

Magnetic entropy change of the layered perovskites $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$

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Magnetocaloric properties of perovskite-type manganese oxides with double Mn-O layers of composition $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.33$ and 0.4) have been investigated. A broad peak of magnetic entropy change ($-\Delta S_M$) was observed at the Curie temperature. The shape of $-\Delta S_M$ is strongly dependent on the Sr concentration. In contrast to $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ perovskites, the distinct curvilinear shape of $-\Delta S_M$ for perovskites with double Mn-O layers shows different magnetic mechanisms arising from magnetocrystalline anisotropy. © 2005 American Institute of Physics.
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I. INTRODUCTION

Solid-state magnetic refrigeration has been attracting the attention of scientists due to many advantages over gas refrigeration.¹ The essential working principle of magnetic refrigerators is based on the magnetocaloric effect (MCE), i.e., the magnetic entropy change (ΔS_M) produced by changing the magnetic field applied to the system. However, in the temperature region $T > 10$ K, because the effect of the lattice heat capacity and the thermal agitation energy is enhanced, the application of magnetic refrigeration using solid working substances has been seriously restricted. Some efforts have been made to search for new solid refrigerants which produce a large magnetic entropy change, and a magnetic refrigeration cycle corresponding to the Ericsson cycle was chosen in order to remove the effect of the large heat capacity of the lattice.^{2,3} Recently, much attention in this field has been focused on ferromagnetic substances for MCE applications at high temperatures.^{4,5}

The intense interest in perovskite-type manganese oxides $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (Ln : rare-earth ion, A : divalent alkaline-earth metal) was prompted by the observation of colossal magnetoresistance (CMR).^{6,7} These manganese oxides have also demonstrated a potential to increase the working temperature range and to reduce the field requirements of cryogenic magnetic refrigeration, because large entropy changes were observed in isotropic perovskite-type ferromagnetic oxides

$\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$.^{8–11} For manganites of the type $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, the magnetic entropy change can reach 4.3 J/kg K at T_C in a field of 1.5 T.⁸ In addition, for $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, the maximum entropy change value obtained for a variation of 3 T in the magnetic field is 5.15 J/kg K.¹⁰ This value is about 80% of that of pure gadolinium metal. Ceramic perovskite-type manganese oxides are good candidates to work as magnetic refrigerants in a wide temperature interval since the magnetocaloric effect in these materials is large and tunable.¹¹ The relationships between both the isothermal entropy change and adiabatic temperature change have been analyzed.¹²

For the manganites with the formula $\text{Ln}_{2-2x}\text{A}_{1+2x}\text{Mn}_2\text{O}_7$ (the $n=2$ member of the Ruddlesden–Popper series¹³), studies have shown the existence of the CMR effect as well.^{14,15} In contrast to three-dimensional (3D) perovskite-type manganese oxides, the perovskite manganites with this general formula have double Mn-O layers and quasi-two-dimensional crystal structures. The Mn-O magnetic bilayers are a large distance apart and are separated by insulating spacers. One of the most distinctive features of the manganites with Mn-O bilayers is their anisotropic charge-transport and magnetic properties. Experiments have shown that these manganites, with structure which can be described by $(\text{La}_{1-x}\text{Sr}_x\text{MnO}_3)\text{-SrO-(La}_{1-x}\text{Sr}_x\text{MnO}_3)$, exhibit an anomalous low-field magnetization plateau between the Curie temperature (T_C) and 250 K,¹⁶ which implies short-range order above T_C . This plateau is presumably due to short-range magnetic order, associated with the lower dimensionality of

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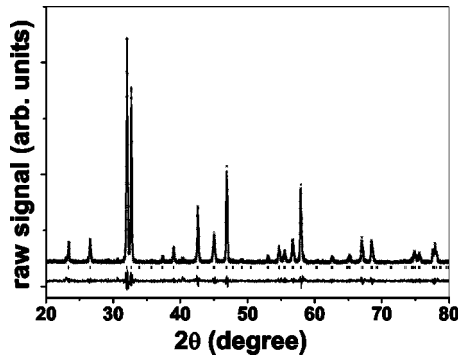


FIG. 1. X-ray refinement for $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.33$). Upper curve: data and fit, with difference plot below. The ticks show peaks indexed according to the bilayer perovskite structure.

the materials. It has been known that the anisotropy and dimensionality effects play a crucial role in the CMR behavior for the layered perovskite structure, but it is still unclear how the anisotropy and dimensionality affect the magnetocaloric effect.

In the present paper, we report our studies of magnetocaloric properties for the $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ perovskites with double Mn-O layers. In the temperature dependence of the magnetic entropy change ($-\Delta S_M$), we observe a broad peak for the $x=0.33$ and 0.4 samples. The width of this peak is greater than that of the 3D perovskite-type manganese oxides, and the asymmetric peak shape is dependent on the Sr concentration. The Mn-O bilayer perovskites therefore exhibit a potential for application as a working substance in magnetic refrigeration because the broad magnetic entropy peak has advantages for magnetic refrigeration using the Ericsson cycle.

II. EXPERIMENT

Polycrystalline samples of $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ were prepared by a solid-state reaction. The sol-gel method was applied to prepare starting powders in order to enable high purity and homogeneity. X-ray powder diffraction patterns showed nearly single-phase $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ for the two compositions prepared, $x=0.33$ and 0.4. All of the strong peaks were indexed according to the tetragonal space group $I4/mmm$ (No. 139). There was no trace of the ABO_3 phase. X-ray refinement was performed by using the GSAS software package.¹⁷ As shown in Fig. 1, the experimental pattern is in good agreement with the simulated one for the $x=0.33$ sample. The R values for the fit are $R_{wp}=0.073$ and $R_p=0.053$. The lattice parameters for $x=0.33$ are $a=0.3874$ nm and $c=2.0139$ nm, which are slightly smaller than that for $x=0.4$ ($a=0.3876$ nm and $c=2.0209$ nm). Magnetization measurements were performed on a superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND DISCUSSIONS

The temperature dependences of the magnetization for samples of the $x=0.33$ and 0.4 samples under an applied field of 0.01 T are shown in Fig. 2. A similar trend was observed for the two samples: from room temperature downward, the magnetization increases slowly then reaches a pla-

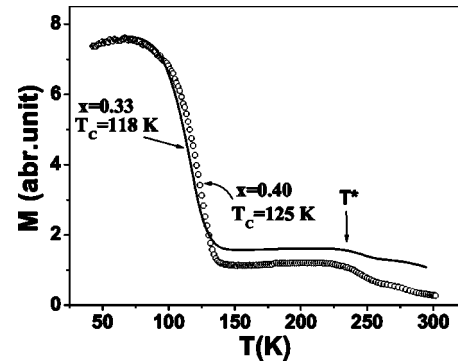


FIG. 2. Temperature dependence of magnetization of $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.33$ and 0.4) under an applied magnetic field of 0.01 T.

teau at about 235 K. The rounded shoulder appearing at about 235 K is labeled as T^* in Fig. 2. With further temperature decrease below about 140 K, the magnetization increases rapidly as the two samples go through a ferromagnetic transition. The $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ samples are known to display T_C variations dependent on the Sr concentration. In our case, the T_C , defined as the temperature of maximum slope in dM/dT , was found to be 118 and 125 K for the $x=0.33$ and 0.4 samples, respectively. The plateau of the M - T curves can be explained by the appearance of two-dimensional (2D) short-range magnetic order in the temperature range between T_C and T^* .^{18,19} With decreasing temperature, three-dimensional long-range magnetic order occurs, leading to a sharp increase of magnetization at T_C . A similar phenomenon was previously observed in $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ [$x=0.3$ (Ref. 18) and $x=0.3, 0.35$, and 0.4 (Ref. 19)].

In order to investigate the magnetocaloric properties, isothermal magnetization measurements were performed up to 5 T at different temperatures. Based on thermodynamic theory, the magnetic entropy change $\Delta S_M(T, H)$ is given by

$$\begin{aligned} \Delta S_M(T, H) &= S_M(T, H) - S_M(T, 0) \\ &= \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH. \quad (\text{Refs. 2 and 10}) \end{aligned}$$

Thus by obtaining M - H measurements we could calculate the magnetic entropy change.

