Compositional dependence of the magnetocaloric effect in $La_{1-x}Ca_xMnO_3$ ($0 \leqslant x \leqslant 0.52$)

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(Received 2 January 2004; revised manuscript received 16 June 2004; published 7 September 2004)

A detailed investigation of the thermodynamic properties of $La_{1-x}Ca_xMnO_3$ ($0 \leqslant x \leqslant 0.52$) for possible applications in magnetic refrigeration is presented. The adiabatic magnetic entropy change $|\Delta S|$ is determined for a 2 Tesla change in magnetic field using magnetization measurements. A broad double peak behavior as a function of x is observed with maximum absolute values $|\Delta S|_{\max}$ near 5.5 J/kg K for $x \approx 0.28$. The largest $|\Delta S|_{\max}$ values do not coincide with the maximum value of the ferromagnetic transition temperature T_c. The relatively large adiabatic magnetic entropy change is moderated by a large heat capacity, which leads to a modest adiabatic temperature change of about 2 K for the $x=0.28$ specimen. The largest contribution to $|\Delta S|_{\max}$ occurs for magnetic field changes in the range $0 \leqslant H \leqslant 2$ Tesla; increasing the magnetic field range to 3 Tesla only increases $|\Delta S|_{\max}$ by about 20%.

DOI: 10.1103/PhysRevB.70.094403 PACS number(s): 75.30.Sg, 65.40.Gr, 65.40.Ba

I. INTRODUCTION

Magnetic cooling has been used for decades to attain very low temperatures (below 1 K) using paramagnetic salts. In general it is very efficient below about 10 K because the lattice heat capacity C_L is small. Its possible use at high temperatures would require ferromagnetic materials with large magnetocaloric effects. A substantial amount of research in this area has been conducted.[1–3] The future use of magnetic refrigeration in technology will be strongly influenced by the discovery of new magnetocaloric materials. For example, recent measurements of $Gd_5(Si_2Ge_2)$ reveal a magnetocaloric effect (MCE) that is nearly a factor of 2 larger than that exhibited by any known material.[4] This anomalously large MCE appears to be strongly influenced by the close proximity of a first-order phase transition to the ferromagnetic transition.[5] Since 1996, there have been numerous reports of exceptionally large magnetocaloric effects in ferromagnetic perovskite manganese oxides.[6–10] However, it appears that the large heat capacity of these materials has a moderating effect that leads to a fairly small MCE.[11,12] A maximum temperature change $|\Delta T|$ of about 2 K has been estimated for a magnetic field change of about 2 Tesla.[11] This is most clearly explained by Pecharsky and Geschneidner, who point out that the large heat capacity of the manganese oxides relative to Gd, for example, leads to a small $|\Delta T|$ even though the adiabatic magnetic entropy change $|\Delta S|$ is quite large; for example, a magnetic field change of 3 Tesla leads to $|\Delta T|$ values of about 2 K in $La_{0.6}Ca_{0.4}MnO_3$ and 8 K in Gd.[12] Although this finding indicates that these manganese oxides may not be ideally suited for magnetocaloric applications, some more detailed investigations are still of value. For example, the finding that a structural transition residing close to the ferromagnetic transition[5] might enhance the magnetocaloric effect is very important since manganese peroviskites often exhibit structural transitions nearby to the ferromagnetic transition.[14–16] With these previous findings in mind, we undertook a very detailed investigation of the magnetocaloric effect in $La_{1-x}Ca_xMnO_3$ ($0 \leqslant x \leqslant 0.52$). Our goals here are: (1) to determine the dependence of Ca concentration on $|\Delta S|$, (2) to find the Ca composition which exhibits the largest $|\Delta S|$ and investigate its magnetocaloric effect in some detail using heat capacity measurements, and (3) to establish whether or not charge-ordering compositions[17] such as $x=0.5$ exhibit an anomalous magnetocaloric effect. Our results reveal a strong compositional dependence of $|\Delta S|$ on x with maximum $|\Delta S|$ values near 5.5 J/kg K at $x=0.28$, and a value of $|\Delta T| \approx 2$ K for a 2 Tesla change in field for $x=0.28$. A very small value of $|\Delta S|$ near the charge-ordering composition is observed. These findings are discussed within the framework of prior reports.

