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Field-tuned magnetocaloric effect in metamagnetic manganite system

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We have investigated the origin of the huge magnetocaloric effect in a manganite system with ferro–antiferromagnetic phase mixture at low temperatures. We carried out magnetic measurements in fields up to 100 kOe in order to show that both a high hysteretic behavior and a metamagnetic transition in the antiferromagnetic state are responsible for the large magnetic entropy change. The temperature where the maximum of the magnetic entropy change occurs can be tuned by varying the maximum value of the applied magnetic field to the system. This last procedure can open a new perspective for charge-ordered manganite applications to magnetic refrigeration at low temperatures. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1827926]

Extensive research about the magnetocaloric effect (MCE) has being carried out over the last decades,[1] and nowadays the main goal is related to its potential for magnetic refrigeration.[2] The MCE in paramagnets or ferromagnets is characterized by an increasing (decreasing) temperature of the magnetic material when it is submitted to a positive (negative) magnetic field change. Quantitatively, this effect is directly related to the magnetic entropy change ΔS_{mag} and the adiabatic temperature change $\Delta T_{\mathrm{adiab}}$, that are minimum near the Curie temperature T_C of the material.[3] Usually, the desired magnetocaloric properties are obtained by changing the stoichiometry and composition of the sample, in such way controlling the magnetic transition temperature and the value of ΔS_{mag} and $\Delta T_{\mathrm{adiab}}$. This imposes serious restrictions to the use of the single materials in the Ericsson cycle, where ΔS_{mag} must be as constant as possible in the desired temperature range of refrigeration, in order to avoid energy losses. In order to overcome this problem, a composite material based on a collection of the single materials with slightly different T_C has been proposed. However, ΔS_{mag} observed in composite systems is several times smaller than those presented by a single magnetic material.[4]

Among the magnetic materials potentially useful for magnetic cooling devices, manganites are reported in the literature as promising, due to its low cost of preparation, nonactive chemical property (no oxidation), high electric resistance and, obviously, the high values of magnetic entropy change.[5–9] In addition, some manganites present a coexistence of ferromagnetic (FM) and antiferromagnetic (AFM) phases. In this sense, $\mathrm{Pr}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ manganites are of particular interest, presenting a strong phase coexistence around $x=0.30$ and a charge-ordering phenomenon for $0.30<x<0.90$ as well as colossal magnetoresistence.[10]

The samples of the series with $x=0.20$, 0.25, 0.32 were prepared by the conventional ceramic route with the following pure stoichiometric quantities: $\mathrm{Pr}_2\mathrm{O}_3$ (99.99%) CaCO_3 (>99%), and MnO_2 (>99%). The stoichiometric mixture was heated in air, with five cycles of crushing and pressing. To complete the fabrication process, the powder was compressed and sintered in air at 1350 °C for 45 h. All samples with phase coexistence have presented a large MCE. In this letter, hereafter, we focus on the sample with $x=0.32$ on which we have observed the largest MCE.

The lattice parameters obtained from Rietveld analysis are $a=5.4379(5)$ Å, $b=5.4607(6)$ Å, and $c=5.4399(5)$ Å. This analysis confirmed the orthorhombic structure of *Pbnm* space group.[11] Below 210 K, the sample is charge ordered, and for temperatures lower than the Neel temperature ($T_N=113$ K) an antiferromagnetic arrangement arises. Below a critical temperature (T^*), successive ferromagnetic/antiferromagnetic sheets coexist[12] in a cabbage structure with the degradation of the charge-ordering.[13]

Figure 1(a) shows a characteristic fully saturated hysteresis curve, after a zero field cooling (ZFC), for $T=25\ \mathrm{K}<T^\star$. The behavior of this curve can be described as follows: from zero up to 10 kOe we have mainly the contribution of the intrinsic multidomain FM sheets that tend to saturate in the magnetic applied field. Beyond this FM saturation and up to 25 kOe we have the coexistence of FM single-domain and AFM phases. The susceptibility of the latter is primarily responsible for the slope of the magnetization curve observed in this range of magnetic field. For higher values of magnetic field, there is the onset of an irreversible metamagnetic transition, which has the microscopic effect of decreasing (increasing) gradually the thickness of the AFM (FM) sheets, until the system reaches a fully FM metallic phase, with $M_{\mathrm{sat}}=107$ emu/g. In addition, we define a critical magnetic field H_{SF}, that represents the inflection point in the metamagnetic transition of the M versus H isotherm curve.

Taking advantage of the isothermal irreversibility, we measured several M versus H curves up to a certain value of magnetic field H_{max}. Actually, we followed the approach of stopping the isothermal magnetization at the beginning of the metamagnetic transition; this procedure enabled us to access a new initial magnetic state for each subsequent isothermal

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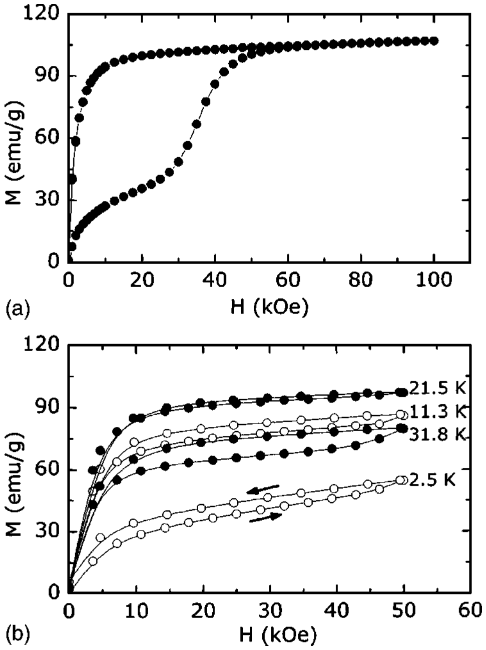

FIG. 1. (a) Isotherm magnetization curve at 25 K and up to 100 kOe, presenting the complete irreversible metamagnetic transition. (b) Isotherm magnetization curves for several values of temperature and up to the beginning of the metamagnetic transition.

curve as we increased the temperature. For instance, the measurements performed in fields up to 50 kOe, which are shown in Fig. 1(b). Note the unusual behavior of magnetization, which increases for higher values of temperature. It is a consequence of the above-noted procedure that gradually increases the proportion of the FM phase. In other words, each isothermal magnetization curve transforms a small amount of AFM phase into FM phase, increasing the FM fraction for the next M versus H curve. This effect is cumulative up to a critical temperature T_0, above which the isothermals are reversible. For the case in Fig 1(b), with $H_{\mathrm{max}}=50$ kOe, $T_0=21.5$ K. At this temperature, the sample is almost completely saturated, as can be observed. For $T>T_0$, the thermal energy contribution starts to reduce the alignment induced by the magnetic field, and the system returns to the AFM phase.

The magnetic entropy change ΔS_{mag} can be derived from the Maxwell relations, and can be written as follows:

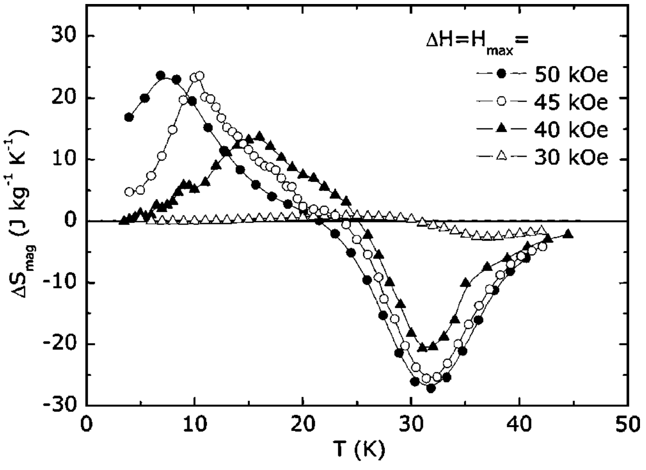

FIG. 2. Magnetic entropy change for several values of $H_{\mathrm{max}}=\Delta H$.

