms in the vicinity of $T_C$ and draw the isotherm plots of $H/M$ versus $M^2$ (the Arrott plots). The sweep rate of field is slow enough to ensure that these curves are recorded in an isothermal process. According to the Banerjee criterion, a negative slope in a relatively small $M^2$ region above $T_C$ indicates a first-order character of phase transition. As shown in the Fig. 2, this is actually observed for both the $ab$-plane and $c$-direction, confirming the first-order nature of the magnetic phase transition. From the Arrott plots, we can also testify that the Curie temperature is about 110 K, consistent with the results from Fig. 1.

The MCE in a magnetic material is generally evaluated by the magnetic entropy change $\Delta S_M$ at a constant pressure, which is a function of the absolute temperature $T$ and the change of external magnetic fields ($\Delta H = H_f - H_i$), where $H_f$ and $H_i$ are the final and initial magnetic fields, respectively. According to the Maxwell equation

$$\left[ \frac{\partial S_M(T, H)}{\partial H} \right]_T = \left[ \frac{\partial M(T, H)}{\partial T} \right]_H$$

(1)

Fig. 1. Temperature dependence of magnetization along $ab$-plane and $c$-direction of La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal under applied magnetic field of 1 kOe.

Fig. 2. Arrott plots of the La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal in the vicinity of the Curie temperature with the direction of the magnetic field along (a) $ab$-plane and (b) $c$-direction.
the isothermal magnetic entropy change for a field change of $\Delta H$ is

$$\Delta S_M(T, \Delta H) = \int_{H_i}^{H_f} \left[ \frac{\partial M(T, H)}{\partial T} \right]_H dH. \quad (2)$$

In practice, the integral in Eq. (2) can be approximately calculated using isothermal $M - H$ curves that are measured at small temperature intervals.

Fig. 3(a) and (b) show the magnetic entropy changes $|\Delta S_M|$ of La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal determined by Eq. (2), with magnetic field along $ab$-plane and $c$-direction, respectively. For both directions, $|\Delta S_M|$ shows a peak around 112 K (near $T_C$). The half-height width of the peak broadens toward higher temperature regions with increasing field, coinciding with the other experimental results [11]. The maximum of $|\Delta S_M|$ reaches 5 J/kg K for $ab$-plane and 4.4 J/kg K for $c$-direction under 50 kOe magnetic field, which are larger than that (3.7 J/kg K) reported for the polycrystalline sample with same component [11]. It is apparent that the magnetic entropy change is anisotropic, with a larger value in the $ab$-plane, especially in low magnetic fields. Fig. 3(c) plots the difference of magnetic entropy changes between the two crystallographic directions under a 10 kOe magnetic field. The maximum difference exceeds 1.6 J/kg K. This particular character may be used to enhance the refrigerant capacity in practice (see below).

In Fig. 4, we compare the peak values of $|\Delta S_M|$ between $ab$-plane and $c$-direction as a function of magnetic field in La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal. In the whole field range from 0 to 50 kOe, $|\Delta S_M|$ in $ab$-plane is larger than that along $c$-direction. The maximum difference (about 2 J/kg K) occurs in 15 kOe. The large anisotropic magnetic entropy change in La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal is ascribed to the strong magnetocrystalline anisotropy. Lima et al. [20] have proposed a way to increase the refrigerant capacity by using the anisotropic magnetization in single crystals of some RAl$_2$ and RNi$_2$ (R = lanthanides) compounds. In the first approach, the external magnetic field is initially oriented to the easy magnetizing direction of the anisotropic crystal, and then the crystal is rotated while the variation of magnetic field is synchronized with the variable easy magnetization direction in order to keep the magnetization direction fixed. In the second approach, the crystal is fixed while the magnetic field is rotated from the hard magnetizing to the easy magnetizing direction. The theoretical calculation indicated that the refrigerant capacity by using the materials' own anisotropic properties can be considerably increased. So, it is possible to increase the refrigerant capacity in practice by utilizing strong anisotropy in our own La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal when the sample undergoes a spin reorientation.

Another interesting result is that a large low-field magnetic entropy change along $ab$-plane of the crystal is observed (Fig. 4). The maximum values of $|\Delta S_M|$ are about 1.1, 2.3, and 3.2 J/kg K for a magnetic field change of 5, 10, and 15 kOe, respectively. These values of $|\Delta S_M|$ are in the same magnitude as that of Gd in the low-field range from 0

![Fig. 3. Magnetic entropy change $\Delta S_M$ as a function of temperature for the magnetic field along (a) $ab$-plane and (b) $c$-direction of the La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal. (c) Temperature dependence of the difference of magnetic entropy change between two directions in a 10 kOe magnetic field.](image)

![Fig. 4. Maximum of magnetic entropy change along $ab$-plane and $c$-direction as a function of magnetic field. The difference between two directions is also plotted.](image)
to 20 kOe [10,19]. In comparison, the maximum value of $|\Delta S_M|$ is only about 1.5 J/kg K for a magnetic field change of 10 kOe in polycrystalline samples of La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ and 1 J/kg K for a magnetic field change of 10 kOe in polycrystalline La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ [11]. The low-field $|\Delta S_M|$ in our sample is also larger than that in many cubic perovskite manganites [10]. This low-field MCE is beneficial for the practical application of MCE because the low fields can be directly supplied by Nd$_2$Fe$_{14}$B or other permanent magnets. The low-field large magnetic entropy change in the La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ crystal is due to the rapid change of magnetization near the critical temperature in the easy magnetizing plane. In La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$, there are two exchange interactions, i.e., the intralayer exchange interaction $J_{ab}$ and the interlayer exchange interaction $J_c$. Because $J_{ab}$ is much stronger than $J_c$, the magnetic moments tend to lie in the $ab$-plane. At the vicinity of $T_c$, a small magnetic field along $ab$-plane can easily promote the paramagnetic to ferromagnetic transition, which causes a rapid change of magnetization. As a result, a low magnetic field can induce considerable magnetic entropy change.

4. Conclusions

In conclusion, we have studied the MCE in a La$_{4/3}$Sr$_{5/3}$Mn$_2$O$_7$ single crystal. Due to the strong magnetocrystalline anisotropy, the crystal shows anisotropic magnetic entropy change. The difference of magnetic entropy change between two crystallographic directions can be as high as 2 J/kg K. A large low-field MCE, reaching 3.2 J/kg K for a magnetic field change of 15 kOe, is observed when the magnetic field is applied in the $ab$-plane, which is attributed to the rapid change of magnetization in the easy magnetizing plane in response to external magnetic fields.

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References