II. EXPERIMENT

Thirty-one polycrystalline samples of $La_{1-x}Ca_xMnO_3$ ($0 \leqslant x \leqslant 0.52$) were synthesized using standard solid-state reaction. Stoichiometric quantities of La_2O_3 (dried at 200 °C), $CaCO_3$, and MnO_2 were weighed and mixed for 10 min in an agate mortar followed by reaction in an alumina crucible at 1100 °C overnight. The samples were then reground for 10 min, placed in the crucible, and reacted at 1150 °C for 20 h. This last step was repeated 2 times with reaction temperatures of 1250 °C and 1300 °C. Finally, the samples were pressed into pellets and reacted at 1350 °C for 20 h followed by slow cooling in air (for $0.28 \leqslant x \leqslant 0.52$) at a rate of 1.5 °C/min. A similar method was used for samples with $0.0 \leqslant x \leqslant 0.26$, except that all reactions were done in flowing Ar gas in order to minimize the formation of chemical defects. All samples were investigated with powder x-ray diffraction and found to exhibit only the perovskite phases typical to these compounds, and no secondary impurity phases.

Thermodynamic measurements were conducted using a Quantum Design Physical Properties Measurement System (PPMS) which can measure the magnetic properties with a vibrating sample magnetometry option that operates at 40 Hz. In measuring the magnetization M versus T, samples are warmed slowly, stabilized at the desired temperature, and M is measured. The heat capacity was measured using a thermal relaxation technique.

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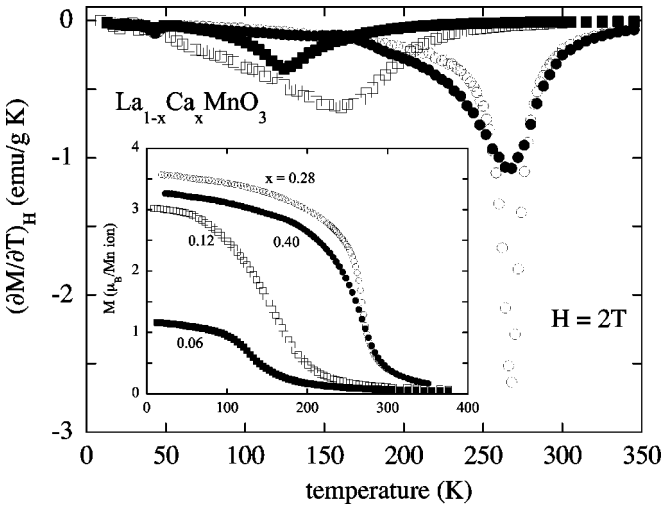

FIG. 1. The derivatives of magnetization $M(T)$ data, $(\partial M/\partial T)_H$, are shown for four compositions. In the inset the magnetization versus temperature in an applied magnetic field of 2 Tesla is shown for four samples of $La_{1-x}Ca_xMnO_3$.

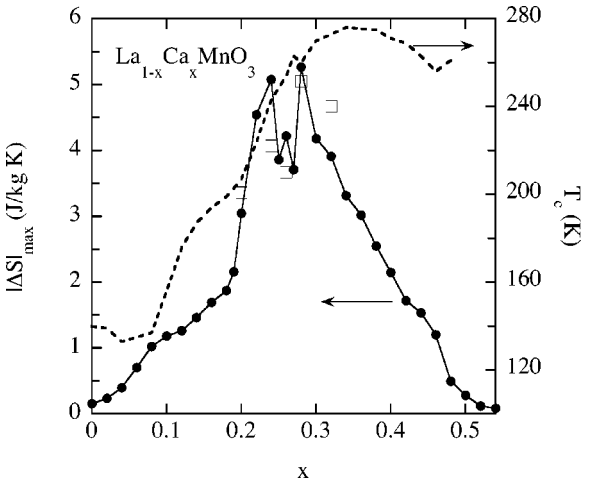

FIG. 2. The maximum value of ΔS, $|\Delta S|_{\max}$, for a magnetic field change of 2 Tesla plotted versus composition for 31 compositions of $La_{1-x}Ca_xMnO_3$ ($0 \leqslant x \leqslant 0.52$) is shown by the solid circles; these values were obtained using the approximation method described in the text. Also shown (right abscissa) by the dashed line is the ferromagnetic transition temperature T_c versus x. The open squares are the $|\Delta S|_{\max}$ values obtained from the data in Fig. 3 using more detailed measurements.