Figure 3 shows $[-\Delta S_M(T)]$ under different applied fields for the $x=0.33$ and 0.4 samples. A large asymmetric peak

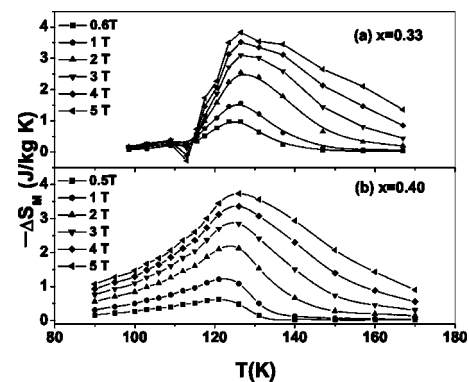


FIG. 3. Magnetic entropy change $-\Delta S_M$ for $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.33$ and 0.4) under different applied fields.

appears in a rather wide temperature region. The half-height width of this peak is about 40 K under 5 T. A direct comparison shows that both samples have a maximum of ($-\Delta S_M$) occurring at $T_{\max} \sim 126$ K. The peak shifts somewhat with an applied field. The $[-\Delta S_M(T, H)]$ maximum reaches 3.7 J/kg K under 5 T, which is slightly smaller than that reported for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($-\Delta S_M = 4$ J/kg K).²⁰ There are some obvious differences between the two samples. For $x = 0.33$, the ($-\Delta S_M$) peaks include only the temperature region above 115 K, with ($-\Delta S_M$) rapidly decreasing when the temperature falls below T_C . For $x = 0.4$, the peaks cover a lower temperature range. However, for $T > T_{\max}$ ($-\Delta S_M$) decays more slowly for $x = 0.33$ than that for $x = 0.4$. As discussed below, these differences originate from the structural and magnetic anisotropies, which are dependent on the Sr concentration.

For the Mn-O bilayer perovskite $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, the ($-\Delta S_M$) peak shape is different from that of the $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ perovskite.¹⁰ In particular, the curve extending above T_C arises from 2D short-range magnetic order, and covers a wider temperature range, extending towards T^* . For the perovskites with double Mn-O layers, it is obvious that the different Sr concentration results in the different ($-\Delta S_M$) peak shapes for the $x = 0.33$ and 0.4 samples. The magnetocrystalline anisotropy is also heavily dependent on the crystallographic structure and composition. Studies of the temperature dependence of the lattice parameters for $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ with $x = 0.3-0.45$ showed previously an anomalous two-dimensional expansion.^{21,22} For $x < 0.36$, a large and sudden decrease in c and a small increase in a was observed within a narrow temperature range below T_C (this range is denoted as $\Delta T'$), while for $x > 0.36$, the sign of the anomaly was reversed: c expands and a contracts. $\Delta T'$ corresponds precisely to the temperature range over which ($-\Delta S_M$) drops rapidly for $x = 0.33$.²¹ As the effect of dynamical structural anisotropy, the magnetic exchange interactions of in-plane (J_{\parallel}), intra-bilayer (J_{\perp}), and inter-bilayer (J') bonds are different for samples with $x < 0.36$ and $x > 0.36$ in the range $\Delta T'$. J_{\parallel} increases slightly, while J_{\perp} and J' decrease with decreasing temperature in the range of $\Delta T'$ for $x < 0.36$. On the contrary, J_{\parallel} decreases slightly, while J_{\perp} and J' increase with decreasing temperature over the range of $\Delta T'$ for $x > 0.36$. Since J_{\parallel} is stronger than J_{\perp} and J' ,²³ these differences in magnetocrystalline anisotropy results in the contrasting magnetic entropy behavior for the $x = 0.33$ and 0.4 samples.

