Field-tuned magnetocaloric effect in metamagnetic manganite system

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(Received 21 April 2004; accepted 28 September 2004)

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 been carried out over the last decades, and nowadays the main goal is related to its potential for magnetic refrigeration. The MCE in paramagnets or ferromagnets is characterized by an increasing temperature as promising, due to its low cost of preparation, non-magnetic cooling devices, manganites are reported in the literature of the magnetic material when it is submitted to a 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.

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. Below 210 K, the sample is charge ordered, and for temperatures lower than the Neel temperature \( (T_N = 113 \text{ K}) \) an antiferromagnetic arrangement arises. Below a critical temperature \( (T') \), successive ferromagnetic/antiferromagnetic sheets coexist in a cabbage structure with the degradation of the charge-ordering.

Figure 1(a) shows a characteristic fully saturated hysteresis curve, after a zero field cooling (ZFC), for \( T = 25 \text{ K} < T' \). 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 \( M_{sat} = 107 \text{ emu/g} \). In addition, we define a critical magnetic field \( H_{sr} \) 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.
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 $H_{\text{max}}=50$ 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 $\Delta S_{\text{mag}}$ can be derived from the Maxwell relations, and can be written as follows:

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

Figure 2 presents the mentioned quantity as a function of temperature, for several values of $H_{\text{max}} = \Delta H=30, 40, 45, \text{and } 50 \text{ kOe}$. The position of the maximum and vanishing $\Delta S_{\text{mag}}$ are dependent on $H_{\text{max}}$, 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 $H_{\text{max}}$.

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 $H_{\text{max}}$. The ratio of the values of this presaturation (before the metamagnetic transition) and the fullsaturation (after the metamagnetic transition, $M_{\text{sat}}=107 \text{ emu/g}$), is a direct measure of the FM fraction present in the system for such temperature and $H_{\text{max}}$, and are shown in Fig. 3. This figure also includes the ZFC case ($H_{\text{max}}=90$ 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 $H_{\text{max}}$. In the $H_{\text{max}}=30$ 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

<table>
<thead>
<tr>
<th>$H_{\text{max}}$ (kOe)</th>
<th>$T_\text{max}$ (K)</th>
<th>$\Delta S_{\text{mag}}^{\text{max}}$ (J kg$^{-1}$ K$^{-1}$)</th>
<th>$T_\text{min}$ (K)</th>
<th>$\Delta S_{\text{mag}}^{\text{min}}$ (J kg$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>23.0</td>
<td>0.97</td>
<td>37.0</td>
<td>-2.6</td>
</tr>
<tr>
<td>40</td>
<td>16.0</td>
<td>13.0</td>
<td>31.0</td>
<td>-20.7</td>
</tr>
<tr>
<td>45</td>
<td>10.0</td>
<td>23.2</td>
<td>31.4</td>
<td>-25.7</td>
</tr>
<tr>
<td>50</td>
<td>6.9</td>
<td>23.6</td>
<td>31.8</td>
<td>-27.2</td>
</tr>
</tbody>
</table>

Figure 3. Ferromagnetic fraction as a function of temperature for several values of $H_{\text{max}}$, including the ZFC case. Inset: Comparison between $\Delta S_{\text{mag}}$ and derivative of the FM curve obtained with $H_{\text{max}}=50$ kOe.
the $H_{\text{max}}$ is increasing inside the metamagnetic transition.

Three characteristic temperatures emerge from the ferromagnetic fraction curves: $T_{\text{sf}}$, 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 transition critical temperature. Moreover, this temperature corresponds to the one where $H_{\text{sf}}$ assumes the exact value of $H_{\text{max}}$, and also can be identified as the maximum in $\Delta S_{\text{mag}}(T)$, (see the inset in Fig. 3). As suggested by Tishin et al., a maximum in $\Delta S_{\text{mag}}(T)$ corresponds to a transition with the same character of the one proposed here, corroborating our interpretation.

The second temperature, that we can remark from these 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 $T_{\text{sf}}$, 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 $\Delta S_{\text{mag}}(T)$ (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 $T^*$. Here again, the sign of this feature in the $\Delta S_{\text{mag}}(T)$ 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 $T_{\text{sf}}$ and $T_{\text{sf}}$ are dependent on $H_{\text{max}}$, and this fact plays a significant role for MCE applications. In this direction, in Fig. 4 we show $T_{\text{sf}}$ as a function of $H_{\text{max}}$, as well as the temperature dependence of $H_{\text{sf}}$, the inflection point in the ZFC isotherms. Note the wide range of temperatures (5 up to 30 K), in which the maximum of $\Delta S_{\text{mag}}$ can lie, by simply varying $H_{\text{max}}$. 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 $\Delta S_{\text{mag}}$, 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.

The authors would like to thank P. B. Tavares for assistance during the sample preparation and L. Ghivelder for the help in the measurements. The authors also acknowledge FCT/Portugal (POCTI/CTM/35642/00), ICCTI/CAPES in Brasil-Portugal bilateral collaboration, CT-Petro/CNPq and Faperj for financial support.