III. RESULTS

Our investigation begins with measurements of the magnetization M versus temperature in constant magnetic field. Some example data are shown in the inset of Fig. 1, where M versus T is plotted for 4 specimens of $La_{1-x}Ca_xMnO_3$ with $x=0.06$, 0.12, 0.28, and 0.40. The units of M are given as μ_B/Mn-ion to clearly indicate the degree of magnetic order. The magnetic Mn ions exist in either Mn^{3+} or Mn^{4+} valence states which possess magnetic moments of 4 μ_B and 3 μ_B, respectively. Thus, the $x=0.28$ specimen in Fig. 1 should theoretically display $M=3.72$ μ_B/Mn-ion at T near 0 K, which agrees very well with our observation suggesting that this sample is ferromagnetic. The $x=0.06$ sample, on the other hand, exhibits $M(10\ \mathrm{K})$ near 1.2 μ_B/Mn-ion indicating that it is not fully ferromagnetic and probably consists of a canted antiferromagnetic type of order.[18,19]

The magnetocaloric effect can be evaluated by measuring the magnetization and heat capacity with the use of the theory of thermodynamics. The Maxwell relation

$$\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T, \tag{1}$$

where M is the magnetization, T is the temperature, S is the magnetic entropy, and H is the magnetic field provides the connection between the entropy change and the magnetization. Thus, the change in magnetic entropy associated with a change in magnetic field can be obtained from

$$\Delta S = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right)_H dH. \tag{2}$$

To determine $|\Delta S|$ we take the derivative of data similar to those in the inset of Fig. 1 and find the area under the $(\partial M/\partial T)_H$ versus H curve. Example derivatives of the data for $x=0.06$, 0.12, 0.28, and 0.40 are shown in Fig. 1. It is interesting to note that the slope of $M(T)$ near the ferromagnetic transition temperature T_c plays an important role in the maximum value of $|\Delta S|$ and its shape. Furthermore, the saturation moment M_{sat} (value of M at the lowest temperature in the inset of Fig. 1) is less important (M_{sat} is comparable for $x=0.28$ and 0.40, but $(\partial M/\partial T)_H$ is 2.5 times larger for $x=0.28$).

We make an estimate of the maximum value of $|\Delta S|$, $|\Delta S|_{\max}$, by using $(\partial M/\partial T)_H$ determined at 2 Tesla, and multiplying by the magnetic field $H=2$ Tesla. From Eq. (2), it is evident that this approximates the area under the $(\partial M/\partial T)_H$ versus H curve as a rectangle. The obtained curve of $|\Delta S|$ versus T exhibits a peaklike behavior; the maximum of this curve is defined as $|\Delta S|_{\max}$. Although this is a crude approximation, it allows us to estimate $|\Delta S|_{\max}$ for a large number of samples without collecting an excessive amount of magnetization data. For a number of specimens near the peak in $|\Delta S|_{\max}$ we measured $M(T)$ at 6 magnetic fields to provide a more precise determination of $|\Delta S|_{\max}$; these values (open squares in Fig. 2), will be discussed in detail below, they agree exceedingly well with the results obtained with our estimation method. Figure 2 displays the results of our estimate of $|\Delta S|_{\max}$ for the 31 polycrystalline specimens in this investigation (filled circles in Fig. 2). We find that $|\Delta S|_{\max}$ exhibits a broad peak when plotted versus composition. Near the maximum, a double-peak structure is evident. This double peak structure is not as pronounced when more detailed measurements of $|\Delta S|_{\max}$ are used (open squares in Fig. 2). The dashed line in Fig. 2 displays the ferromagnetic transition temperature T_c. It is interesting to note that the sample with maximum T_c does not have the maximum $|\Delta S|_{\max}$ value.