In summary, measurements of magnetocaloric properties for the Mn-O bilayer perovskite $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.33$ and 0.4) reveal a broad peak of magnetic entropy change ($-\Delta S_M$) around T_C . The shape of ($-\Delta S_M$) is strongly dependent on the Sr concentration, which can be related to

different magnetic mechanisms arising from magnetocrystalline anisotropy. The peaks of ($-\Delta S_M$) are broadened somewhat differently versus temperature and magnetic field for the manganites $x = 0.33$ and 0.4, and this material may have the potential to increase the working temperature range or to reduce the field requirements of cryogenic magnetic refrigeration.

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- ¹A. F. Lacaze, R. Beranger, G. Bon Mardion, G. Claudet, and A. A. Lacaze, *Cryogenics* **23**, 427 (1983).
- ²T. Hashimoto, T. Numasawa, M. Shino, and T. Okada, *Cryogenics* **21**, 647 (1981).
- ³R. D. McMichael, J. J. Ritter, and R. D. Shull, *J. Appl. Phys.* **73**, 6946 (1993).
- ⁴K. A. Gschneidner, Jr., V. K. Pecharsky, A. O. Pecharsky, and C. B. Zimm, *Mater. Sci. Forum* **315**, 69 (1999).
- ⁵O. Tegus, E. Bruck, K. H. J. Buschow, and F. R. de Boer, *Nature (London)* **415**, 150 (2002).
- ⁶R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, *Phys. Rev. Lett.* **71**, 2331 (1993).
- ⁷S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnact, R. Ramesh, and T. H. Chen, *Science* **264**, 423 (1994).
- ⁸Z. B. Guo, Y. W. Du, J. S. Zhu, H. Huang, W. P. Ding, and D. Feng, *Phys. Rev. Lett.* **78**, 1142 (1997).
- ⁹P. Chen and Y. W. Du, *Chin. J. Phys. (Taipei)* **39**, 357 (2001).
- ¹⁰X. Bohigas, J. Tejada, M. L. Marinéz-Sarrión, S. Tripp, and R. Black, *J. Magn. Magn. Mater.* **208**, 85 (2000).
- ¹¹X. Bohigas, J. Tejada, E. del Barco, X. X. Zhang, and M. Sales, *Appl. Phys. Lett.* **73**, 3, 390 (1998).
- ¹²V. K. Pecharsky and K. A. Gschneidner, *J. Appl. Phys.* **90**, 4614 (2001).
- ¹³Y. Tokura, *Annu. Rev. Mater. Sci.* **30**, 541 (2000).
- ¹⁴M. Kubota, H. Fujioka, K. Ohoyama, K. Hirota, Y. Moritomo, H. Yoshizawa, and Y. Endoh, *J. Phys. Chem. Solids* **60**, 1161 (1999).
- ¹⁵T. Kimura, A. Asamitsu, Y. Tomioka, and Y. Tokura, *Phys. Rev. Lett.* **79**, 3720 (1997).
- ¹⁶S. D. Bader, R. M. Osgood, D. J. Miller, J. F. Mitchell, and J. S. Jiang, *J. Appl. Phys.* **83**, 6385 (1998).
- ¹⁷B. H. Toby, *J. Appl. Crystallogr.* **34**, 210 (2001); C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LAUR 86-748, 2000.
- ¹⁸T. Kimura, Y. Tomioka, H. Kuwahara, A. Asamitsu, M. Tamura, and Y. Tokura, *Science* **274**, 1698 (1996).
- ¹⁹T. I. Arbutova, S. V. Naumov, and V. L. Arbutov, *Phys. Solid State* **45**, 1513 (2003).
- ²⁰T. K. Bose, R. Chahine, B. R. Gopal, M. Foldealli, A. Barmant, M. Gosh, S. K. De, and S. Chatterjee, *Cryogenics* **38**, 849 (1998).
- ²¹T. Kimura, Y. Tomioka, A. Asamitsu, and Y. Tokura, *Phys. Rev. Lett.* **81**, 5920 (1998).
- ²²M. Medarde, J. F. Mitchell, J. E. Millburn, S. Short, and J. D. Jorgensen, *Phys. Rev. Lett.* **83**, 1223 (1999).
- ²³K. Hirota, S. Ishihara, H. Fujioka, M. Kubota, H. Yoshizawa, Y. Moritomo, and S. Maekawa, *Phys. Rev. B* **65**, 064414 (2002).