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Influence of grain size and sintering temperature grain size on the critical behavior near the paramagnetic to ferromagnetic phase transition temperature in $La_{0.67}Sr_{0.33}MnO_3$ nanoparticles

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ABSTRACT

We have undertaken a systematic study of critical behavior in $La_{0.67}Sr_{0.33}MnO_3$ nanoparticles, sintered at different temperatures (*L6*, *L8*, *L10* and *L12* sintered at 600 °C, 800 °C, 1000 °C, 1200 °C respectively), by magnetization measurements. The critical exponents are estimated by various techniques such as the Modified Arrott plot, Kouvel–Fisher plot and critical isotherm technique. Compared to standard models, the critical exponents are close to those expected by the Mean-field model (with $\beta = 0.5$ $\gamma = 1$, and $\delta = 3$) for (*L6*, *L8*, and *L10*) samples and by the (3D) Heisenberg model ($\beta = 0.365$, $\gamma = 1.336$ and $\delta = 4.80$) for *L12* sample. We conclude that the reduction of grain size strongly influences the universality class.

1. Introduction

Nanotechnology, which involves the manipulation of matter at nanometer length scales to produce new structures and devises, has been shown to revolutionize the industry of today [1,2]. Most of the past attention has focused on nanoscale manganites with the view of exploring the various properties and technological applications at the nanoscale [3–5].

A typical example is the recent attention on nanosized perovskite manganites with the $Ln_{1-x}A_xMnO_3$ formula (where Ln and A are rare earth and alkaline earth, respectively. The properties of mixed valence manganites are expected to depend on material size due to both the nanoscale phase inhomogeneity inherent to bulk materials and additional surface [6–8]. Out of all the doped manganites, the $La_{1-x}Sr_xMnO_3$ (LSMO) nanoparticle is of a great interest, since it has very high phase transition temperature (about of 370 K) and manifests very high value of a colossal magnetoresistive (CMR) effect [9,10].

One of the most controversial issues is the universality class related to the paramagnetic (PM) to ferromagnetic (FM) transition in manganites. The universality class does not depend on microscopic details of the system, but also on global information such as the dimension of the order parameter and space [20]. The ferromagnetism and CMR of manganites have been explained with the magnetic double exchange model. The critical behavior in the double-exchange (DE) model was first described with long-range mean-field theory [11–13]. However, more recent investigations have brought forward the ferromagnetic phase transition itself [14–16]. Therefore, for better understanding of this issue, it is necessary to investigate the critical behavior at the phase transition temperature in detail. Critical phenomena in manganites have been described earlier within the framework of mean-field theory [17]. Controversy still remains on the experimental estimates pertaining to the critical exponents and even the order of the magnetic transitions including three dimensional 3D-Heisenberg interaction, 3D-Ising values, mean-field values, and those which cannot be classified into any universality class ever known [18–20]. Here, our motivation is to further understand the effect of annealing temperature and size reduction on the magnetic behavior of nanosized perovskite-type manganites, especially on the critical behavior of $La_{0.67}Sr_{0.33}MnO_3$ nanoparticle with different crystallite sizes.

2. Experimental details

Nanocrystalline sample of nominal composition $La_{0.67}Sr_{0.33}MnO_3$ were prepared according to the citrate gel method and sintered at different temperatures with the similar heat treatment as reported in Ref. [39]. Magnetic measurements were realized with the BS1 magnetometer developed at Néel Institute (CNRS-Grenoble). The isothermals *M vs. H* data used for the present survey are corrected by a demagnetization factor that has been determined by a standard

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procedure from low-field dc magnetization measurement. In fact, the internal field H used for the scaling analysis has been corrected for demagnetization, $H = H_{app} - DM$, where D is the demagnetization factor obtained from M *vs.* H measurements in the low-field linear-response regime at low temperature.

3. Scaling analysis

According to the scaling hypothesis, the second-order phase transition around the Curie point T_C could be described by the critical parameters β, γ and δ corresponding to spontaneous magnetization $M_S(T)$, inverse initial susceptibility $\chi_0^{-1}(T)$ and magnetization isotherm as given below:

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

where $\varepsilon = (T - T_C)/T_C$ and M_0 is a critical amplitude. γ is the isothermal magnetic susceptibility exponent defined as

$$\chi_0^{-1}(T) = (h_0/M_0)\varepsilon^{\gamma}, \quad \varepsilon > 0 \tag{2}$$

where χ_0^{-1} is the inverse zero-field susceptibility, and h_0 is a critical amplitude. δ is the critical isotherm exponent:

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

where H is the demagnetization adjusted applied magnetic field, and D is a critical amplitude. Note that Eqs. (1) and (2) are strictly valid in the limit $\varepsilon \to 0$, i.e., in the asymptotic critical region. Eq. (3) is valid exactly at $T = T_C$. Clearly, the accurate determination of T_C is of uttermost importance.

Moreover, these critical parameters β, γ, and δ follow Widom's scaling relation [29]:

$$\delta = 1 + \gamma/\beta \tag{4}$$

Using this scaling relation and the estimated values of β and γ, the value of δ is obtained.