The potential caveats in our estimation of $|\Delta S|_{\max}$ can be better appreciated after inspection of Fig. 3, where more de-

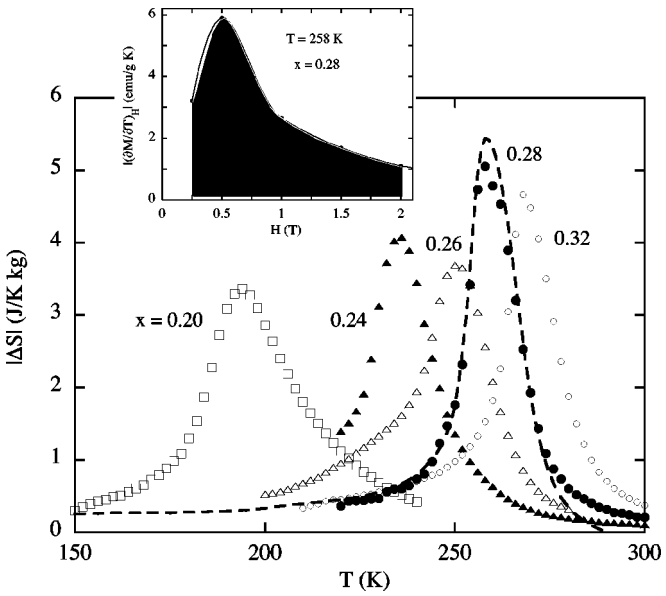

FIG. 3. Detailed measurements of $|\Delta S|$ determined for a magnetic field change from 0.25 to 2 Tesla using magnetization data, plotted versus temperature in the region where it reaches its maximum value for $La_{1-x}Ca_xMnO_3$ with $x=0.20$, 0.24, 0.26, 0.28, and 0.32. The dashed line indicates $|\Delta S|$ determined from the heat capacity data of Fig. 4. In the inset an example curve of $(\partial M/\partial T)_H$ versus magnetic field H is shown for $x=0.28$; the shaded area under the curve corresponds to the $|\Delta S|$ value at 258 K of the main figure.

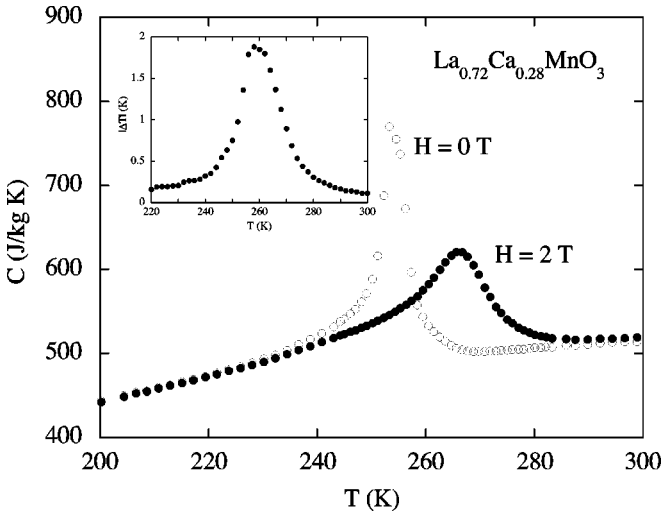

FIG. 4. Heat capacity C versus temperature at 0 and 2 Tesla for $La_{0.72}Ca_{0.28}MnO_3$. In the inset the magnitude of the temperature change due to the magnetocaloric effect is plotted versus temperature in the region near T_c. $|\Delta T|$ was calculated using Eq. (3) with the $M(T)$ and $C(T)$ data at 0.25, 1, 1.5, and 2 Tesla.

