

## Field-induced entropy change in the manganite with significant short-range magnetic order

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Effects of short-range magnetic order on magnetic entropy change have been studied for the manganese oxide  $\text{Eu}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ . Superparamagnetic clusters composed of seven to ten Mn ions, depending on applied field, have been derived in the paramagnetic state of the compound based on the analysis of dc susceptibility. The presence of short-range magnetic order greatly depresses the magnetic entropy of the paramagnetic phase; thus the entropy changes at the field-induced paramagnetic to ferromagnetic phase transition. The maximum entropy change detected is only  $\sim 7$  J/kg K for a field change of 0–5 T, about one-fifth of the theoretical expectation. The experimental results can be well elucidated within the mean field theory. It is suggested that a way of destroying the short-range order would enhance the magnetic entropy change greatly. © 2006 American Institute of Physics. [DOI: 10.1063/1.2355441]

Magnetocaloric effects of the materials can be used to develop a magnetic refrigeration technique, a green one with high energy efficiency. The discovery of significant magnetic entropy change in  $\text{Gd}_5\text{Si}_{4-x}\text{Ge}_x$ ,<sup>1,2</sup>  $\text{La}(\text{Fe}, \text{Co})_{13-x}\text{Si}_x$ ,<sup>3</sup> and  $\text{MnFeP}_x\text{As}_{1-x}$  (Ref. 4) demonstrated the possibility of applying this technique near room temperature and aroused extensive exploration of potential magnetocaloric materials in recent years.

One of the important criteria for promising refrigerants is that the material should exhibit large field-induced entropy change. Based on the local magnetic moment model, the utmost magnetic entropy change for a material would be  $\Delta S = Nk_B \ln(2J+1)$ , where  $N$  is the number of spins,  $J$  the quantum number of the spin, and  $k_B$  the Boltzmann constant. This is the entropy released by the system when the material transforms from a completely ordered magnetic state to a disordered magnetic state. However, experimentally detected entropy change is usually much lower than the theoretical expectation. Taking Gd as an example, its entropy change is  $\sim 10$  J/kg K for a field change of 0–5 T,<sup>5</sup> while the theoretical value is  $\sim 110$  J/kg K. It is generally believed that the field-induced magnetization change is much smaller than that produced by a full order-disorder transition. As a result, the entropy change is not large.

In addition to these, other possible factors affecting the entropy also deserve further investigation considering the complexity of a practical material, in which short-range magnetic order near and above  $T_C$  as well as structural and electronic degrees of freedom could be in action. It is obvious that a comprehensive study on these aspects will help us to understand and control the magnetocaloric effects of the materials.

It may be a proper starting point to establish a quantitative relation between magnetization and magnetic entropy, so that the information about the entropy release at the phase transition could be retrieved by comparing the experimental and theoretical results. However, no such investigation has been reported.<sup>6</sup> For a material that experiences a first-order

magnetic transition, an applied field can drive the Curie temperature upwards or downwards.<sup>7</sup> In this case the field-induced magnetization change could be very large because of the sudden change of magnetic order at  $T_C$ .  $\text{Eu}_{1-x}\text{Sr}_x\text{MnO}_3$  is a compound showing a field-sensitive magnetic behavior, especially an ideal first-order phase transition that results in a great magnetization drop/jump.<sup>8</sup> It is therefore a proper system for the above mentioned studies.

Polycrystalline sample  $\text{Eu}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$  (ESMO) was prepared by the conventional solid-state-reaction method. Well mixed stoichiometric  $\text{Eu}_2\text{O}_3$ ,  $\text{SrCO}_3$ , and  $\text{MnO}_2$  were calcinated at 900 °C for 10 h. The resultant product was ground, pelletized, and sintered at 1350 °C for 48 h. with an intermediate grinding for homogenization. Phase purity and crystal structure of the sample were studied by powder x-ray diffraction performed on a Rigaku x-ray diffractometer with a rotating anode and  $\text{Cu } K\alpha$  radiation. A superconducting quantum interference device magnetometer (MPMS-7) was used for the magnetic measurements. Heat capacity was determined by a physical property measurement system (PPMS-14H). All the data presented here were collected in the warming process after zero-field cooling the sample to preset temperatures.

The sample thus obtained is single phase as confirmed by the x-ray diffraction study and exhibits a complex magnetic behavior. Figure 1 shows the temperature-dependent magnetization under the fields of 0.1 and 5 T (top panel). The sample is paramagnetic (PM) at high temperatures and behaves as a spin glass at low temperatures under  $H=0.1$  T. Increasing the magnetic field stabilizes the ferromagnetic (FM) order, and a field of 5 T induces a FM transition that leads to a nearly fully spin-polarized state. The detected magnetization is  $M \approx 87.1$  emu/g at 5 K, while the saturated magnetization is  $M_s \approx 87.7$  emu/g. As the magnetic field drives the system from the PM to the FM state, the magnetization change is as high as  $\Delta M/M_s \approx 85\%$  even near  $T_C$ . The bottom panel of Fig. 1 is a phase diagram of ESMO in the  $H$ - $T$  plane.

Large magnetization change implies large entropy change. The latter can be derived from the heat capacity data based on the formula  $\Delta S = \int_0^T [C_p(T, 5T) - C_p(T, 0)] dT/T$ .<sup>9</sup>

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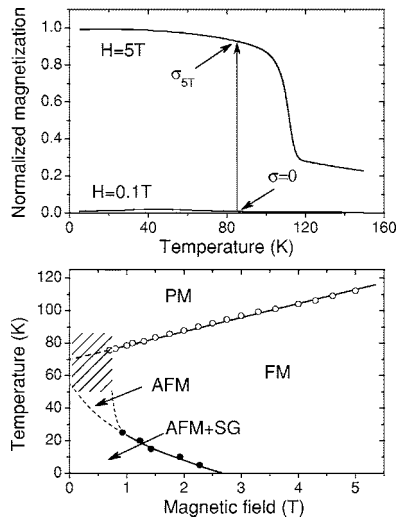


FIG. 1. Temperature dependence of the magnetization measured under the fields of  $H=0.1$  and  $5$  T (top panel) and the phase diagram of ESMO in the  $H$ - $T$  plane (bottom panel). The arrow in the figure marks the increase of magnetization after the magnetic field is applied. Hatched area marks unidentified phases. AFM=antiferromagnetic and SG=spin glass.

Figure 2 presents the heat capacity measured under the fields of  $H=0$  and  $5$  T (top panel). The heat capacity is rather smooth without external field while displaying an obvious thermal anomaly near  $\sim 110$  K, corresponding to the field-induced magnetic transition, under the field of  $5$  T. The resultant entropy change is shown in the bottom panel of Fig. 2. It exhibits first a sharp increase at  $T_C$  and then a gradual decrease, after the broad peak at  $\sim 85$  K, with the decrease of temperature. The maximum entropy change is only  $\sim 7$  J/kg K, much smaller than the theoretical expectation [ $\Delta S = Nk_B \ln(2J+1) \sim 55$  J/kg K].

To get a complete picture about this discrepancy, it may be helpful to establish a quantitative relation between magnetization and magnetic entropy. As shown in Figs. 1 and 2, the  $\sigma = M/M_s$  to  $S$  correlation is obvious: Entropy increases from  $S(\sigma_{5T})$  to  $S(0)$  as the magnetization drops from  $\sigma_{5T}$  to  $0$ . Such a correlation exists at any temperature below  $T_C$ . Based on these data, a quantitative relation between

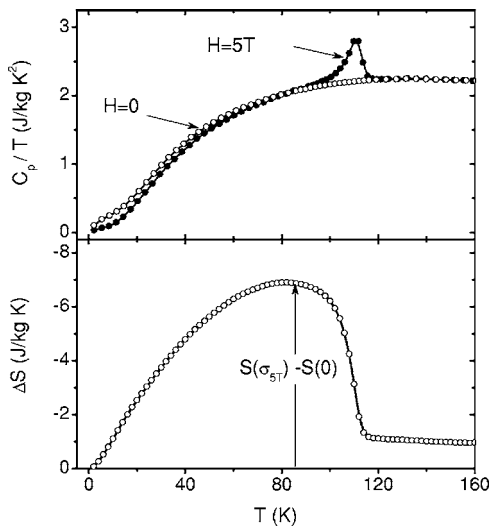


FIG. 2. Heat capacity measured under the fields of  $H=0$  and  $5$  T (top panel) and the corresponding entropy change (bottom panel). The arrow in the bottom panel marks the change of magnetic entropy after the field is applied.