TABLE I. Maxima and minima values of ΔS_{mag} and the corresponding temperatures.

H_{max} (kOe)	T^{max} (K)	$\Delta S_{\mathrm{mag}}^{\mathrm{max}}$ (J kg^{-1} K^{-1})	T^{min} (K)	$\Delta S_{\mathrm{mag}}^{\mathrm{min}}$ (J kg^{-1} K^{-1})
30	23.0	0.97	37.0	−2.6
40	16.0	13.7	31.0	−20.7
45	10.0	23.2	31.4	−25.7
50	6.9	23.6	31.8	−27.2

$$\Delta S_{\mathrm{mag}}(T,H)=\int_0^H\left(\frac{\partial M}{\partial T}\right)_H dH. \tag{1}$$

Figure 2 presents the mentioned quantity as a function of temperature, for several values of $H_{\mathrm{max}}=\Delta H=30$, 40, 45, and 50 kOe. The position of the maximum and vanishing ΔS_{mag} are dependent on H_{max}, whereas the minimum is not (see Table I). These features can be analyzed in terms of the FM–AFM phase coexistence and the ratio between these phases when submitted to different values of H_{max}.

Subtracting the AFM linear susceptibility from each isothermal magnetization curve, we are able to access a presaturation value of the FM phase, related to each H_{max}. The ratio of the values of this presaturation (before the metamagnetic transition) and the fullsaturation (after the metamagnetic transition, $M_{\mathrm{sat}}=107$ emu/g), is a direct measure of the FM fraction present in the system (for such temperature and H_{max}), and are shown in Fig. 3. This figure also includes the ZFC case ($H_{\mathrm{max}}=90$ kOe), in which the system is always warmed up to room temperature, and then zero field cooled between the magnetization isotherms. This procedure provides the intrinsic FM–AFM phase coexistence, contrary to the case of direct and successive M versus H isotherms, where the fraction of coexisting phases can be controlled through the value of H_{max}. In the $H_{\mathrm{max}}=30$ kOe case, the percentage of FM phase is not significantly changed because the maximum value of magnetic applied field is not sufficiently large to reach the onset of the metamagnetic transition, therefore not producing the accumulation of the ferromagnetic phase. It is interesting to note the remarkable change in the ferromagnetic fraction for the cases in which

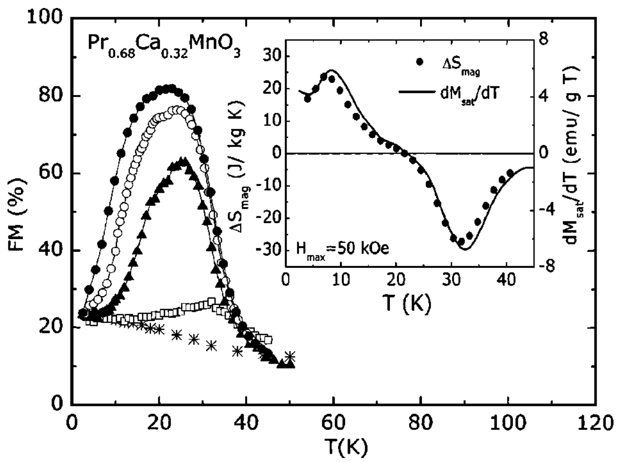

FIG. 3. Ferromagnetic fraction as a function of temperature for several values of H_{max}, including the ZFC case. Inset: Comparison between ΔS_{mag} and derivative of the FM curve obtained with $H_{\mathrm{max}}=50$ kOe.

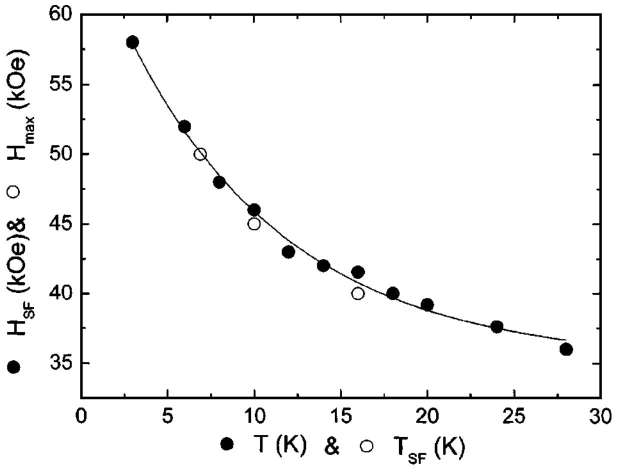

FIG. 4. T_{sf} as a function of H_{max}, as well as the temperature dependence of H_{sf}, the inflection point in the ZFC isotherms.

the H_{max} is increasing inside the metamagnetic transition.

Three characteristic temperatures emerge from the ferromagnetic fraction curves: T_{sf}, here defined as the inflection point at lower temperature. Since this temperature is connected to the huge increase of the FM fraction, at a first glance we can interpret it as an AFM→FM transition critical temperature. Moreover, this temperature corresponds to the one where H_{sf} assumes the exact value of H_{max}, and also can be identified as the maximum in $\Delta S_{mag}(T)$. (see the inset in Fig. 3). As suggested by Tishin *et al.*,[14] a maximum in $\Delta S_{mag}(T)$ corresponds to a transition with the same character of the one proposed here, corroborating our interpretation. The second temperature, that we can remark from theses curves, is the one that corresponds to the maximum. The obvious interpretation for this temperature is that it is associated with the maximum amount of the FM phase that can be accumulated by the system, as early defined T_0, and it corresponds to the temperature for which the isothermal curve presents full reversible behavior [as for the 50 kOe example, see Fig. 1(b)]. The last critical temperature that could be identified from the FM fraction curves is the temperature of the inflection point at higher temperature, which is associated with a decrease of the FM fraction. This temperature can be interpreted as a transition of the FM phase back to the AFM one. This temperature is the same as the minimum of the $\Delta S_{mag}(T)$ (see the inset in Fig. 3). In analogy to the way of defining T_C from M versus T with a nonzero applied magnetic field, we can define this inflection point as $T^{\star}$. Here again, the sign of this feature in the $\Delta S_{mag}(T)$ curve is in agreement with the prediction of Ref. 14. As expected for this kind of transition, this temperature is not field dependent.

Due to the energy balance between Zeeman and thermal energy, both T_{sf} and T_0 are dependent on H_{max}, and this fact plays a significant role for MCE applications. In this direction, in Fig. 4 we shown T_{sf} as a function of H_{max}, as well as the temperature dependence of H_{sf}, the inflection point in the ZFC isotherms. Note the wide range of temperatures (5 up to 30 K), in which the maximum of ΔS_{mag} can lie, by simply varying H_{max}.[15] This behavior can be used alternatively to the composites, and there useful for technological applications. In addition, with a suitable magnetic cycle it will be possible to take advantage of the huge maximum (positive) and minimum (negative) values of ΔS_{mag}, and also considering they can be made closer to each other, if required.

The magnetocaloric effect in $Pr_{0.68}Ca_{0.32}MnO_3$ reveals a rich means of understanding the magnetic phases at low temperatures. The high values of the magnetic entropy change, as well as the full control of the temperature where it occurs, make this material promising for magnetic refrigeration at low temperatures. The same behavior is expected to be present in any system that shows a metamagnetic transition. A future challenge is to find magnetic systems that present the same behavior around room temperature.

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