tailed measurements of the $x=0.20$, 0.24, 0.26, 0.28, and 0.32 specimens are shown, and consideration of the data shown in the inset of Fig. 1. Measurements of the magnetization of the samples in Fig. 3 were taken in magnetic fields of 0.25, 0.5, 1, 1.5, and 2 Tesla. Magnetic fields below 0.25 Tesla are not used because magnetic domain rotation dominates the temperature dependence of M for $T \leqslant T_c$. The $M(T)$ data were differentiated to obtain a series of $(\partial M/\partial T)_H$ versus H curves at numerous temperatures; an example of one of these curves at 258 K for $x=0.28$ (inset of Fig. 3) illustrates how $(\partial M/\partial T)_H$ versus H shows a maximum. These curves were then integrated, according to Eq. (2). Since the region below 0.25 Tesla is not used in our calculation, it is important to realize that our $|\Delta S|$ values are smaller than they would be if the measurements and calculations included a 0 Tesla value. It is evident in the inset of Fig. 3 that $(\partial M/\partial T)_H$ displays a complex behavior as a function of H. This results from the strong sensitivity of the magnetization to magnetic field in the region near T_c. Magnetic field has the effect of shifting the M versus T curve to higher temperature, for example, at a temperature slightly below T_c (in zero field) the slope $(\partial M/\partial T)_H$ increases and then decreases. With this in mind, one can imagine the shape of the $(\partial M/\partial T)_H$ versus H curves over the entire temperature range. There is also a broadening of the $M(T)$ curves as the magnetic field is increased due to fluctuation effects, this tends to decrease the maximum observed $(\partial M/\partial T)_H$ value. The approximate $|\Delta S|_{\max}$ values displayed in Fig. 2 (solid circles) for the $x=0.20$, 0.24, 0.26, 0.28, and 0.32 specimens agree well the maximum value for $|\Delta S|$ in Fig. 3 (shown by the open squares in Fig. 2). However, the temperature at which $|\Delta S|_{\max}$ occurs is slightly different because of the above mentioned shift in the maximum value of $(\partial M/\partial T)_H$ with magnetic field. For example, in a magnetic field of 2 Tesla the maximum value of $(\partial M/\partial T)_H$ (and therefore the temperature of the $|\Delta S|_{\max}$ value of Fig. 2) occurs at 268 K for $x=0.28$ whereas the maximum value of $|\Delta S|$ in Fig. 3 occurs at 258 K. We believe this good agreement between the estimated value in Fig. 2 and the maximum value of $|\Delta S|$ in Fig. 3 can be appreciated through this change in shape of the $M(T)$ curves in magnetic field. Finally, increasing the magnetic field range to 3 Tesla (i.e., a 50% increase in field) only adds about 20% to the $|\Delta S|_{\max}$ value in Fig. 3 for $x=0.28$, thus, the field region below 3 Tesla is the most important for the magnetocaloric effect in these materials.

Although measurements of ΔS provide a guide to the magnetocaloric effect's magnitude, it is essential that heat capacity measurements be used as well to make a complete evaluation. The importance of this has been illustrated by the measurements of Bohigas *et al.*[11] and discussed by Pecharsky and Geschneidner.[12] We use

$$\Delta T = -\int_0^{H_{\max}} \left(\frac{T}{C(T,H)}\right)\left(\frac{\partial M}{\partial T}\right)_H dH, \tag{3}$$

to calculate the temperature change $|\Delta T|$ realized by a change in magnetic field. In Eq. (3) $C(T,H)$ is the heat capacity. Inspection of this equation should make it clear that specimens with larger heat capacity will exhibit smaller $|\Delta T|$ values. We have measured heat capacity C in magnetic fields of 0, 0.25, 0.5, 1, 1.5, and 2 Tesla for our $La_{0.72}Ca_{0.28}MnO_3$ specimen (see Fig. 4), and used Eq. (3) to calculate $|\Delta T|$ with data in the magnetic field range $0.25 \leqslant H \leqslant 2$ Tesla. Our results for $|\Delta T|$ versus T are plotted in the inset of Fig. 4. We

find $|\Delta T|$ to exhibit a broad peak with a maximum value of about 2 K. The magnitude of this $|\Delta T|$ value is comparable to values reported previously[11] for $La_{0.6}Ca_{0.4}MnO_3$ and estimated[12] for some other Mn perovskite compounds. The heat capacity data in Fig. 4 were also used to determine $|\Delta S|$, to check against the data determined using magnetization data. The C/T versus T data from 5 K to 300 K (in constant magnetic field) are integrated in order to find the temperature-dependent entropy change ΔS_T using

$$\Delta S_T(H) = \int_{T_{\min}}^{T_{\max}} \left(\frac{C(T,H)}{T} \right) dT. \quad (4)$$

$|\Delta S|$ is then determined from $|\Delta S_{T,H=2\ \mathrm{Tesla}} - \Delta S_{T,H=0\ \mathrm{Tesla}}|$; the resulting data are plotted as the dashed line in Fig. 3 illustrating the excellent agreement between the two methods. Similar comparisons between $|\Delta S|$ values obtained from heat capacity measurements and magnetization measurements were presented[13] by Pecharsky and Geschneidner for $ErAl_2$ and Gd.

IV. DISCUSSION AND CONCLUSIONS

Our results reveal fairly large values of $|\Delta S|$ for manganese perovskite compounds, in agreement with prior reports.[6–9] Thus, it can be concluded that a reasonable change in magnetic entropy occurs in these materials close to the ferromagnetic transition when they are subjected to moderate (a few Tesla) changes in applied magnetic field. In calculating $|\Delta T|$, $(\partial M/\partial T)_H$ must be divided by the total heat capacity (not just magnetic heat capacity), multiplied by T, and integrated according to Eq. (3) to obtain the heat increase or decrease associated with the change in applied magnetic field. Thus, the large heat capacity of the manganese perovskites has a moderating effect on the overall temperature change that occurs due to the magnetocaloric effect. Physically, this heat energy is spread out over the many degrees of freedom of the system, which in this compound, contains many atoms which do not participate in the magnetic entropy change and their associated lattice and electronic contributions to the heat capacity. Although the findings of Pecharsky and Geschneidner[12] regarding the large heat capacity of manganese oxides and its influence on $|\Delta T|$ through Eq. (3) are true, this effect can be partially negated through the refrigeration cycle. Brown has shown, for example, that a Gd-based magnetic refrigerator can achieve a reduction in temperature of 47 K using a magnetic Stirling cycle (7 T field) that removes the lattice and electronic heat loads with a regenerator.[2] Note that this is possible although the maximum $|\Delta T|$ for Gd in a comparable field is[2,12] only 14 K. Thus, the argument regarding the large heat capacity's negative influence on the MCE of ferromagnetic manganese perovskites may be too simplistic. A rather interesting aspect arises upon consideration of the shape of the $(\partial M/\partial T)_H$ versus H curve shown in the inset of Fig. 3. The slope $(\partial M/\partial T)_H$ becomes quite small at high field resulting in a very modest contribution to $|\Delta S|$ for fields larger than 2 Tesla. This is also evident upon consideration of measurements of $|\Delta T|$ for magnetic field changes of 6 Tesla,[20] which yield $|\Delta T|$ values near 2 K. Apparently, this is not the case in Gd where $|\Delta T|$ increases almost linearly[12] with the change in magnetic field ΔH. Thus, ferromagnetic manganese perovskites are actually quite good magnetocaloric materials for modest magnetic field changes in the range 0–2 Tesla. A further advantage of the manganese oxides is the wide tunability of the ferromagnetic transition temperatures T_c which can easily be altered through doping from[12,21,22] 100 K to 375 K. Furthermore, the influence of structural transitions[21] on $|\Delta S|$ appears to broaden $|\Delta S|$, when compared to the behavior revealed in Fig. 3. This should be investigated further in order to establish whether or not anomalously large $|\Delta S|$ values might also occur in ferromagnetic manganese perovskites, similar to what is observed[4] in $Gd_5(Si_2Ge_2)$.

In conclusion, we have presented a detailed investigation of the magnetocaloric effect in $La_{1-x}Ca_xMnO_3$ ($0 \leqslant x \leqslant 0.52$). We find the maximum MCE to occur at $x=0.28$. The maximum MCE does not occur at the maximum T_c ($x \approx 0.36$). The MCE near the charge-ordering composition of $x=0.50$ was found to be extremely small. Our detailed investigation of the $x=0.28$ specimen reveals a maximum value of $|\Delta T| \approx 2$ K for a magnetic field change $\Delta H=2$ Tesla. We also discuss the fact that magnetic fields larger than 2 Tesla are not very advantageous in enhancing the MCE in ferromagnetic manganese perovskites. Finally, although the MCE in these compounds is moderated by their large heat capacity, the choice of an appropriate regenerative refrigeration cycle could make their application feasible.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grants Nos. DMR 0244058 (REU-Site) and DMR 0301166 (CAREER).

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