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Experiment, mean field theory and Monte Carlo simulations of the magnetocaloric effect in $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ compound

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ABSTRACT

Magnetic properties and magnetocaloric effect (MCE) of the $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ compound are studied by means experiment, mean field theory and Monte Carlo simulations (MCSs). The temperature dependence of the magnetic entropy change and of the adiabatic temperature is also obtained. We have used the experiment results, mean field theory and MCSs. The Curie temperature of $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ compound has been deduced. The field dependence of relative cooling power (RCP) of $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ compound has been given.

1. Introduction

Perovskite-type manganites with the general formula $LaAMn_{1-x}T_xO_3$ (A: divalent alkali element such as Ba, Sr, Ca etc, and T=Fe, Co, Ti, etc,) have many important effects for example magnetocaloric effect (MCE), colossal magnetoresistance (CMR) effect, charge ordering, orbital ordering, isotope effect, etc, have been observed by introduction of the rare earth or alkaline earth ions in to the A-sites, these behaviors of original probably occurs in the systems due to the mixed-valence state of Mn^{3+}/Mn^{4+}. Which explains, a large number of study have been devoted to the substitution of Mn-site by other elements preferably 3d-ferromagnetic transition metals [1–3].

The magnetocaloric effect in $NdMnO_3$ perovskite is investigated using the Monte Carlo simulations [4] and Mn_2NiAl is studied by ab initio calculations and Monte Carlo simulations [5]. The magnetic entropy change (ΔS_M) and the critical exponents in the double perovskite manganite Y_2NiMnO_6 with a ferromagnetic to paramagnetic transition T_C = 85 K have been investigated by experiment measurement [6]. The measurements of the heat exchanged along the hysteresis loop and the return branches of barium ferrite of composition $BaFe_{12}O_{19}$ have been discussed by Ref. [7]. Nevertheless, the MCE in these simple is defined by the isothermal magnetic entropy change (ΔS_M) or the adiabatic temperature change (ΔT_{ad}) that is a function of magnetic field and temperature. There are three principal methods to assess MCE. The first one direct measurements of adiabatic temperature change (ΔT_{ad}) is carried out by exposing a thermally insulated material to the magnetic field. The second one based on Maxwell equations, it is possible to calculate the ΔS_M starting from magnetization measurements. Finally heat capacity measurements respectively in the following two cases: magnetic fields zero and non-zero magnetic fields, both are used to calculate ΔS_M and ΔT_{ad} thanks to determining the context of the total entropy. In an experimental study [8,9], the ferroelectric properties of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films have studied.

In this paper, we investigate based on the mean field theory and from a classical measurement of the variation of the magnetization as a function of temperature M(T), it is possible to estimate if our new compounds exhibits significant magnetocaloric properties or not. To compare our results with the other results, we have used the Monte Carlo simulation to study the magnetic entropy change and the adiabatic temperature of $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ compound. The Curie temperatures of this compound have been obtained. The relative power cooling of $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ compound has been also found [10,11].

2. Experiment technical

The perovskite manganites $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ were prepared by sol-gel method. Stoichiometric ratio of La_2O_3, MnO_2, BaO and SrO (99.9% purity) were initially dissolved excellently in nitric acid (HNO_3) and distilled water to obtain a homogeneous mixture. The solution was then heated between 80 and 90 °C on a hotplate under constant stirring to eliminate the excess nitric and to obtain a homogeneous solution. Then, ethylene glycol $(CH_2OH)_2$ and citric acid $C_6H_8O_7$ were added under thermal agitation to obtain a viscous gel. The gel was then dried

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at 300 °C and calcinated at 600 °C for 5 h resulting in fine powder. Finally, the obtained powders were ground and mixed evenly in a mortar for 10 min and then compressed into pellets 12 mm in diameter and 2 mm thick. The pellets of $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ compound were finally sintered at 1100 °C for 3 h.

The structural information was obtained by XRD studies on Siemens D5000 X-ray diffractometer, with monochromatized Cu Ka1 radiation in the 2θ range of 20–80°. The X-ray diffractometer pattern has been analysed using Rietveld technique employing the Fullproof Suite program [12] using the *Pnma* space group.

The magnetic as a function of temperature M(T) and the isothermal magnetization curves M(H) in applied magnetic fields up to 6 T were obtained using the SQUID (Quantum Design) unit at Louis Neel Laboratory of Grenoble. Isothermal curves around the ferromagnetic ordering transition temperature (T_C) of the samples were obtained in steps of 0.05 T, and temperature variations of 2–5 K between successive isotherms. The temperature dependence of the magnetocaloric effect MEC was calculated from the isothermal magnetization measurements versus applied magnetic fields up to 5 T.

3. Theoretical and model

3.1. Mean field theory

A rapid and simple procedure for the determination of the MEC especially in magnetic materials like our sample, both experimental and theoretical approaches was used. According to the phenomenological model (Mean field theory) [13], the variation of magnetization with temperature and Curie temperature T_C is presented by:

$$M(T) = \frac{M_i - M_f}{2}\tanh(A(T_c - T)) + BT + C \tag{1}$$

M_i/M_f is an initial/final value of magnetization at ferromagnetic–paramagnetic transition as shown in Fig. 1;

The parameters A, B and C are given by:

$$\begin{cases} A = \frac{2(B - S_C)}{M_i - M_f} \\ B = \left(\frac{dM}{dT}\right)_{T \approx T_i} \\ S_C = \left(\frac{dM}{dT}\right)_{T = T_C} \\ C = \frac{M_i + M_f}{2} - BT_C \end{cases} \tag{2}$$

The parameters B and S_c are the magnetization sensitivity $\frac{dM}{dT}$ at the ferromagnetic state before transition and at Curie temperature T_C, respectively.

From the expression (1) of M(T), we can obtain:

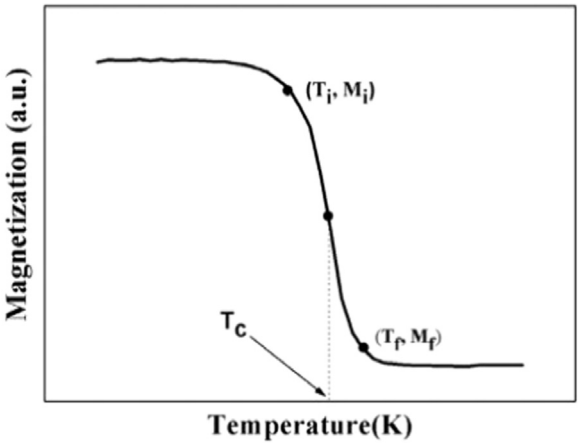

Fig. 1. (Color online) Temperature dependence of magnetization for $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ compound under constant applied field.

Magnetic entropy change:

$$\Delta S_M = \int_0^{H_{Max}} \left(\frac{\partial M}{\partial T}\right)_H dH \tag{3}$$

From where [10]:

$$\Delta S_M = H_{Max}\left(-A\frac{M_i - M_f}{2}\mathrm{sech}^2(A(T_C - T)) + B\right) \tag{4}$$

Relative cooling power (RCP) based on magnetic entropy change

$$RCP = -(\Delta S_M)_{Max} * \delta T_{FWHM} \tag{5}$$

Maximum entropy change obtained at T = T_C is given by:

$$(\Delta S_M)_{Max} = \Delta S_M(T = T_C) = H_{\max}\left(-A\frac{M_i - M_f}{2} + B\right) \tag{6}$$

Full width at half maximum δT_{FWHM} is given by [14,15]:

$$\delta T_{FWHM} = \frac{2}{A}\cosh^{-1}\left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}}\right) \tag{7}$$

where from [16,17]:

$$RCP = H_{MAX}\left(M_i - M_f - 2\frac{B}{A}\right)\cosh^{-1}\left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B)}}\right) \tag{8}$$

Magnetization-related change of the specific heat at constant pressure and field [18,19]:

$$\Delta C_{p,H} = T\left(\frac{\Delta S_M}{\Delta T}\right)_{p,H} \tag{9}$$

where from

$$\Delta C_{p,H} = TA^2H_{\max}(M_i - M_f)\tanh(A(T_C - T))\mathrm{sech}^2(A(T_C - T)) \tag{10}$$

3.2. Ising model

Starting with the well known Ising model, the Hamiltonian of the system is given by:

$$H' = -J_1\sum_{<i,j>} S_iS_j - J_2\sum_{<<i,k>>} S_iS_k - H\sum_i S_i^z \tag{11}$$

In this work we consider the nearest neighbour (*nn*) and next nearest neighbour (*nnn*) interactions J_1 and J_2 respectively. The values of J_1 = 42.5 and J_2 = 37.5 K are obtained using the mean field theory [20]. H is the external magnetic field applied in z-direction and $\vec{S}_{i(j\ or\ k)}$ is the spin operator localized at the site i(j or k) and the magnetic moment of Mn^{3+} is S = 2.

4. Monte Carlo simulations

The standard sampling MC simulation has been applied to simulate the Hamiltonian given by Eq. (11) for $La_{0.6}7Ba_{0.22}Sr_{0.11}MnO_3$. The MCs update was performed by choosing random spins and then flipped from current state S_i to opposite state -S_i with Boltzmann based probability. This can be done using the Metropolis algorithm (MA) [21] i.e. $P_{metro} = \exp(-\Delta E/k_BT)$, where ΔE is the energy difference between the before and the after flip and $\beta = 1/(k_BT)$ where T denotes the absolute temperature and k_B is the Boltzmann's constant. However, since the actual MA suffers from large correlation time especially close to the critical point [22]. The cyclic boundary conditions on the structure were imposed and the configurations were generated by sequentially traversing the structure and making single-spin flip attempts. Then, the next 10^4 configurations were also taken for the extraction of the magnetization per spin of Mn in $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$. The magnetization of $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$ compound is: