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Abstract

The structural, magnetic, and magnetocaloric properties of the manganite $La_{0.7}Ca_{0.3}MnO_3$ have been studied. Change in the giant magnetic entropy was observed without any noticeable magnetic hysteresis but with small thermal hysteresis losses. We observed a first order magnetic phase transition around 251 K. The magnetic entropy change observed in this work is estimated to be 5.27 J/kg K for field changes from 0 to 1.5 T based on magnetization measurements. This value is about twice as large as those for other perovskite manganites and is even larger than for Gd-based magnetic materials at low fields. In addition, the entropy change was estimated by using the heat capacity method, which can be well explained by the Maxwell relation.

Keywords

Giant, magnetic, entropy, change, colossal, magnetoresistance, La0, 7Ca0, 3MnO3, material, low, field

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Giant magnetic entropy change in colossal magnetoresistance in $La_{0.7}Ca_{0.3}MnO_3$ material in low field

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The structural, magnetic, and magnetocaloric properties of the manganite $La_{0.7}Ca_{0.3}MnO_3$ have been studied. Change in the giant magnetic entropy was observed without any noticeable magnetic hysteresis but with small thermal hysteresis losses. We observed a first order magnetic phase transition around 251 K. The magnetic entropy change observed in this work is estimated to be 5.27 J/kg K for field changes from 0 to 1.5 T based on magnetization measurements. This value is about twice as large as those for other perovskite manganites and is even larger than for Gd-based magnetic materials at low fields. In addition, the entropy change was estimated by using the heat capacity method, which can be well explained by the Maxwell relation. © *2010 American Institute of Physics*. [doi:10.1063/1.3359808]

I. INTRODUCTION

Interest in the rare-earth manganites has been considerable due to the occurrence of colossal magnetoresistance (CMR) in these materials. The magnetocaloric effect (MCE) that is present in some of these materials is a crucial factor for practical application in magnetic refrigeration. So far, Gd-based magnetic materials have been primarily considered because of their large MCE property near room temperature. Doping can be used to modify the relevant intrinsic properties, however, i.e., for a CMR material, the Curie temperature (T_C), and the saturation magnetization properties. Even so, much more effort and attention are still needed to find candidates for application in energy-efficient refrigeration. Recently, some promising new candidates have been suggested such as $Gd_5(Si_xGe_{1-x})_4$,[1] Gd_2PdSi_3,[2] $Ni_{51.5}Mn_{22.7}Ga_{25.8}$,[3] $(Tb_{1-x}Gd_x)A_{12}$,[4] and the hole-doped perovskite manganites.[5]

In the literature, most of the previous studies have concentrated on indirect calculation of the isothermal magnetic entropy change. However, it can be directly determined by using the heat capacity method. In this study, therefore, we evaluated the calculation of entropy change in $La_{0.7}Ca_{0.3}MnO_3$ on the basis of magnetization and heat capacity measurements. The aim of this study is to find correlations between different methods and provide a quantitative description.

II. EXPERIMENTAL

The manganite $La_{0.7}Ca_{0.3}MnO_3$ was prepared by the conventional solid-state reaction method. The crystal structure analysis was performed by x-ray diffraction (XRD) and the lattice parameters of the *a*- and *c*-axes were obtained from Rietveld refinement. The magnetization measurements were performed using a physical properties measurement system (14 T) in the temperature range of 5–300 K. The entropy change was evaluated from the magnetization isotherms and the heat capacity.

III. RESULTS

From XRD analysis, perovskite single phase with orthorhombic structure was observed. Structural parameters of lanthanum manganite $La_{0.7}Ca_{0.3}MnO_3$ in this work were estimated to be $a=5.4835$ Å, $b=5.4752$ Å, $c=7.7325$ Å, and $V=232.16$ Å,[3] respectively. Figure 1 shows the low field magnetization in the zero-field cooled (ZFC) and in the field cooled cooling (FCC) and field cooled warming (FCW) processes. We estimated the Curie temperature (T_C) to be 251 K. It can be clearly seen that there is a drastic change in the magnetization around T_C. Under ZFC, the magnetic domain wall pinning causes the low magnetization, and a small part of the particle surface shows a spin-glass behavior, which may be the reason for the separation of the curves at low

