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Magnetocaloric effect and its correlation with critical behavior in $La_{0.5}Ca_{0.4}Te_{0.1}MnO_3$ manganese oxide

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ABSTRACT

The critical behavior of $La_{0.5}Ca_{0.4}Te_{0.1}MnO_3$ compound is investigated based on the data of static magnetic measurements in the vicinity of its critical temperature T_C. The estimated critical exponents for $La_{0.5}Ca_{0.4}$ $Te_{0.1}MnO_3$ are found to be 3D-Ising model ($\beta = 0.343$ and $\gamma = 1.261$ at an average $T_C = 260$ K through various techniques such as modified Arrott plot (MAP), Kouvel–Fisher (KF) method and critical isotherm analysis (CIA). The reliability of the critical exponents' values was confirmed by the Widom scaling relation (WSR) and the universal scaling hypothesis. We noted that the critical exponents γ are almost similar to the value of the mean-field theory which can be explained by the existence of a long-range dipole–dipole interaction. Following the Harris criterion, we deduced that the disorder in our case is relevant, which could be the cause of the change in the universality class.

The magnetic phase transition and the magnetic entropy change ($-\Delta S_m$) in the $La_{0.5}Ca_{0.4}$ $Te_{0.1}MnO_3$ manganite is investigated by measuring the magnetization as a function of temperature. By investigating the field dependence of RCP and ($-\Delta S_m$), it was possible to evaluate the critical exponents of the magnetic phase transitions. Their values are in good agreement with those obtained from the critical exponents by Widom scaling relation (WSR) using the modified Arrott and Kouvel–Fisher methods.

1. Introduction

The colossal magnetoresistance (CMR) manganites with the general formula $A_{1-x}B_xMnO_3$ (where A is a rare-earth ion and B is a divalent alkali) have attracted growing attention due to their potential application in high-density magnetic heads [1–4]. The appearance of the ferromagnetic and metallic states in these systems is attributed to the double-exchange effect between the Mn^{3+} and Mn^{4+} ions and the Jahn-Teller effect [5–7]. Therefore, to understand the relationship between the insulator-metal transition and CMR effect, two substantial questions on the PM-FM transition need to be clarified: the first one deals with the phase transition order; the second one copes with the common universality class. To clarify these issues, it is important to examine the details of the critical behavior at the phase transition temperature. The critical behavior in the DE model was described first with long-range average field theory [8]. However, recent theoretical calculations have predicted that the 3D-Heisenberg model is to understand short-range interaction in manganites [9,10]. The critical-exponent analysis, is considered as a powerful tool, has been widely employed in magnetism near the PM-FM phase transition, using a variety of techniques, and has given a range of values for the critical exponent β of the magnetization [11–13]. The values range, from about 0.3 to 0.5, includes the mean-field ($\beta = 0.5$), the 3D isotropic nearest-neighbor Heisenberg ($\beta = 0.365$) and the 3D Ising ($\beta = 0.325$) estimates.

In recent years, extensive research has been carried out on the magnetocaloric effect (MCE) in manganites, which are considered to be likely candidates for magnetic refrigeration [14–20]. Nowadays, there is a need for new advanced magnetic materials with a second-order magnetic phase transition (SOMT), showing a large reversible magnetic entropy change ($-\Delta S_m$) at low applied fields. For this reason, it is necessary to know the field dependence of ($-\Delta S_m$) of a given magnetic refrigerant material. From a more fundamental perspective, understanding this field dependence may display other indices to improve the performance of refrigerant materials in a lower field range. Thus, the MCE study is not only indispensable for potential applications but it also provides a tool to understand the intrinsic properties of a material. The

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magnetic phase transition details and critical behavior, in particular, can be obtained through the magnetocaloric effect.

Recent studies reported a correlation between the MCE and critical exponents near the SOMT in magnetocaloric materials [21–23]. They also introduced a new method to evaluate the critical exponents from the field dependence of the magnetic entropy and the dependence of the exponent n with the critical exponents β, γ, and δ.

In the present work, we focus on the studies of the critical behavior in $La_{0.5}Ca_{0.4}Te_{0.1}MnO_3$ at its PM–FM transition via the detailed measurement of the dc magnetization. We found that the critical exponents for this sample are close to those theoretically predicted for the 3D-Ising model. We also investigate the field dependence of the magnetic entropy change ($-\Delta S_m$) as well as the relative cooling power RCP. The critical exponents' values are in accord with those obtained using modified Arrott plot (MAP) and Kouvel-Fisher (KF) methods.

2. Experimental details

The $La_{0.5}Ca_{0.4}Te_{0.1}MnO_3$ sample was prepared using the sol-gel method [24] and annealed in air at 1173 K for 24 h. In order to verify the percentage of Mn^{3+} and Mn^{4+} ions in $La_{0.5}Ca_{0.4}Te_{0.1}MnO_3$ sample and hence the oxygen stoichiometry, we used the conventional chemical technique. First, we dissolved our powder in oxalic acid dihydrate ($H_2C_2O_4$, $2H_2O$) and concentrated sulfuric acid (H_2SO_4). Subsequently, the resulting solutions were titrated by the potassium permanganate ($KMnO_4$). Finally, by a simple calculation based on the chemical reaction in play, we found the percentage of Mn^{4+} ions in this sample (%Mn^{4+}theoretical = 30%, %Mn^{4+}experimental = 29.2%). The results of chemical analysis confirmed well the Mn^{4+} rate in this sample and the oxygen stoichiometry. Phase purity and homogeneity were determined by X-ray diffraction (XRD) using a Siemens D5000 Diffractometer. A monochromator, in front of the detector, selected out the Cu-Kα_1 radiation (λ_{Cu} = 1.5406 Å) at room temperature in the 2θ range of 10–90° with steps of 0.02°.

Magnetization measurements versus temperature and versus magnetic applied field were carried out using a superconducting quantum interference device (SQUID) magnetometer in the temperature range from 5 to 300 K. To extract the critical exponents of the samples accurately, the magnetic isotherms for our sample were measured in the range of 0–5 T and with a temperature interval of 2 K in the vicinity of their Curie temperatures (T_C).

3. Results and discussion

Fig. 1 illustrates the observed, calculated and difference profiles for $La_{0.5}Ca_{0.4}Te_{0.1}MnO_3$ compound. The results of refinement are listed in Table 1. In this table, the residuals for the weighted pattern R_{WP}, the pattern R_P and the goodness of fit χ^2 are also reported.

The structural refinements were carried out using the FULLPROF Rietveld program [25] at room-temperature. X-ray diffraction patterns show that our sample crystallizes in the orthorhombic structure with *Pnma* space group.

The second order magnetic phase transition near the Curie point is characterized by a set of critical exponents β (associated with the spontaneous magnetization), γ (relevant to the initial magnetic susceptibility), and δ (associated with the critical magnetization isotherm) [26]. The mathematical definitions of the exponents from magnetization measurements can be defined by the following relation [27,28]:

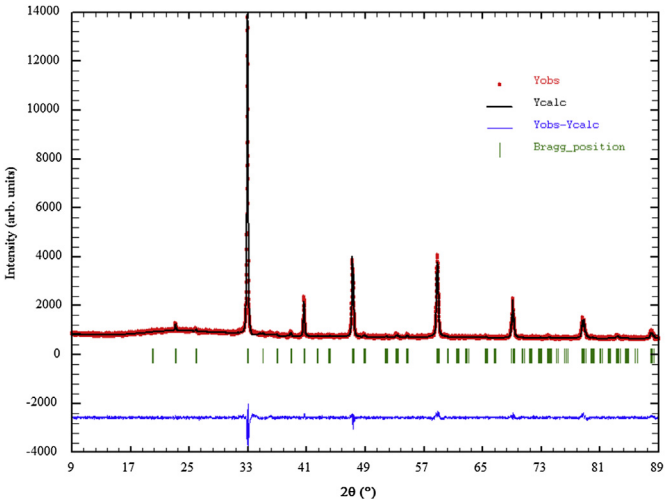

Fig. 1. Rietveld refinement for $La_{0.5}Ca_{0.4}Te_{0.1}MnO_3$. Experimental data in red, calculated data in black, difference between them in blue and Bragg positions in green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Refined structural parameters of $La_{0.5}Ca_{0.4}Te_{0.1}MnO_3$ compound.

Space group	*Pnma*
a (Å)	5.43
b (Å)	7.67
c (Å)	5.45
V (Å^3)	56.85
R_P	4.14
R_{WP}	5.53
$\chi 2$	1.93

- Below T_C, the temperature dependence of the spontaneous magnetization $M_S(T) = \lim_{H\to 0}(M)$ is governed by β exponent through the relation:

$$M_S(T) = M_0(-\varepsilon)^{\beta};\ \varepsilon<0,\quad T < T_C \tag{1}$$

- Above T_C, the inverse initial susceptibility $\chi_0^{-1}(T) = \lim_{H\to 0}(H/M)$ is given by

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

- At T_C, M and H are related by the following equation:

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

where M_S, χ_0^{-1} and $\varepsilon = (T - T_C)/T_C$ are the spontaneous magnetization, inverse initial susceptibility, and reduced temperature, respectively. M_0, h_0, and D are the critical amplitudes (constants) well describing the Eqs. (1)–(3) associated with the exponents β, γ and δ [29–31].

The magnetic equation of state is a relationship between the variables M (H, ε), H and T. From the scaling hypothesis this can be written as: