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A comparison study of the entropy changes in materials with and without short-range magnetic order

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Abstract

The effects of short-range magnetic order (SRMO) on magnetic entropy changes have been studied for the compounds $Sm_{0.55}Sr_{0.45}MnO_3$, $Eu_{0.55}Sr_{0.45}MnO_3$ and the rare-earth metal Gd. Ferromagnetic clusters composed of ∼8 Mn ions are found to be formed in the paramagnetic phase of the manganites based on the analysis of susceptibility. As a result, the entropy change for a field variation of 0–5 T is ∼6 J kg^{-1} K^{-1} for $Sm_{0.55}Sr_{0.45}MnO_3$ and ∼7 J kg^{-1} K^{-1} for $Eu_{0.55}Sr_{0.45}MnO_3$, well below the values expected without considering the effect of SRMO. (The maximum entropy change will be ∼56 J kg^{-1} K^{-1} for both compounds.) Assuming the presence of sizable magnetic clusters, the field-induced entropy change, not only its peak value but also its temperature dependence, can be well reproduced by the mean field theory. The average cluster size is found to be $m \approx 8$, in agreement with the result obtained from a Curie–Weiss analysis of the susceptibility. The presence of SRMO reduces the entropy change by ∼80%. In contrast, the mean field theory gives a good description of the entropy change in Gd, for which no significant SRMO is observed. The present work reveals the important role of SRMO in modifying the magnetocaloric properties of the magnetic materials.

Magnetic refrigeration, based on the magnetocaloric effect (MCE) of magnetic materials, has attracted much attention because of its considerable advantages over conventional refrigeration techniques. One of the key problems for the practical application of this technique is the availability of efficient refrigerants. The possibility of applying this technique near room temperature has been demonstrated by the discovery of $Gd_5Si_xGe_{4-x}$, $LaFe_xSi_{13-x}H_y$ and MnAs [1–6], which show a strong MCE around the temperature of the magnetic phase transition.

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Despite significant progress in the study of the MCE in recent years, there is still a great difference between the obtained entropy change and the expected one. According to the formula $\Delta S_{\mathrm{M}} = Nk_{\mathrm{B}} \ln(2J + 1)$, the ultimate magnetic entropy changes will be of the order of 100 J kg^{-1} K^{-1} in magnitude for the materials mentioned above, where N is the number of magnetic atoms in 1 kg of material, k_{B} is the Boltzmann constant and J the quantum number of spins. However, no such strong MCE has ever been observed in any magnetic materials up to now[2].

There are many factors that can affect the entropy of materials, especially for compounds that experience a first-order phase transition. In this case, changes in lattice and electronic entropies could be significant. There is evidence for the important role of lattice entropy in affecting the MCE property of the materials [7, 8]. The lattice entropy change is believed to be significant in those compounds that experience a large change in phase volume accompanying the magnetic transition, such as $LaFe_{13-x}Si_x$ and $Tb_5Si_2Ge_2$.

In addition to lattice contraction/expansion, short-range magnetic order (SRMO) in the paramagnetic (PM) state was recently found to be an alternative factor affecting magnetic entropy [9]. A primary analysis revealed that the presence of sizable ferromagnetic (FM) clusters in the PM state will prevent the complete release of magnetic entropy and, as a result, depress the entropy change associated with the PM–FM transition.

SRMO may exist, to different extents, in many magnetic materials. How the SRMO affects the magnetic entropy is therefore an interesting problem which has not been clearly addressed before. In fact, in our previous work only the relation between ΔS–$\Delta\sigma$ (σ = normalized magnetization) was established, and two questions still remain to be answered. The first one is whether this relation is general or, equivalently, whether the conclusion drawn from the ΔS–$\Delta\sigma$ relation still holds when cluster size changes or the compound involved is different. The second one is whether the experimental relation $\Delta S(T, H)$ can be well reproduced by assuming the presence of magnetic clusters. It is obvious that the $\Delta S(T, H)$ dependence can provide a detailed description for the dependence of entropy change on temperature and magnetic field and, therefore, contains much more information than the simple ΔS–$\Delta\sigma$ relation.