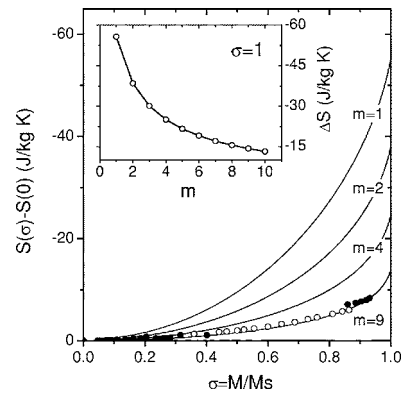


FIG. 3. Entropy change against reduced magnetization. Experimental and the theoretical results are represented by symbols and solid curves, respectively. The full and empty circles correspond to the data from magnetic and thermal measurements, respectively. Inset is a plot showing the variation of magnetic entropy with cluster size.

$\Delta S = S(\sigma_{5T}) - S(0)$  and  $\sigma_{5T}$  can be found.<sup>10</sup> With the help of the mean field theory, a theoretical relation can also be established:

$$\Delta S = S(\sigma) - S(0) = -Nk_B \left[ \ln(2J+1) - \ln \left( \frac{\sinh((2J+1)x/2J)}{\sinh(x/2J)} \right) + x\sigma \right], \quad (1)$$

where  $\sigma = B(x)$  is the Brillouin function with  $x = gJ\mu_B(H + \lambda\sigma)/k_B T$  and  $\mu_B$  and  $g$  have the conventional meanings. Although Eq. (1) was obtained based on the molecular field assumption ( $H_{\text{eff}} \propto \sigma$ ), it is exactly true for any effective fields of the form  $H_{\text{eff}} \propto f(\sigma)$ , even for a first-order transition, which can be realized by properly choosing  $f(\sigma)$ .<sup>11</sup>

Figure 3 exemplifies the  $\Delta S$ - $\sigma$  relations thus obtained.<sup>12</sup> The most remarkable observation is the obvious difference between the experimental (symbols) and theoretical ( $m=1$  solid curve) entropy changes: the former is much smaller than the latter. Simply extrapolating the experimental data to  $\sigma=1$ , it is easy to see that the upper limit of the entropy change is  $\sim 10$  J/kg K, greatly overestimated by the theory ( $\sim 55$  J/kg K).

It has been experimentally proven that the change of unit cell volume at the magnetic transition is rather small in ESMO, only  $\sim 0.1\%$ . Therefore, the corresponding lattice and electronic entropy changes will be smaller than  $\sim 1$  J/kg K.<sup>13</sup> This rules out the possibility that the magnetic entropy change is partially compensated by the lattice and electronic contributions. With these in mind, the discrepancy between the experimental and theoretical results raises an interesting question: Where is the missed magnetic entropy?

To get a deep insight into this problem, the magnetic data obtained under different fields were further analyzed. It is found that the dc susceptibility can be fitted by the Curie-Weiss law  $\chi = N\mu_{\text{eff}}^2/3k_B(T - T_\theta)$  quite well using the parameters  $T_\theta = 4.85$  K and  $\mu_{\text{eff}} = 11.22\mu_B/\text{Mn}$  (Fig. 4). The latter is unreasonably larger than that expected for a Mn ion (the average magnetic moment is  $0.55 \times 4 + 0.45 \times 3 = 3.55\mu_B$  for each Mn ion in ESMO and the corresponding effective magnetic moment will be  $\sim 4.4\mu_B$ ) and implies a strong correlation between magnetic moments. To a first approximation, we assume that neighboring magnetic moments group together, fluctuating as a superparamagnetic (SPM) cluster. This leads to an amplified Curie-Weiss constant of the form

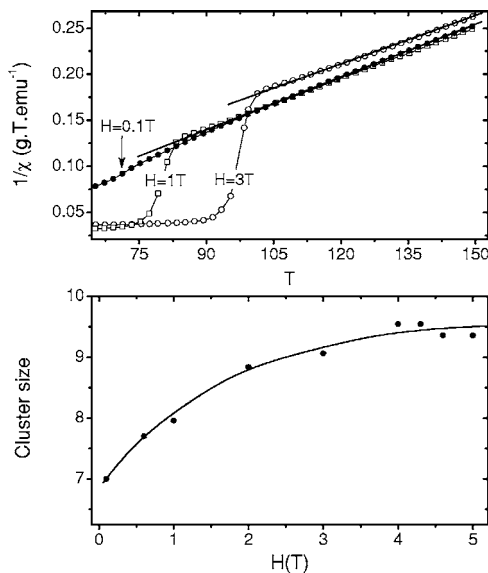


FIG. 4. Reciprocal dc susceptibility as a function of temperature (top panel) and the SPM cluster size against magnetic field (bottom panel). Solid lines are guides for the eye.

$Nm\mu_{\text{eff}}^2/3k_B$ , where  $m$  is the number of Mn ions in each SPM cluster. It is easy to obtain that  $m \approx 7$  if the magnetic moment of the Mn ion is set to  $3.55\mu_B$ . Magnetic field causes a slight growth of the SPM cluster from  $\sim 7$  for  $H = 0.1$  T to  $\sim 9.5$  for  $H = 5$  T (bottom panel of Fig. 4). The corresponding spatial cluster size will be  $\sim 1$  nm. These results are interesting in the sense that they reveal an intrinsic magnetic inhomogeneity in ESMO. We would like to point out that the cluster size derived here is an effective size, and a perfect spin alignment in the cluster has been assumed. The practical cluster size could be even large considering the fact that noncollinear spin arrangements in the cluster are possible. Although the presence of SPM clusters has been suggested in the manganite,<sup>14</sup> their size is quite small, generally below three Mn ions. The big clusters in ESMO could be indicative of the field-sensitive character of the compound and are expected to have a strong impact on the magnetic entropy of the PM phase.

It is easy to calculate that the magnetic entropy of the PM phase with the SPM cluster will be  $(Nk_B/m)\ln(2mJ+1)$ , which gives a value smaller than  $Nk_B\ln(2J+1)$ . The presence of SPM cluster impedes the complete release of magnetic entropy. In fact, the entropy change corresponding to any magnetization state can be calculated when SPM clusters exist, and the results are also presented in Fig. 3. A rapid decrease of entropy change with cluster size is observed. This effect is especially salient when clustering begins, and the formation of the cluster of two Mn ions can reduce the entropy change from  $\sim 55$  to  $\sim 38$  J/kg K (inset in Fig. 3). An excellent agreement of the experimental and theoretical results is obtained when the cluster size is set to 9 without size distribution, which is close to the size predicted by susceptibility analysis. In this case, the entropy change is only one-sixth to one-fifth of the theoretical value. It is therefore the SPM clusters that hinder the entropy change at the FM-PM transition.

With the progress of relevant studies, it becomes clear that availability of efficient magnetocaloric materials is the key problem for the practical application of the magnetic cooling technique. Although great advance in material explo-

ration has been made, materials with a strong magnetocaloric effect are still desired. In fact, besides the manganite, there is evidence of the presence, to different extent, of the short-range magnetic order in many materials. The present work suggests a promising perspective: It is possible that experimentally detected entropy change is only a small fraction of the total value held by the material, and if we can find a way to prevent or destroy the short-range order, magnetic entropy change will be greatly enhanced.

In summary, effects of short-range magnetic order on the magnetic entropy change have been studied for the manganese oxide  $\text{Eu}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ . Superparamagnetic clusters of the size between seven and ten Mn ions, varying with applied field, have been found in the paramagnetic phase of the compound based on an analysis of dc susceptibility. The presence of short-range magnetic order greatly depresses the magnetic entropy of the paramagnetic phase; thus the entropy changes at the field-induced paramagnetic to ferromagnetic phase transition. The maximum entropy change detected is only  $\sim 7$  J/kg K for a field change of 0–5 T, about one-fifth of the theoretical expectation. The experimental results can be well reproduced by the mean field theory when the cluster size is set to approximately nine Mn ions. It is possible that if a method of decomposing the short-range order can be found, the magnetic entropy change will be greatly enhanced.

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<sup>12</sup>Only the experimental data above 85 K were considered. In the low temperature range, significant antiferromagnetic order occurs in the compound without magnetic field. In this case, the field-induced phase transition is from the antiferromagnetic state to the ferromagnetic state and may obey a different rule. Partial results calculated by the Maxwell relation based on the magnetic data are also presented for reference (full symbols).

<sup>13</sup>Variation of the Debye temperature due to the phase transition can be approximated by  $\Delta\Theta/\Theta = -\eta\Delta V/V$ , where  $\eta$  is the Grüneisen parameter.  $\Theta$  is  $\sim 400$  K for the manganites,  $\eta$  is  $\sim 3$  for the solids, and the relative volume change of the unit cell at the FM phase transition is  $\sim -0.045\%$  for ESMO. Therefore, lattice entropy change can be estimated based on the Debye approximation, and it is  $\sim 0.1$  J/kg K. The electronic entropy change will be  $\Delta\gamma T_c \sim 0.7$  J/kg K, where  $\gamma$  is determined by electron heat capacity.

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