Inverse magnetocaloric effect in polycrystalline \( \text{La}_{0.125}\text{Ca}_{0.875}\text{MnO}_3 \)

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Abstract

Recently the inverse magnetocaloric effect has been observed in different compounds. However, it is very rare for any manifestation of the effect to be seen in manganites. We have found the inverse magnetocaloric effect in the case of polycrystalline \( \text{La}_{0.125}\text{Ca}_{0.875}\text{MnO}_3 \). Such a phenomenon is attributed to the stabilization of the antiferromagnetic state associated with inherent magnetic inhomogeneous phases for this compound.

(Some figures in this article are in colour only in the electronic version)

The magnetocaloric effect (MCE) has been a subject of intense research owing to its possible application in magnetic refrigeration [1–18]. It has been widely observed that magnetic entropy reduces with the application of magnetic field for different materials, including some paramagnetic salts [1]. The cooling can be possible by utilizing those materials subject to exposure in a magnetic field followed by adiabatic demagnetization. However, there has been a recent report on the discovery of materials with an inverse situation in which the magnetic configuration entropy increases due to the application of the magnetic field [4]. Such an effect is known as the inverse magnetocaloric effect (IMCE). For the materials exhibiting IMCE, the attaining of low temperature can be possible by only just magnetizing them adiabatically [4]. Some of the examples of such materials are NiMnSn, FeRh, TbNiAl, DySb, Tb$_2$Ni$_2$Sn, NiMnSb, etc [4, 19–25]. The materials which show IMCE can be used as a heat-sink for heat generated when the magnetic configuration entropy increases due to the application of the magnetic field [4].

The refrigeration efficiency can be enhanced by using materials exhibiting IMCE in composites with conventional magnetic refrigerants [4]. Therefore searching for suitable materials, which display IMCE, is an important issue in the ongoing research related to magnetic refrigeration. Our present study is based on the magnetocaloric property of polycrystalline \( \text{La}_{0.125}\text{Ca}_{0.875}\text{MnO}_3 \). We have observed IMCE with quite a large change of magnetic entropy (\( -\Delta S \)) in this compound.

The perovskite manganites with general formula \( \text{R}_{1-x}\text{B}_x\text{MnO}_3 \) (R is rare-earth, B is a bivalent ion) are considered potential magnetic refrigerants [2, 13–17]. \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) is a manganite system, which has a very rich phase diagram depending on the values of \( x \) [26]. Although some works regarding the magnetocaloric properties of this system with \( x \sim 0.2–0.5 \) have been reported, there is hardly any such study for high doping concentration of bivalent ion [2]. In fact, little attention has been paid to the study of MCE for other manganite systems in the high doping region (i.e. a high value of \( x \)). We have chosen \( \text{La}_{0.125}\text{Ca}_{0.875}\text{MnO}_3 \) for two main reasons. Firstly, it is a system with a high doping concentration of bivalent ions. Secondly, its position in the phase diagram of \( \text{La}_{0.1-x}\text{Ca}_x\text{MnO}_3 \) is at a phase boundary between antiferromagnetic (AFM) and canted antiferromagnetic (CAF) phases [26]. Therefore this compound provides an opportunity to study the effect of the phase boundary on the magnetocaloric properties of a system as well.

The polycrystalline \( \text{La}_{0.125}\text{Ca}_{0.875}\text{MnO}_3 \) was prepared by the sol–gel method. The details of the sol–gel method have been described in our previous article [29]. At the end of the sol–gel process, the decomposed gel was annealed at 1400 °C for 36 h. The x-ray powder diffraction study has confirmed the formation of the sample with a single crystallographic phase with PNMA space group. The lattice parameters are determined as, \( a = 5.347 \text{ Å}, b = 7.442 \text{ Å}, \) and \( c = 5.318 \text{ Å} \).

A commercial SQUID magnetometer was utilized for the magnetization study. The temperature dependence of dc susceptibility (figure 1) shows clear antiferromagnetic...
transition at \( \sim 120 \text{ K} \). The transition temperature is consistent with the phase diagram of the sample [26]. The magnetization measurement has been performed in the presence of 100 Oe magnetic field in a zero field cooled protocol. We have also carried out a specific heat study using the semi-adiabatic heat pulse method. The transition is manifested by the observed maxima in the temperature dependence of specific heat as well (inset of figure 1).

The isothermal magnetic field dependence of magnetization \([M(H)]\) at different temperatures has been studied for the sample (figure 2). To get intricate details of \( M(H) \), we have examined Banerjee’s plot [30] i.e. \( H/M \) versus \( M^2 \) behavior around the transition temperature (inset figure 2). The negative slope of Banerjee’s plot is evident in the high magnetic field region (above \( \sim 35 \text{ kOe} \)), which is characteristic of a first-order transition [30]. From the isothermal \( M(H) \) curves, the change of the magnetic entropy (\( -\Delta S \)) was estimated for various magnetic fields by using Maxwell’s relation [1],

\[
\left( \frac{\partial S}{\partial H} \right)_T = \left( \frac{\partial M}{\partial T} \right)_H. 
\]

The temperature dependence of \( -\Delta S \) for different magnetic fields is shown in figure 3. A minimum in \( -\Delta S(T) \) has been observed at \( \sim 120 \text{ K} \), where antiferromagnetic transition occurs. One important feature of \( -\Delta S(T) \) is that the value of \( -\Delta S \) remains negative for all the magnetic fields at the transition temperature for this sample. The negative value of \( -\Delta S \) increases with the increase of magnetic field (i.e. the magnetic configuration entropy increases) and it reaches \( \sim -6.4 \text{ J kg}^{-1} \text{ K} \) for the magnetic field change 0–70 kOe. The increase of the negative value of \( -\Delta S \) with magnetic field at the transition temperature is shown in inset (b) of figure 3. From the magnetocaloric behavior of the sample, it seems that although there is a change of slope in Banerjee’s plot at high magnetic field, the antiferromagnetism still exists in the field up to \( \sim 70 \text{ kOe} \). Recently, Ranke et al, put forward a theoretical framework of the magnetocaloric properties of an antiferromagnetic system [31]. The temperature dependence of \( -\Delta S \) for \( \text{La}_{0.125}\text{Ca}_{0.875}\text{MnO}_3 \) follows that theoretical model quite convincingly. Previously, we have also observed small negative \( -\Delta S \) at antiferromagnetic transition temperature for other manganite systems at magnetic field below the required field for quenching the antiferromagnetism [14].

Now a question arises about the origin of the enhancement of magnetic configuration entropy with the increase of magnetic field. According to the phase diagram (temperature
versus $x$) of La$_{1-x}$Ca$_x$MnO$_3$, La$_{0.125}$Ca$_{0.875}$MnO$_3$ is situated at the phase boundary between the antiferromagnetic and inhomogeneous canted antiferromagnetic (CAF) states [26]. It is obvious that the CAF phase may have an influence on the magnetic state of the sample, as a result of which the magnetically inhomogeneous phase with mixed magnetic exchange interactions can be stabilized at the antiferromagnetic transition temperature. The enhancement of the magnetic configuration entropy with the application of magnetic field can occur for such a system giving rise to IMCE [4] with a large value of $-\Delta S$. We have also studied the magnetocaloric property of another La$_{1-x}$Ca$_x$MnO$_3$, with a slightly different value of $x$ ($x \sim 0.83$). That sample is of polycrystalline form and is prepared under similar conditions to La$_{0.125}$Ca$_{0.875}$MnO$_3$. IMCE is also observed for that compound at its antiferromagnetic transition temperature (inset (a), figure 3). However, the value of $-\Delta S$ is considerably less for La$_{0.175}$Ca$_{0.83}$MnO$_3$ in comparison with La$_{0.125}$Ca$_{0.875}$MnO$_3$. According to the phase diagram of La$_{1-x}$Ca$_x$MnO$_3$, the magnetic transition in the case of La$_{0.175}$Ca$_{0.83}$MnO$_3$ is paramagnetic to antiferromagnetic, in which case there is no influence of the CAF phase [26]. From the comparison of the magnetocaloric properties of the two compounds, it can be argued that the presence of the magnetically inhomogeneous CAF state plays a vital role in IMCE and the magnetic entropy change becomes significantly enhanced because of the influence of such a state.

To summarize, we have observed IMCE in the case of polycrystalline La$_{0.125}$Ca$_{0.875}$MnO$_3$ with a large value of $-\Delta S$ at the antiferromagnetic transition temperature. Possibly the stabilization of the inhomogeneous magnetic state for this compound at its antiferromagnetic transition temperature causes the increase in magnetic entropy in the presence of magnetic field. The observation of the enhancement of magnetic configuration entropy with the increase of magnetic field is very rare especially for manganites.

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