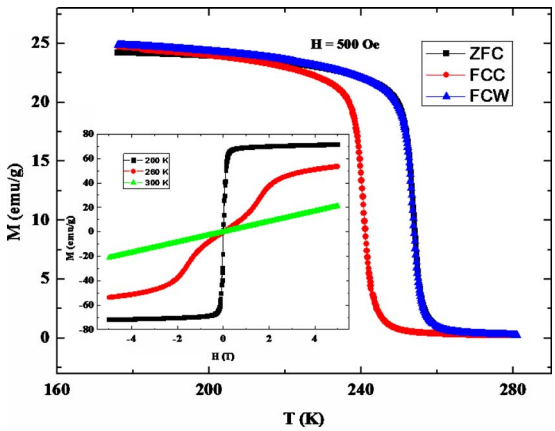

FIG. 1. (Color online) Magnetization as a function of temperature in the ZFC, FCC, and FCW processes with an applied field of 500 Oe for $La_{0.7}Ca_{0.3}MnO_3$. The inset shows a magnetic field dependence of the magnetization of the sample.

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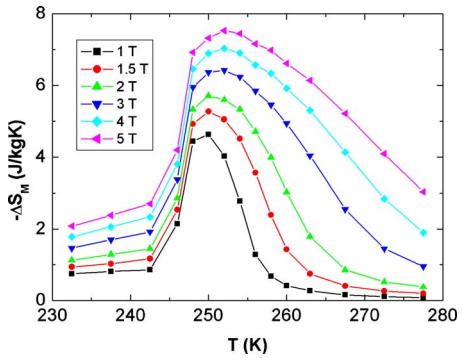

FIG. 2. (Color online) Magnetic entropy change as a function of temperature under magnetic field changes from 0 to 1, 1.5, 2, 3, 4, and 5 T.

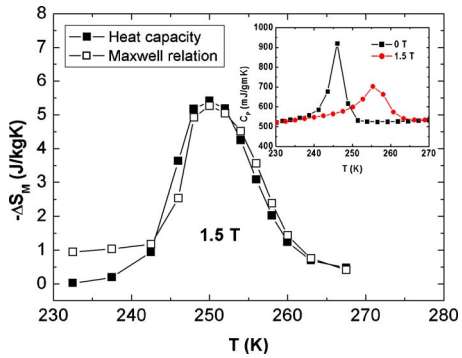

FIG. 3. (Color online) The temperature dependence of the entropy changes in the sample calculated from the heat capacity and the Maxwell relation. The inset shows the temperature dependence of the heat capacity of the $La_{0.7}Ca_{0.3}MnO_3$ sample for 0 and 1.5 T field.

temperature. It can be seen that the FCC and FCW curves follow different path at the transition temperature, which is one of the features of a first order transition. So, we think that the thermal hysteresis at the transition temperature is due to the first order phase transition. At and near T_C, however, the magnetization also shows an S-shape, which is unusual for the lanthanum manganites, indicating a large magnetic entropy change. In addition, the Arrott plots derived from M (H) over a broad temperature range around T_C (not shown) provide evidence that the slopes of the H/M versus M^2 curves are negative in the complete M^2 range. According to the Banerjee[6] criterion, the transition is confirmed as first order and is also an indication of a large magnetic entropy change.

Magnetic entropy change versus temperature at various applied fields (1–5 T) is presented in Fig. 2. At or near the Curie temperature (T_C), the maximum entropy changes were about 4.63, 5.27, 5.71, 6.42, 7.03, and 7.53 J kg^{-1} K^{-1} for field changes from 0 to 1, 1.5, 2, 3, 4, and 5 T, respectively. It should be noted that these values were about two times larger than those of other perovskite manganites[7–9] and even larger than for Gd-based magnetic materials at low fields.[10] From the results, the material studied in this work is characterized by large magnetic entropy changes induced by low magnetic field change, which is also beneficial for the household application of active magnetic refrigerant materials.

As mentioned above, the entropy change was also determined by using the heat capacity method. The heat capacity of the sample at different fields (0 and 1.5 T) is plotted against temperature and is shown in the inset of Fig. 3. The entropy changes determined by the heat capacity and the Maxwell relation are shown in Fig. 3. Quite interestingly, the entropy change determined by using the heat capacity method almost dovetails with that from the Maxwell relation. The quantitative value from the heat capacity is also in good agreement with that from the magnetization.

The adiabatic temperature change (ΔT_{ad}) for the temperature range of 230–275 K is shown in Fig. 4. The estimated ΔT_{ad} values are 2.02, 2.69, and 3.62 K for field changes from 0 to 1, 2, and 5 T, respectively. The ΔT_{ad} value for 1 T is 1.5 times larger that those reported in Ref. 8 and is nearly same as for Gd. It is well known that the presence of either no or low hysteresis is an important criterion for magnetic refrigeration without loss. The magnetic isotherms of the sample at the temperatures of 200, 260, and 300 K were measured with an increasing and decreasing field from 5 to −5 T, respectively (see the inset in Fig. 1). Almost no magnetic hysteresis was observed, which indicates that the MCE is fully reversible. The magnetization of the sample, when measured in cooling and then heating cycles at 500 Oe (Fig. 1), shows a small thermal hysteresis of about 6 K, which is consistent with the Arrott plot, indicating a first order transition near T_C.

IV. DISCUSSION

The magnetization isotherms of $La_{0.7}Ca_{0.3}MnO_3$ at and above T_C appear to exhibit an unusual dependence for lanthanum manganites, which is evidenced by the S-shaped magnetization curves, as mentioned above. It is believed that a large low-field value of $(\delta M/\delta T)$, which is caused by the S-shape of the magnetization, gives rise to the giant low-field magnetic entropy change. It is well known that itinerant electron metamagnetism (IEM) materials show the S magnetization shape.[11,12] The properties are well described by the Landau energy expansion $\Delta F = aM^2 + bM^4 + cM^6 - HM$ with a negative M^4 prefactor.[13] Due to the peculiarity of the exchange interaction and the magnetoelastic coupling (MEC), the b prefactor in the Landau expansion can, in fact, be negative, and phenomena similar to IEM are possible. Again, in Nagaev,[14] it is mentioned that metamagnetism is possible in magnetic systems, which include giant magnetoresistance

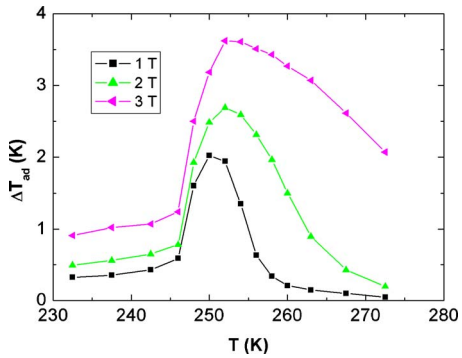

FIG. 4. (Color online) Temperature dependence of the adiabatic temperature change in the sample for a field change from 0 to 1, 2, and 5 T.

manganites, as a result of both the spin-phonon interaction and the influence on spin exchange due to the Jahn–Teller (JT) ordering of the electron orbits. This S-shaped magnetization was recently observed in the manganite $La_{0.7}Y_{0.7}Ca_{0.3}MnO_3$ (Refs. 15 and 16) as well and was clearly explained by the magnetoelastic contribution to the magnetic part of the free energy. Therefore, we can conclude that the observed giant magnetic entropy changes, following the strong manifestation of S-shaped magnetization, are caused by a metamagnetic transition. A change in the nature of the magnetic transition suggests a variation in the nature of the magnetic coupling. Goodenough suggested that in manganites, the static-cooperative JT distortions are replaced in the ferromagnetic phase by dynamic JT distortions that introduce vibrational modes into the spin-spin interaction, giving rise to an extra superexchange term.[15,16] That is, in our case, there is a strong influence of lattice effects in the sample, which is reflected in strong variations in several physical properties.[17] The anomalous volume change at T_C in the sample supports the first order character of the transition. In addition, giant MEC may exist in our sample. This MEC phenomenon has been found in other manganites,[18] which again confirms the lack of any noticeable magnetic hysteresis with a field-induced first order transition.

V. CONCLUSION

In summary, the MCE has been studied in the material $La_{0.7}Ca_{0.3}MnO_3$, and the results show a large magnetic entropy change at low field, associated with a first order transition. No noticeable magnetic hysteresis loss is observed but there is a small thermal hysteresis loss. Magnetic materials that show a first order magnetic phase transition, especially at the low fields that are obtainable from a permanent magnet, are good candidates for magnetic refrigeration.

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