In the critical region, magnetization and internal field should obey the universal scaling behavior and the magnetic equation of state can be written as:

$$M(H,\varepsilon)|\varepsilon|^{-\beta} = f_{\pm}(H|\varepsilon|^{-(\beta+\gamma)}) \tag{5}$$

where f_+ and f_- are regular analytical functions for $\Sigma > 0$ and $\Sigma < 0$ respectively.

4. Results and discussions

In Fig. 1, we plotted the isothermal magnetization curves in the vicinity of Curie temperature T_C, M *vs.* H, after correcting the external magnetic field for demagnetizations effects. These curves reveal a gradual ferromagnetic (*FM*)-to-paramagnetic (*PM*) transition [21]. The saturation of magnetization is not fully reached. This behavior which was found in other compounds [21], is characteristic of samples without true long-range-order ferromagnetism.

Conventional method to determine the critical exponents and critical temperature involves the use of Arrott plot [22]. In accordance with this method, M^2 vs. H/M isotherms near T_C of our system should show a series of parallel lines and the line for $T = T_C$ passes through the origin. It can be mentioned that Arrott plot assumes the critical exponents following mean-field theory ($\beta = 0.5$, $\gamma = 1$, $\delta = 3$). These curves (M^2 vs. H/M isotherms) give a positive slope in the complete M^2 range, which confirms that our samples exhibit a second-order PM-FM phase transition, according to the Banerjee criterion [23]. Hence, linear behavior of isotherms

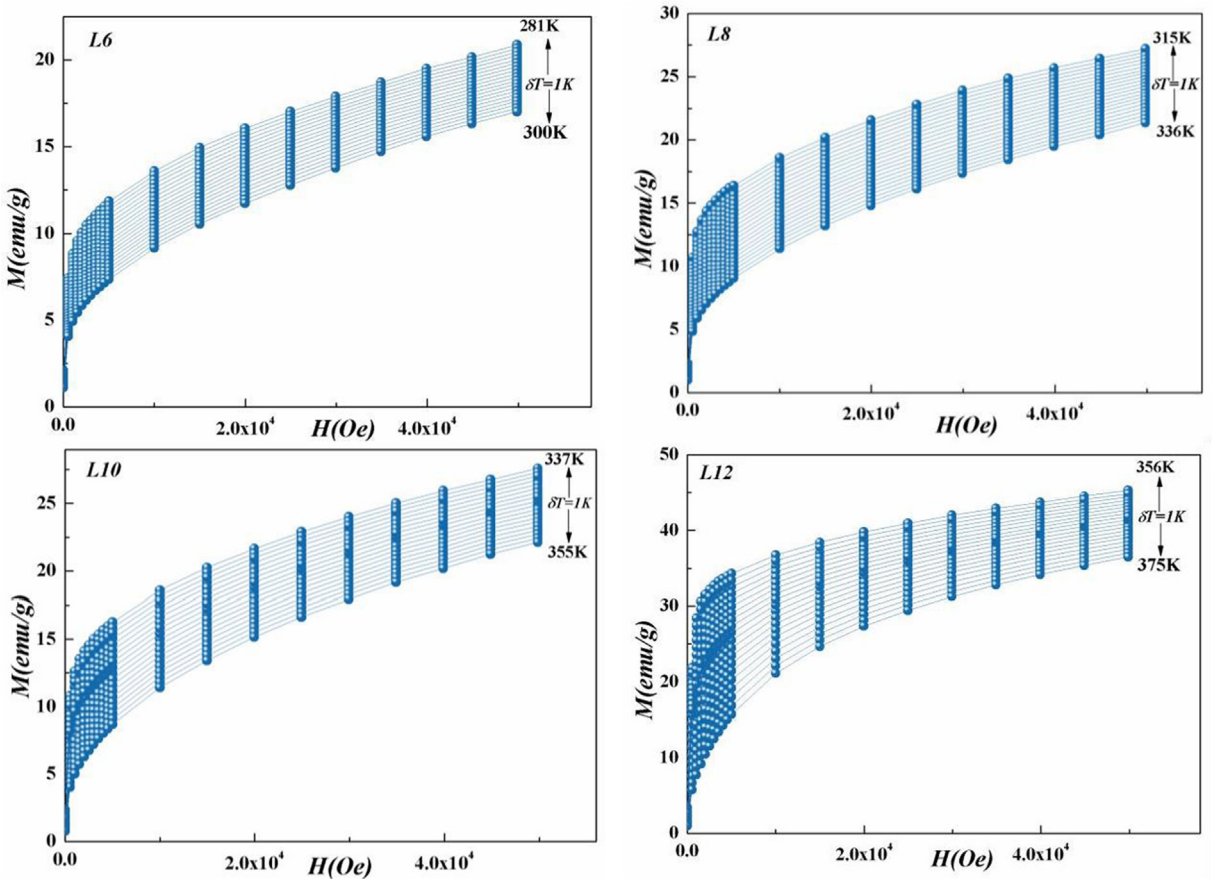

Fig. 1. Isotherms M *vs.* H at different temperatures for *L6*, *L8*, *L10*, and *L12* samples.