To get a thorough understanding of these problems, in this paper two compounds, $Sm_{0.45}Sr_{0.55}MnO_3$ (SSMO) and $Eu_{0.45}Sr_{0.55}MnO_3$ (ESMO) and a rare-earth metal, Gd, were chosen to study the effects of SRMO. The SRMO is strong in the first two compounds and weak in Gd, and it would be worthwhile to perform a comparison study on the entropy changes in these materials. Special attention has been paid to the temperature dependence of entropy changes. Entropy changes determined by magnetic measurements and mean field calculation are compared. Satisfactory agreements are observed for the rare-earth metal Gd. In contrast, the presence of SRMO greatly depresses the entropy changes, and an agreement is obtained only when the FM clusters in the PM phase are considered.

The two polycrystalline samples of SSMO and ESMO were prepared by the conventional solid state reaction method. Well mixed stoichiometric Sm_2O_3, Eu_2O_3, $SrCO_3$ and MnO_2 were calcinated at 900 °C for 10 h. The resultant products were ground, pelletized and sintered at 1350 °C for 60 h with an intermediate grinding for homogenization. X-ray diffraction was performed to check the phase purity and crystal structure of the samples. A SQUID magnetometer (MPMS-7) was used for the magnetic measurements. Data for Gd were obtained from the literature [10].

The obtained samples are single phase as confirmed by the x-ray diffraction study. To eliminate the effects of magnetic history, all of the data were collected in the warming process

[2] It was recently reported that the entropy change in $Mn_{1-x}Fe_xAs$ is as high as ~300 J kg^{-1} K^{-1} for a field variation of 0–5 T. This result was obtained based on magnetic measurements and there is no evidence from the calorimetric data.

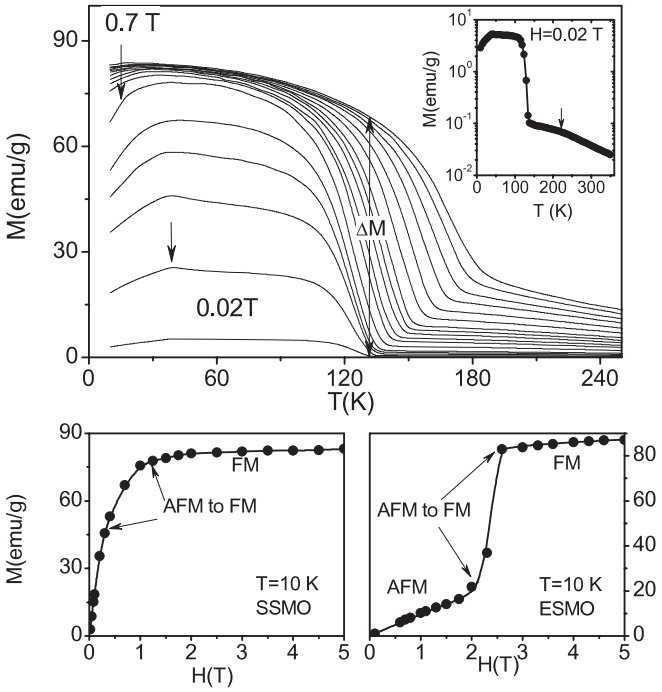

Figure 1. Top panel: temperature dependence of magnetization under different fields for SSMO. The inset plot is a close view of the magnetization under a field of 0.02 T and the arrowhead denotes the charge-order temperature. Bottom panels: isothermal magnetization of SSMO and ESMO at $T = 10$ K respectively. Solid lines are guides for the eye.

after zero-field cooling the samples to pre-set temperatures. Figure 1 shows the thermal magnetization $M(T)$ of SSMO measured under different fields (top panel). The sample is PM at high temperatures. With the decrease of temperature, a charge-ordering transition takes place at ∼220 K [11], as demonstrated by the arrowhead in the inset plot of figure 1. FM ordering appears below $T_C \sim 120$ K. T_C can be remarkably modified by magnetic field, rising from ∼123 K for $H = 0.7$ T to ∼167 K for $H = 5$ T. This reveals the first-order nature of the magnetic transition. The visible anomaly at ∼40 K, when the magnetic field is small, indicates an antiferromagnetic (AFM) transition, which leads to the coexistence of FM and AFM phases [11]. The AFM phase is unstable, and a field above ∼0.3 T can induce a gradual AFM–FM transition (the left bottom panel in figure 1). Essentially similar $M(T)$ curves are observed in ESMO [9]. Different from SSMO, the ground state of ESMO is AFM under low fields, and the FM transition does not take place until the magnetic field exceeds ∼2 T (the right bottom panel of figure 1).

The field-induced entropy change (ΔS) can be calculated by the Maxwell equation based on the magnetic data, and the results corresponding to field changes of 0–2 and 0–5 T are shown in figure 2. We take the results under the field of 5 T as an example. It is found that ΔS is negligibly small at high temperatures, starts to increase at ∼187 K and arrives at its peak value of ∼6.2 J kg^{-1} K^{-1} at ∼132 K. The temperature span of ΔS is ∼47 K (width at half height). Essentially similar behavior is observed for the field change of 0–2 T except for a lower ΔS peak and a narrower temperature width. Similarly, the entropy change of ESMO is not large either, ∼7 J kg^{-1} K^{-1} for the field change of 0–5 T [9].

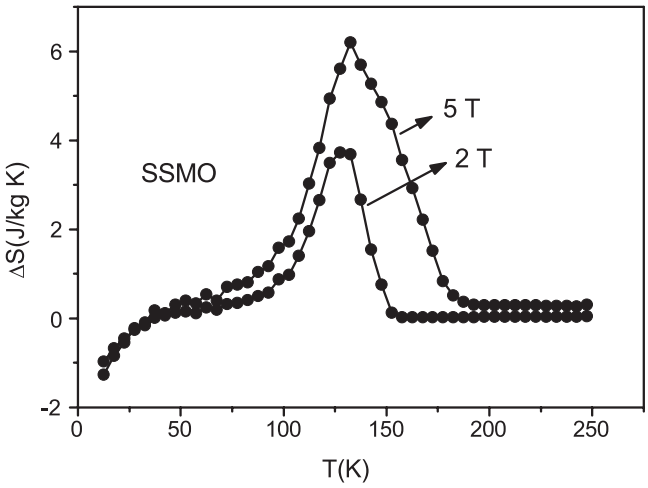

Figure 2. Entropy changes of SSMO for the field variations of 0–2 and 0–5 T.

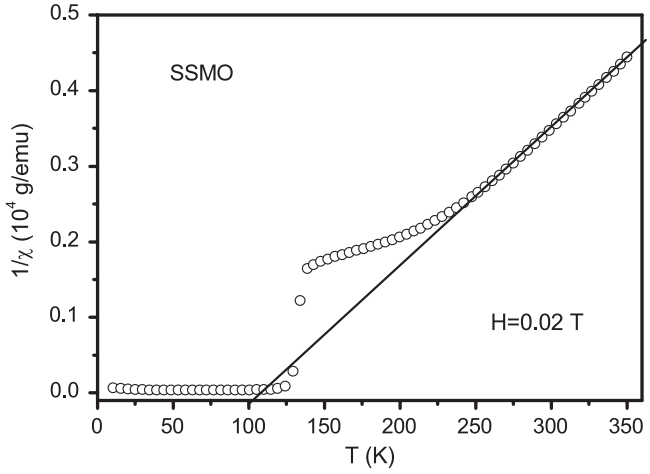

Figure 3. Reciprocal dc susceptibility as a function of temperature for SSMO under a field of 0.02 T.

Based on the mean field theory, the ultimate magnetic entropy change will be $\Delta S = Nk_{\mathrm{B}} \ln(2J + 1) \sim 56\ \mathrm{J\,kg^{-1}\,K^{-1}}$ for SSMO and ESMO without SRMO, corresponding to a transition from the fully FM state to the PM state, where the idealized value of $J = 2 \times 0.55 + 3/2 \times 0.45 = 1.775$ has been used for the calculation (2 and 3/2 are the quantum numbers of the core spins of Mn^{3+} and Mn^{4+} ions, respectively). From figure 1, it is easy to see that the peak value of ΔS is produced by the magnetization change from 0 to ∼83%. Although 83% is not a fully FM order, the expected ΔS should not be far from the theoretical result. However, the observed magnetic entropy change is only ∼12% of the theoretical value, which implies the occurrence of entropy loss during the phase transition.

