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Critical properties in Dy-doped $La_{0.7-x}Dy_xSr_{0.3}MnO_3$ (x=0.00, 0.03) manganites

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ABSTRACT

The critical properties of $La_{0.7-x}Dy_xSr_{0.3}MnO_3$ (x=0.00 and 0.03) manganites elaborated using sol-gel method have been investigated around the ferromagnetic-paramagnetic (FM-PM) phase transition. The X-ray diffraction characterizations show that the parent compound (x=0.00) crystallized in the rhombohedral structure with R-3C space group without any detectable impurity, while doped sample with (x=0.03) crystallized in the orthorhombic structure with *Pnma* space group. Various techniques such as modified Arrott plots, Kouvel-Fisher method and critical isotherm analysis were used to determine the values of the Curie temperature T_C, as well as the critical exponents β (corresponding to the spontaneous magnetisation), γ (corresponding to the initial susceptibility) and δ (corresponding to the critical magnetisation isotherm). The estimated results are close to those expected by the mean-field model for both samples. The obtained values from critical isotherm $M(T_C, \mu_0H)$ are close to those determined using the Widom scaling relation, and all data fall on two distinct branches, one for $T < T_C$ and the other for $T > T_C$, indicating that the critical exponents obtained in this work are accurate.

1. Introduction

The magnetocaloric effect (MCE) has been extensively investigated during the last twenty years, not only due to its potential applications for active magnetic refrigeration but also for further understanding the fundamental properties of the manganites materials [1–7]. The MCE has been used for many years to obtain low temperatures through adiabatic demagnetization of paramagnetic salts [8]. At present the magnetic refrigeration around room temperature is of particular interest because of potential impact on energy savings as well as environmental concerns. The observation of giant magnetoresistance (GMR) effects [9–13] in the $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Ca_xMnO_3$ compounds with low doping have revived the interest of the scientific community in such compounds due to possible technological applications.

Particularly, the $La_{0.7}Sr_{0.3}MnO_3$ compound has received much attention due to its interesting magnetic and magnetotransport properties and its promise for future technological applications [14]. Mitra et al. [15] have investigated the effect of gradually dysprosium substituting, at the lanthanum site in $La_{0.7}Sr_{0.3}MnO_3$ and Chau et al. [16] have studied the structure, magnetic and magnetocaloric properties of $La_{0.7}Sr_{0.3}MnO_3$ perovskite with small amount of Cu substitution in the Mn site. They have found that these materials exhibit maximum magnetic entropy change around Curie temperature, T_C~350 K.

Experimental studies [17,18] of the critical behaviors and the universality class around T_C have indicated that the critical exponents play important role in elucidating interaction mechanisms which are responsible for the phase transition near T_C.

The critical behavior in the double-exchange (DE) model was first described with long-range mean-field theory [19,20]. Sequentially, Motome and Furulawa suggested that the critical behavior should be attributed to short range Heisenberg model [21,22]. The experimental results are still controversial concerning the critical exponents and even the order of the magnetic transition including 3D-Heisenberg interaction [23,24], 3D-Ising values [25,26], mean field values [27] and those that cannot be classified into any universality class ever known [28].

In this paper, we focus on the critical behavior of $La_{0.7-x}Dy_xSr_{0.3}MnO_3$ (x=0.00 and 0.03) manganites using the isothermal magnetization around T_C. In view of a sizable magnetic moment of Dy^{3+} ion ($10.63\mu_B$), we think that a slight Dy-substitution for La in the A-site, not only increases some extra magnetic interactions or influences magnetic disordering, but also does not remarkably change the double-exchange effect, which is mainly responsible for the magnetic

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interaction in this system. As an external magnetic field is applied, a large magnetic disordering-ordering transition may be occurring and a considerable or large magnetic entropy change is possibly observed. Small contents of Dy have been chosen to enhance the magneto caloric properties and decrease the T_C. In the present study, the critical exponents: β below T_C, γ above T_C and δ associated with the second order transition have been determined based on various approaches including the modified Arrott plots, the Kouvel-Fisher method and the critical isotherm analysis. Using these exponents, it has been also verified that the scaling hypothesis is perfectly obeyed indicating that they are reliable.

2. Experimental techniques

$La_{0.7-x}Dy_xSr_{0.3}MnO_3$ (x=0.00 and 0.03) powder sample were synthesized using sol-gel method. Starting with La_2O_3, Dy_2O_3, $SrCO_3$ and MnO_2 precursors with high purity (up to 99.9%) according to the reaction:

$$(0.7-x)/2{*}La_2O_3 + x/2Dy_2O_3 + 0.3SrCO_3 + MnO_2 \rightarrow La_{0.7-x}Dy_xSr_{0.3}MnO_3 + \delta CO_2 + \delta' O_2$$

The stoichiometric amounts of precursors were dissolved in dilute nitric acid at 70 C and then a suitable amount of citric acid and ethylene glycol as coordinate agents were added. The resulting gel was decomposed at 300 °C to insure the propagation of a combustion which transforms the gel into a fine powder. Then, the sample was calcined at 600 C. The obtained powder was then pressed into pellets (of about 1 mm thickness under an axial pressure of 4 t for 2 min) and sintered at 900 C for 24 h to improve crystallinity.

