Journal of Alloys and Compounds 504 (2010) 12–15

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Determination of the spontaneous magnetization by analysis of the magnetic entropy change in $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$

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ARTICLE INFO

Article history:
Received 21 April 2010
Received in revised form 12 May 2010
Accepted 21 May 2010
Available online 27 May 2010

Keywords:
Perovskites
Magnetocaloric effect
Magnetic entropy
Spontaneous magnetization

ABSTRACT

The magnetic phase transition and magnetic entropy change ($-\Delta S_M$) in the $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$ perovskite were investigated by measuring the magnetization as a function of temperature. The ferromagnetic transition temperature T_C and the critical exponents β and γ, determined by analyzing the Arrott plots, are found to be $T_C = 191$ K, $\beta = 0.433$, $\gamma = 1.053$ and $\delta = 3.486$. These values for the critical exponents are close to the mean-field values. In order to estimate the spontaneous magnetization $M_s(T)$ at a given temperature, we use a process based on the analysis, in the mean-field theory, of the magnetic entropy change ($-\Delta S_M$) versus the magnetization data. An excellent agreement is found between the spontaneous magnetization determined from the entropy change (($-\Delta S_M$) vs. M^2) and the classical extrapolation from the Arrott curves ($\mu_0 H/M$ vs. M^2), thus confirming that the magnetic entropy is a valid approach to estimate the spontaneous magnetization in this system and in other compounds as well.

1. Introduction

In recent years, magnetic materials with large magnetocaloric effect (MCE) have been extensively studied both experimentally and theoretically due to their great potential applications in magnetic refrigeration [1,2]. The MCE manifests itself as the isothermal magnetic entropy change (ΔS_M) or the adiabatic temperature change (ΔT_{ad}) when a magnetic material is exposed to a varying magnetic field [3]. The MCE can be estimated via the magnetic entropy change $\Delta S_M(T,\mu_0 H)$ as a function of both temperature (T) and magnetic field ($\mu_0 H$), being usually recorded as a function of temperature at a constant $\mu_0 H$.

Significant advances have been made in interpreting the magnetocaloric properties of materials. In fact, the large magnetic entropy change in perovskite manganites is believed to originate from the role of spin–lattice coupling in the magnetic ordering process [4]. Due to strong coupling between spin and lattice, significant lattice change accompanying the magnetic transition in perovskite manganites has been observed [5–7]. The use of phenomenological theories has given us valuable insight in this matter [8–11]. The Landau theory for phase transitions is applied to describe the MCE in ferromagnetic systems with magnetoelastic and magnetoelectronic couplings [12–14]. Moreover, the mean-field theory has established direct relations between magnetic entropy change and magnetization. Whereas, the theory of critical phenomena justifies the existence of a universal magnetocaloric behavior in materials presenting second-order magnetic phase transitions [15,16]. Many experimental studies of critical behavior have been made on some manganites [17–19]. Thus, the critical exponents can supply some useful information about the PM–FM transition.

Therefore, in order to understand the nature of the magnetic transition in $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$, we performed the investigation of the critical behavior of this sample, where the carrier concentration Mn^{3+}/Mn^{4+} and Mn^{3+}/Cr^{3+} are fixed at a ratio of 4/3. In our previous work [20], the magnetic measurements showed a small magnetization of the $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$ sample, in which the moment of Nd^{3+} ions did not contribute to the total moment compared to the total moment of the ferromagnetic (Mn/Cr) network. Consequently, in mean-field model, we utilize the isothermal magnetic entropy change ($-\Delta S_M$) in the $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$ perovskite, obtained from isothermal magnetization measurements, to estimate the spontaneous magnetization of the sample. The results of this approach are compared to results obtained from classical analysis (extrapolation from Arrott curves [21]).

2. Experimental

Polycrystalline $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$ was synthesized by the conventional solid-state reaction method in air [20]. Identification of the crystalline phase and structural analysis were carried out using "PANalytical X'Pert Pro" diffractometer with filtered (Ni filter) Cu radiation ($\lambda_{Cu\ K\alpha 1} = 1.54056$ Å) in Bragg angle range

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doi:10.1016/j.jallcom.2010.05.091

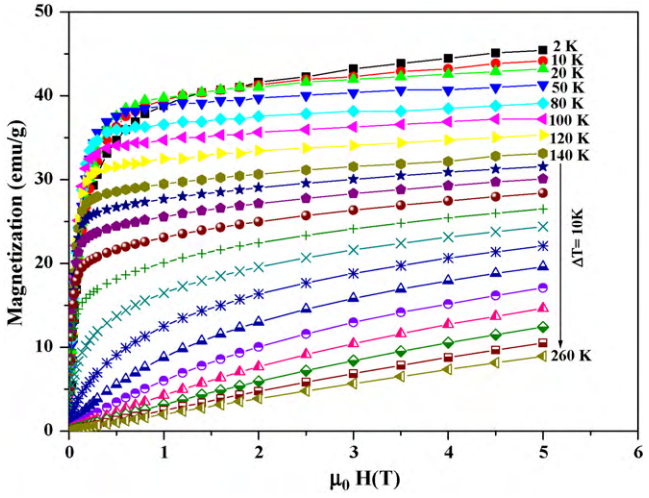

Fig. 1. Isothermal magnetization of $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$ measured at given temperatures.

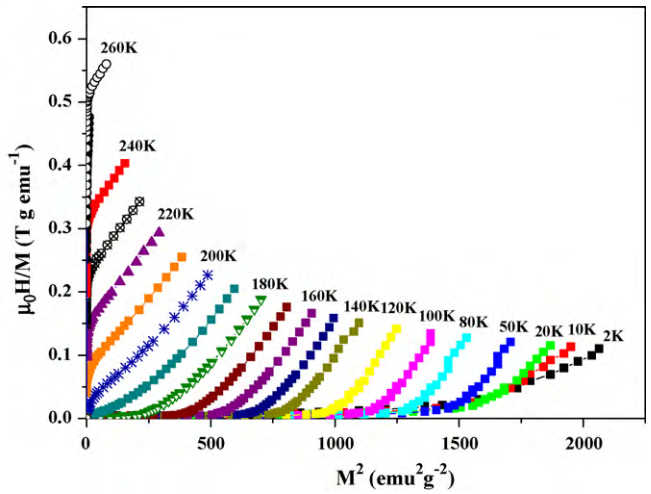

Fig. 2. Arrott plots ($\mu_0 H/M$ vs. M^2) of isothermal magnetization of $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$.

$20^\circ \leq 2\theta \leq 120^\circ$. The data were analyzed by the Rietveld method. Magnetization (M) versus magnetic field ($\mu_0 H$), varying from 0 to 5 T at different temperatures (T), was measured using a MPMS-XL5 Quantum Design SQUID Susceptometer.

3. Results and discussion

Identification of the phase and structural analysis by X-ray diffraction were reported elsewhere [20]. The Rietveld refinement at room temperature revealed the presence of two phases. The major phase, corresponding to $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$ (98.38 wt.% fraction), crystallizes in the orthorhombic structure with *Pbnm* space group. The minority phase (1.62 wt.% fraction), $Ia\bar{3}$ space group, was related to the presence of unreacted Nd_2O_3. Lattice parameters of the perovskite phase are $a = 5.4912(1)$ Å, $b = 5.4517(1)$ Å, $c = 7.7056(2)$ Å, and a cell volume of 230.68(6) Å^3.

The temperature dependence of the magnetization of the field-cooled (FC) and zero-field-cooled (ZFC) modes has been reported by us elsewhere [20]. They show a transition from a ferromagnetic (FM) to a paramagnetic (PM) state at a Curie temperature T_C. Fig. 1 shows the magnetic field dependence of the isothermal magnetization curves $M(T,\mu_0 H)$ at various temperatures, from 2 to 260 K. In order to get a deeper insight of the magnetic transition, the so-called Arrott plots of $\mu_0 H/M$ versus M^2 are presented in Fig. 2. All Arrott plots exhibit a positive slope, indicating that the transition between the ferromagnetic and paramagnetic phases is a second-order transition [22].

In order to understand the nature of the second-order magnetic phase transition near the Curie point, we used Arrott plots to determine the Curie temperature and the critical exponents in the vicinity of the phase transition temperature. The exponents β and γ can be obtained from spontaneous magnetization (M_s) and initial susceptibility (χ_0), below and above T_C, respectively, while δ is the critical isotherm exponent. Those exponents from magnetization measurements are given below [21,23]:

$$M_S(T) = M_0|\varepsilon|^{\beta}, \qquad \varepsilon < 0, \qquad T < T_C \tag{1}$$

$$\chi_0^{-1}(T) = \left(\frac{h_0}{M_0}\right)\varepsilon^{\gamma}, \qquad \varepsilon > 0, \qquad T > T_C \tag{2}$$

$$M = DH^{1/\delta}, \qquad \varepsilon = 0, \qquad T = T_C \tag{3}$$

where $\varepsilon = (T - T_C)/T_C$ is the reduced temperature and M_0, (h_0/M_0) and D are the critical amplitudes.

From the Arrott plots in Fig. 2, the curves below and above T_C can be extended smoothly into the $\mu_0 H/M$ axis to yield reliable values of the $M_s(T,0)$ and $\chi_0^{-1}(T)$. The exponent δ is obtained from the slope of the log(M) versus log($\mu_0 H$) plot at T_C.

By extrapolating the Arrott plots to $\mu_0 H/M = 0$ for $T < T_C$ and $M^2 = 0$ for $T > T_C$, the spontaneous magnetization $M_s(T)$ and the inverse initial susceptibility ($\chi_0^{-1}(T)$) values have been recovered. These results are displayed in Fig. 3. By fitting these data to Eqs. (1) and (2) we obtain $T_C = 191$ K, $\beta = 0.433$ and $\gamma = 1.053$.

In Fig. 4, the critical isotherms M versus $\mu_0 H$ are plotted on a log–log scale at $T = 190$ K, which is close to the T_C. According to Eq. (3), this should be a straight line in the high-field region with the slope $1/\delta$. This gives the δ value of 3.486.

The critical exponents from this static scaling analysis are related to the Widom scaling relation $\delta = 1 + \gamma/\beta$ [24]. Using this relation and the estimated values of β and γ (obtained above) from the mean-field method, we obtain $\delta = 3.432$. This result is around to the estimated $\delta = 3.486$ value obtained from the critical isotherms at 190 K. Thus, the Widom scaling relation is a good tool to check the reasonability of the critical exponents from the experimental data. Moreover, we can note that these values for the critical exponents are close to the mean-field values ($\beta = 0.5$, $\gamma = 1$ and $\delta = 3$) [15]. Hence, we believe that the mean-field model applies very well to our experimental data.

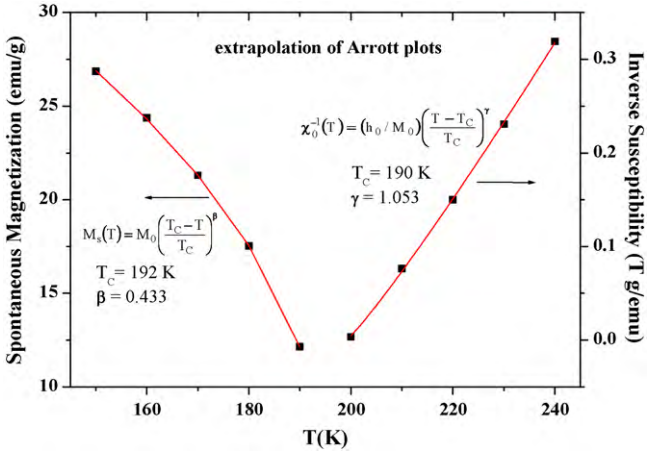

Fig. 3. Spontaneous magnetization and inverse initial susceptibility of $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$, deduced from extrapolation of the Arrott plots ($\mu_0 H/M$ vs. M^2) to $\mu_0 H = 0$ and $M^2 = 0$, respectively. The solid lines are the best fits to Eqs. (1) and (2) in the text.

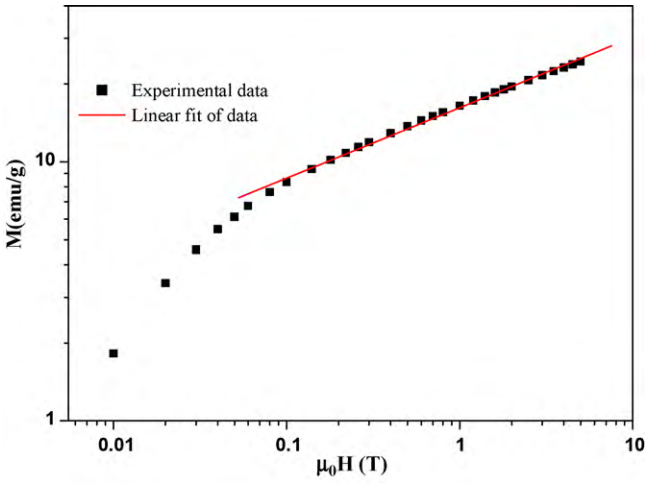

Fig. 4. Critical isotherm on a log–log scale for $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$ at 190 K.

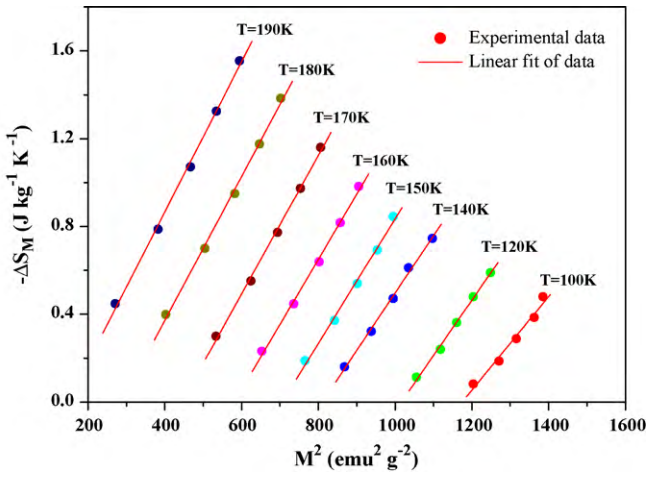

Fig. 5. Isothermal $(-\Delta S_M)$ vs. M^2 curves for $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$. Solid lines are linear fits to data.

An attempt to a theoretical modeling of the spontaneous magnetization issued from a mean-field analysis of the magnetic entropy change was done by Amaral et al. [25]. The dependence of the magnetic entropy $S(\sigma)$ on the relative magnetization can be described in the mean-field theory by [25,26]:

$$S(\sigma) = -Nk_B\left[\ln(2J+1) - \ln\left(\frac{\sinh(((2J+1)/2J)B_J^{-1}(\sigma))}{\sinh((1/2J)B_J^{-1}(\sigma))}\right) + B_J^{-1}(\sigma)\sigma\right] \quad (4)$$

where N is the number of spins, J the spin values, k_B the Boltzmann constant, σ the relative magnetization ($\sigma = M/(g\mu_B JN)$) [10] and B_J the Brillouin function for a given J value.

From a power expansion of Eq. (4), ΔS_M is proportional to M^2 and, from the mean-field model, for small M values [25,27]:

$$-S(\sigma) = \frac{3}{2}\frac{J}{J+1}Nk_B\sigma^2 + 0(\sigma^4) \quad (5)$$

Furthermore, the compound has a spontaneous magnetization below T_C (ferromagnetic state) and consequently the $\sigma = 0$ state is never attained. Explicitly, and considering only the first term of the expansion of Eq. (4), this corresponds to:

$$-\Delta S(\sigma) = \frac{3}{2}\frac{J}{J+1}Nk_B(\sigma^2 - \sigma_s^2) \quad (6)$$

Such result shows that the isothermals $(-\Delta S_M)$ versus M^2 in the ferromagnetic region exhibit a linear variation. By fitting the $(-\Delta S_M)$ versus M^2 curves to $M^2 = 0$ for $T < T_C$, the spontaneous magnetization $M_s(T)$ values have been obtained while, for $T > T_C$, the $(-\Delta S_M)$ versus M^2 plots start at a null M value. Moreover, the slope of $(-\Delta S_M)$ versus M^2 is independent of temperature and is equal to 1/2 of the inverse Curie constant C ($C = (Ng^2\mu_B^2 J(J+1))/3k_B$) [28].

On the other hand, by estimating the accompanying magnetic entropy change, ΔS_M, commonly found through the use of the well known Maxwell relation, it can be assessed:

$$\Delta S_M(T, \mu_0 H) = S(T, \mu_0 H) - S(T, 0) = \int_0^{\mu_0 H}\left(\frac{\partial M}{\partial T}\right)_H \mu_0\, dH \quad (7)$$

This approach utilizes the same isothermal magnetization versus applied field data of Fig. 1.

From the magnetization and the $(-\Delta S_M)$ data $(-\Delta S_M)$ versus M^2 plots are obtained (Fig. 5), showing a clear linear dependence with an approximately constant slope throughout the ferromagnetic region. The obtained slope is approximately 32.8, corresponding to a Curie constant of 0.0152 (emu K T^{-1} g^{-1}). The spontaneous magnetization ($M_s(T)$) is then estimated, and compared to the results obtained from the Arrott curves, as shown in Fig. 6. The

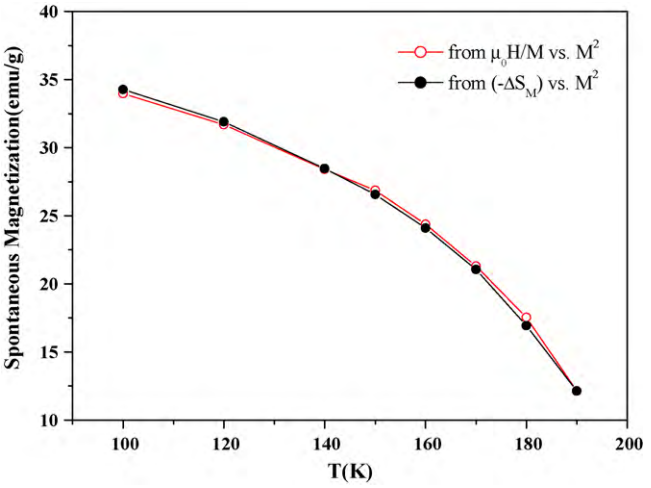

Fig. 6. Spontaneous magnetization of $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$, estimated from the extrapolation of the $(-\Delta S_M)$ vs. M^2 curves (closed circles), and from the Arrott plots ($\mu_0 H/M$ vs. M^2) (open circles).

excellent agreement between the two methods allows to confirm the validity of this process to estimate the spontaneous magnetization using a mean-field analysis of the magnetic entropy change in the $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$ system. The same results are obtained in the case of $La_{0.665}Eu_{0.035}Sr_{0.30}MnO_3$ and $La_{0.638}Eu_{0.032}Ca_{0.33}MnO_3$ systems [25]. The magnetic behavior of those compounds is well described by the classical mean-field theory and might be strong correlated systems.

4. Conclusions

In this work, an excellent agreement was obtained between two different approaches to estimate the spontaneous magnetization of the $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$ perovskite, by using the isothermal data of the magnetization versus applied magnetic field. The estimated critical exponents confirm that the experimental data agree well with the mean-field model. The methodology based on the analysis of the magnetic entropy change $(-\Delta S_M)$ versus M^2, compared with the classical extrapolation of the Arrott curves ($\mu_0 H/M$ vs. M^2), confirm that the magnetic entropy change is a valid method to determine the spontaneous magnetization of the $La_{0.40}Nd_{0.30}Sr_{0.30}Mn_{0.70}Cr_{0.30}O_3$ system and eventually of other compounds.

Acknowledgement

Authors acknowledge the Tunisia–France exchange program DGRS-CNRS project no. 09//R 11-52.

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