There has been a lot of work on lattice and electron entropies for the first-order phase transition in an attempt to reveal the key factors affecting entropy changes, and considerable contributions from lattice entropy have been found when significant changes in phase volume occur around magnetic transition [7, 8]. The phonon and electron entropy changes in SSMO could be small because of the small magnetostriction [12]. Another important factor influencing magnetic entropy may be the SRMO of the compound, the presence of which has been confirmed by various experiments with manganites [9, 13]. To give a definite characterization

of the SRMO in SSMO, the magnetic data were carefully analyzed. It is easy to derive that the Curie–Weiss law will be $\chi = Nm(T, H)g^2J^2\mu_B^2/3k_B(T - T_\theta)$ ($mJ \gg 1$) if FM clusters of the average size of m Mn ions exist, where $g = 2$ is the Landé factor, T_θ is the PM Curie temperature, N is the number of Mn ions in 1 g SSMO and J and k_B have the conventional meanings. It is found that, above the temperature for the charge-ordering transition, the susceptibility obtained under the field of 0.02 T can be excellently fitted by the modified Curie–Weiss law using the parameters $T_\theta \approx 110.7$ K and $m \approx 8$ (figure 3) if the effective magnetic moment of the Mn ion is set to $gJ\mu_B = 3.55\ \mu_B$ (the weighted average of Mn^{3+} and Mn^{4+}). This result reveals the presence of the FM clusters with an effective size of ∼8 Mn ions in the PM state.

ESMO is similar to SSMO in many aspects. For example, the average cluster size is essentially the same, ∼7–9 Mn ions for each cluster [9], and the maximum magnetization drop during the FM–PM transition is ∼85% for ESMO and ∼83% for SSMO. Although $m = 9$ was used in our previous work to fit the experimental ΔS [9], the difference is not significant if $m = 8$ is adopted. Differences also exist between ESMO and SSMO. The low-temperature magnetic state is FM for SSMO but AFM for ESMO. The Curie temperature of SSMO is also much higher than that of ESMO (∼170 K versus ∼112 K under the field of 5 T), which will strongly affect the thermal spin fluctuation near T_C. It is therefore worthwhile comparing the SRMO effects in SSMO and ESMO.

To get a clear concept about the effects of SRMO, it will be helpful to compare the experimental and theoretical entropy changes. Based on the mean field theory, magnetic entropy corresponds to an exclusive magnetic value, that is to say, a relation between magnetic entropy and magnetization can be established [7, 9]:

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

where $\Delta\sigma$ is the normalized magnetization change that can be derived from the relation $\Delta\sigma = \sigma - 0 = B_J(x)$ and $B_J(x)$ is the Brillouin function with $x = gJ\mu_B(H + \lambda\sigma)/k_BT$. With the magnetization being experimentally determined, the theoretical magnetic entropy can be obtained, based on equation (1), as a function of temperature and magnetic field. Figure 4 (top panel) shows a comparison of the theoretical and experimental entropy changes for a field change of 2–5 T (the latter is obtained by directly subtracting $|\Delta S(2\ \mathrm{T})|$ from $|\Delta S(5\ \mathrm{T})|$). Without SRMO, the expected ΔS is ∼20.6 J kg^{-1} K^{-1}, which is much larger than the measured value ∼4.2 J kg^{-1} K^{-1}, though the temperatures where ΔS peaks are similar (∼142 K versus ∼150 K). As discussed above, FM clusters in the PM phase can prevent the complete release of magnetic entropy when the system enters into the PM state. In the presence of Mn clusters, the theoretical relation between ΔS and $\Delta\sigma$ can be obtained by substituting (N/m) and (mJ) for N and J, respectively, in equation (1). A direct calculation reveals that the theoretical ΔS decreases rapidly with the increase of cluster size m, and a good agreement with the experimental results is obtained when m is set to 8: not only the peak value but also the temperature dependence of ΔS are well reproduced (inset in the top panel of figure 4). Noting the fact that the effects of non-collinear spin arrangements in the cluster and cluster size distribution are not considered in our calculation, the agreement between theoretical and experimental results is satisfactory. The theoretical description is applicable only to the PM phase, which may explain the appearance of a visible discrepancy below T_C (marked by the arrowheads in the inset plot).

Similar analyses were performed for the ESMO compound, for which the ΔS corresponding to the field change of 3–5 T was considered. As shown by the bottom panel

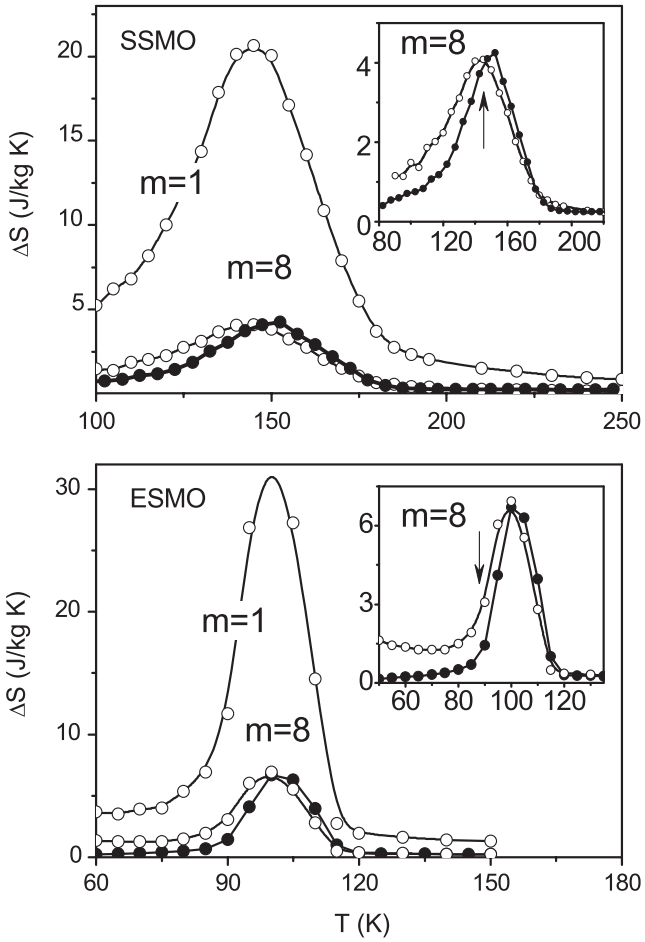

Figure 4. Entropy changes determined by experiments (solid circles) and mean field theory (open circles) with two cluster sizes of $m = 1$ and 8 for SSMO under a field variation of 2–5 T (top panel) and for ESMO under a field variation of 3–5 T (bottom panel). The inset plots show the close views of the entropy change as a function of temperature. The arrowheads mark the Curie temperature.

of figure 4 and the inset plot, the experimental results are reproduced when the cluster size is $m \approx 8$.[3]

To avoid the difficulty of the determination of spontaneous magnetization, here the entropy changes corresponding to the field change of 2–5 T (3–5 T), instead of 0–5 T, are considered. However, the conclusions obtained are general.

It is easy to see that the ultimate entropy change will be $\Delta S = (Nk_B/m)\ln(2mS + 1)$ when FM clusters of the size of m exist in the PM phase. A direct calculation proves that $(Nk_B/m)\ln(2mS + 1) < Nk_B \ln(2S + 1)$. It is interesting to note that the cluster size that reproduces the experimental ΔS is close to that suggested by the susceptibility data. This could be an accidental coincidence. However, it is obvious that the bigger the cluster is, the smaller the entropy change will be.

[3] Although the Maxwell relation fails to give the correct entropy change for ESMO for a field change from 0 to 5 T [14], it works when the field changes from 3 to 5 T. The reason is the depression of the AFM transition in the low-temperature range by the fields above 2.5 T.

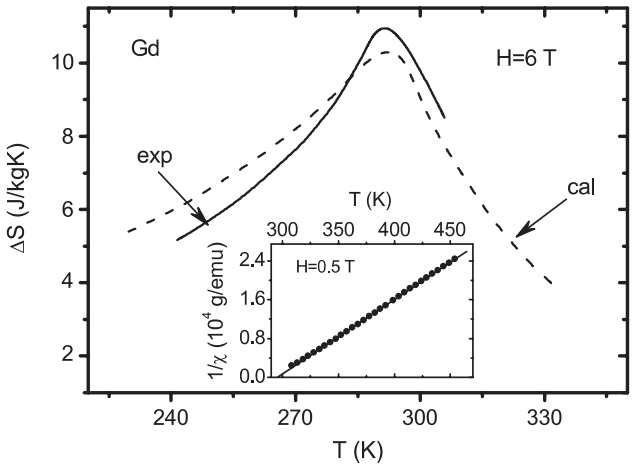

Figure 5. Entropy change of Gd for a field variation of 0–6 T. Solid and dashed lines denote the experimental and theoretical results, respectively [10]. Inset plot shows the reciprocal susceptibility of Gd as a function of temperature measured under a field of 0.5 T.

These analyses show that the $\Delta S(T, H)$ relation can be well reproduced by considering the presence of SRMO in the compound, which reveals the strong effect of SRMO on entropy change. The depression of entropy change due to SRMO is general, occurring in compounds with different magnetic behaviors. These effects are similar to those discussed by Wasilewski in the frame of spin-wave-like excitation of magnetization above T_C [15].

It is natural to ask what would happen without SRMO. The rare-earth metal Gd is a well known material showing significant MCE near the ambient temperature. We measured the magnetization of Gd under a field of 0.5 T in the temperature interval from ∼300 to ∼450 K. (A high magnetic field was used to eliminate the influence of the sample holder and other undesired effects.) A susceptibility analysis based on the Curie–Weiss law gives an effective magnetic moment of ∼8 μ_B, in good agreement with the expected value 7.63 μ_B within experimental errors (inset plot in figure 5). Considering the negligible lattice entropy change around the magnetic transition, Gd is an ideal sample to contrast with SSMO and ESMO.

In fact, the entropy change of Gd has been calculated based on the mean field theory, and compared with the experiment results by Tishin, and the results are shown in figure 5 [10]. The agreement of the two sets of data is satisfactory: the theoretical calculation well reproduces the ΔS–T relation. This result is interesting in the sense that it demonstrates the effectiveness of the mean field theory in describing the magnetic entropy of the compounds without SRMO.

Since the discovery of the giant entropy change in $Gd_5Si_xGe_{4-x}$ series, much effort has been devoted to the exploration of the materials showing strong MCE. There are many factors that affect the entropy of those materials that experience a first-order phase transition. There is obvious evidence for the significant contributions of lattice entropy change to MCE [7, 8]. It is therefore necessary to find out the key factors that affect the MCE of the materials. The present work reveals the dominant role of SRMO in modifying the MCE of the materials. This result is important considering the fact that SRMO is a general feature of magnetic materials, especially for those materials with an inhomogeneous exchange [16, 17], and its effects on entropy change have not been well understood [15, 16]. Another interesting topic is how to release magnetic entropy when SRMO exists, which would be possible if a technique that destroys the SRMO could be found.

In conclusion, the effects of short-range magnetic order (SRMO) on magnetic entropy changes have been studied for the compounds $Sm_{0.55}Sr_{0.45}MnO_3$, $Eu_{0.55}Sr_{0.45}MnO_3$ and the rare-earth metal Gd. Ferromagnetic clusters composed of ∼8 Mn ions are found to be formed in the paramagnetic phase of the manganites based on the analysis of susceptibility. As a result,

the entropy change for a field variation of 0–5 T is ∼6 J kg^{-1} K^{-1} for $Sm_{0.55}Sr_{0.45}MnO_3$ and ∼7 J kg^{-1} K^{-1} for $Eu_{0.55}Sr_{0.45}MnO_3$, well below the values expected without considering the effect of SRMO. (The maximum entropy change will be ∼56 J kg^{-1} K^{-1} for both compounds.) Assuming the presence of sizable magnetic clusters, the field-induced entropy change, not only its peak value but also its temperature dependence, can be well reproduced by the mean field theory. The average cluster size is found to be $m \approx 8$, in agreement with the result obtained from the Curie–Weiss analysis of the susceptibility. The presence of the SRMO reduces the entropy change by ∼80%. In contrast, the mean field theory gives a good description of the entropy change in Gd, for which no significant SRMO is observed. The present work reveals the important role of SRMO in modifying the magnetocaloric properties of magnetic materials.

Acknowledgments

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References

[1] Pecharsky V K and Gschneidner K A Jr 1997 *Phys. Rev. Lett.* **78** 4494
[2] Giguère A, Foldeaki M, Ravi Gopal B, Chahine R, Bose T K, Frydman A and Barclay J A 1999 *Phys. Rev. Lett.* **83** 2262
[3] Pecharsky V K and Gschneidner K A Jr 1998 *Advances in Cryogenic Engineering* vol 43, ed P Kittel (New York: Plenum) p 1729
[4] Provenzano V, Shapiro A J and Shull R D 2004 *Nature* **429** 853
[5] Chen Y F, Wang F, Shen B G, Hu H X, Sun J R, Wang G J and Cheng Z H 2003 *J. Phys.: Condens. Matter* **15** L161
[6] Tegus O, Brück E, Buschow K H and de Boer F R 2002 *Nature* **415** 150
Wada H and Tanabe Y 2001 *Appl. Phys. Lett.* **79** 3302
[7] Jia L, Liu G J, Sun J R, Zhang H W, Hu F X, Dong C, Rao G H and Shen B G 2006 *J. Appl. Phys.* **100** 123904
[8] Morellon L, Arnold Z, Magen C, Ritter C, Prokhnenko O, Skorokhod Y, Algarabel P A, Ibarra M R and Kamarad J 2004 *Phys. Rev. Lett.* **93** 137201
[9] Jia L, Liu G J, Wang J Z, Sun J R and Shen B G 2006 *Appl. Phys. Lett.* **89** 122515
[10] Tishin A M 1990 *Cryogenics* **30** 127
[11] Fisher L M, Kalinov A V, Voloshin I F, Babushkina N A, Khomskii D I, Zhang Y and Palstra T T M 2004 *Phys. Rev.* B **70** 212411
Luzyanin I D, Ryzhov V A, Chernyshov D Yu, Kurbakov A I, Trounov V A, Lazuta A V, Khavronin V P, Larionov I and Dunaevsky S M 2001 *Phys. Rev.* B **64** 094432
[12] Kurbakov A I, Lazuta A V, Ryzhov V A, Trounov V A, Larionov I I, Martin C, Maignan A and Hervieu M 2005 *Phys. Rev.* B **72** 184432
Luzyanin I D, Ryzhov V A, Chernyshov D Yu, Kurbakov A I, Trounov V A, Lazuta A V, Khavronin V P, Larionov I and Dunaevsky S M 2001 *Phys. Rev.* B **64** 094432
[13] De Teresa J M, Ibarra M R, Algarabel P, Morellon L, García-Landa B, Marquina C, Ritter C, Maignan A, Martin C, Raveau B, Kurbakov A and Trounov V 2002 *Phys. Rev.* B **65** 100403
[14] Liu G J, Sun J R, Wang J Z and Shen B G 2006 *Appl. Phys. Lett.* **89** 222503
[15] Wasilewski W 1981 *Phys. Lett.* A **84** 80
Wasilewski W 1982 *Phys. Lett.* A **92** 99
[16] Ouyang Z W, Pecharsky V K, Gschneidner K A Jr, Schlagel D L and Lograsso T A 2006 *Phys. Rev.* B **74** 094404
[17] Sun J Z, Krusin-Elbaum L, Gupta A, Xiao G and Parkin S S P 1996 *Appl. Phys. Lett.* **69** 1002
Borges R P, Ott F, Thomas R M, Skumryev V, Coey J M D, Arnaudas J I and Ranno L 1999 *Phys. Rev.* B **60** 12847
Burgy J, Mayr M, Martin-Mayor V, Moreo A and Dagotto E 2001 *Phys. Rev. Lett.* **87** 277202
De Teresa J M, Ibarra M R, Algarabel P, Morellon L, García-Landa B, Marquina C, Ritter C, Maignan A, Martin C, Raveau B, Kurbakov A and Trounov V 2002 *Phys. Rev.* B **65** 100403
Deisenhofer J, Braak D, Krug von Nidda H-A, Hemberger J, Eremina R M, Ivanshin V A, Balbashov A M, Jug G, Loidl A, Kimura T and Tokura Y 2005 *Phys. Rev. Lett.* **95** 257202