The structure and phase purity were checked by powder X-ray diffraction (XRD) using CuKα radiation (λ=1.54059 Å) at room temperature. The pattern was recorded in the 9°≤2θ≤81° angular range with a step of 0.02°. The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) J3590 mini CFM of Cryogenics. In order to accurately extract the critical exponents of our samples, magnetization isotherms were measured in the range of 0–5 T with a temperature interval of 2 K in the vicinity of the Curie temperature (T_C).

3. Scaling analysis

According to the scaling hypothesis, the critical behavior of a magnetic system showing a second-order magnetic phase transition near the Curie point is characterized by a set of critical exponents, β, γ and δ given by the equation below.

$$M_{SP}(T) = M_0(-\varepsilon)^{\beta}; \quad \varepsilon < 0 \text{ for } T < T_C \tag{1}$$

$$\chi_0^{-1}(T) = (h_0/M_0)\varepsilon^{\gamma}; \varepsilon>0 \text{for} T > TC \tag{2}$$

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

where M_0, h_0/M_0, and D are the critical amplitudes and $\varepsilon=(T-T_C)/T_C$ is the reduced temperature. $M_{SP}(T)$,$\chi_0^{-1}(T)$ and H are the spontaneous magnetization, the inverse of the initial susceptibility and the demagnetization adjusted applied magnetic field respectively. Another independent way to determine the exponents β and γ is by using scaling theory which predicts the existence of a reduced equation of state given by:

$$M(\mu_0 H, \varepsilon)|\varepsilon|^{-\beta} = f_{\pm}(\mu_0 H|\varepsilon|^{-(\beta+\gamma)}) \tag{4}$$

where f_+ and f_- are regular analytical functions for $\varepsilon > 0$ and $\varepsilon < 0$ respectively. Eq. (4) implies that plots of $M(\mu_0 H, \varepsilon)|\varepsilon|^{-\beta}$ vs. $\mu_0 H|\varepsilon|^{-(\beta+\gamma)}$ would lead to universal curves, one for temperatures $T > T_C$ ($\varepsilon > 0$) and the other for $T < T_C$ ($\varepsilon < 0$).

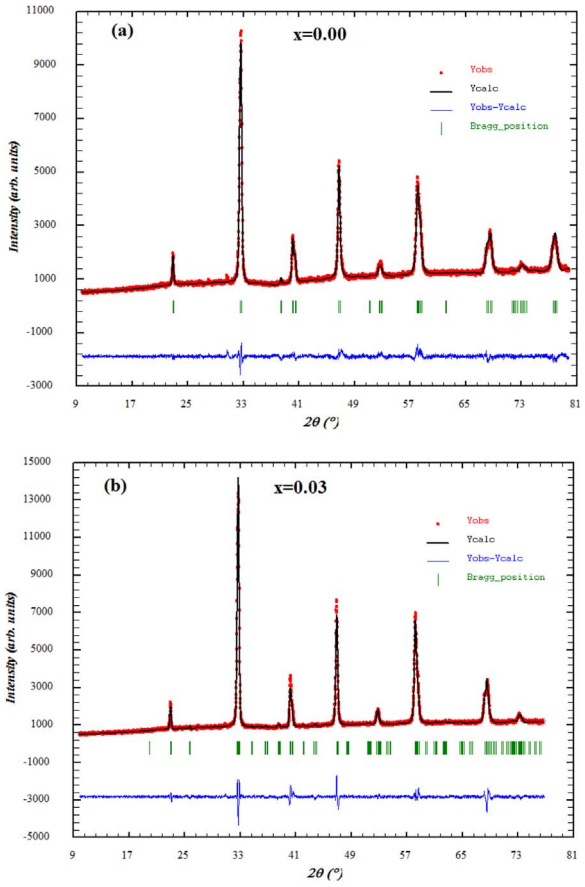

Fig. 1. Observed (the point symbols) and calculated (the solid lines) X-ray diffraction pattern for both samples. Positions for the Bragg reflection are marked by vertical bars. Differences between the observed and the calculated intensities are shown at the bottom of the diagram.

4. Results and discussions

The phase identification and the structural analysis of $La_{0.7-x}Dy_xSr_{0.3}MnO_3$ (x=0.00 and 0.03) manganites samples were carried out using the X-ray diffraction patterns recorded at room temperature. A typical X-Ray diffraction pattern of both samples is shown in Fig. 1(a-b). The two samples are single phase without any detectable impurity. We have refined the structure by the Rietveld method [29] using the Fullprof program [30]. The refinement shows that (x=0.00) crystallized in rhombohedra structure with R-3C space group and (x=0.03) crystallized in orthorhombic structure with *Pnma* space group. The measured manganite density (D) is found to be 5.462 and 5.636 g/cm^3 for (x=0.00) and (x=0.03) respectively. The XRD density (D_{XRD}) was also calculated according to the following formula [31]:

$$DXRD = \frac{Z{*}M}{AV} \tag{5}$$

where: Z: the number of manganite molecules per unit cell; M: molecular mass; A: Avogadro number and V: the unit cell volume.

The result was 6.42 and 6.51 g/cm^3 for (x=0.00) and (x=0.03), respectively. These values are in a typical range for manganites [31,32]. A comparison of the measured density (D) with the XRD density (D_{XRD}) reveals the relatively low porosity (P) defined as [31]:

$$P = 1 - \left(\frac{D}{D_{XRD}}\right) \tag{6}$$

The obtained value is 0.15 and 0.13 for (x=0.00) and (x=0.03), respectively. Such a low porosity gives evidence of the high quality of