# Unconventional critical behavior of magnetic susceptibility as a consequence of phase separation and cluster formation in $La_{0.7}Ca_{0.3}MnO_3$ thin films

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Nonuniversal critical behavior of the dc magnetic susceptibility $\chi^{-1}(T)-\chi^{-1}(T_C)\sim(T/T_C-1)^{\gamma} \equiv \tau^{\gamma}$ is observed near the paramagnetic (PM) to ferromagnetic (FM) transition in $La_{0.7}Ca_{0.3}MnO_3$ film samples. The value of $\gamma\approx1.4$ obtained for $0<\tau<\tau_1$ with $\tau_1\approx0.05-0.09$ corresponds to a three-dimensional Heisenberg spin system and that of $\gamma\approx2.4$ for $\tau_1<\tau<\tau_2$ with $\tau_2\approx0.2-0.3$ to a two-dimensional percolation system. This behavior is attributed to phase separation by presence of FM clusters with temperature dependent correlation length in the PM matrix of the film. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1448309]

$La_{1-x}Ca_xMnO_3$, briefly LCMO, belongs to the class of hole-doped "colossal" magnetoresistance (CMR) materials, exhibiting a huge drop of the resistivity in external magnetic field around the paramagnetic (PM) to ferromagnetic (FM) transition temperature, $T_C$.[1] An intrinsic property of LCMO is phase separation or presence of FM droplets embedded into the PM host material[2–4] due to interplay between orderings of the charge, orbital, and spin degrees of freedom.[5]

Critical magnetic behavior near $T_C$, governed by scaling exponents between those of the mean-field theory ($\beta=0.5, \gamma=1$) and of the three-dimensional (3D) Heisenberg model ($\beta=0.36, \gamma=1.39$)[6] have been observed in $La_{1-x}Sr_xCoO_3$,[7] $La_{0.67}(Ba_xCa_{1-x})_{0.33}MnO_3$,[8] $La_{0.8}Sr_{0.2}MnO_3$,[9] $La_{0.95}Mg_{0.05}MnO_3$,[10] and in LCMO samples with $x<x_b\approx0.18$ and the hole concentration $c<c_b\approx0.23$.[11] However, for $x>x_b$ and $c>c_b$ the values of $\gamma\approx1.64$ were found[11] close to 1.7 characterizing a 3D percolation system.[12] Furthermore, the giant $1/f$ noise observed in $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ (Ref. 13) and the critical behavior of the variable-range hopping conductivity in LCMO with $x=0-0.15$, [14] indicate the features inherent to a percolation PM–FM transition in these compounds.

Comparing with bulk samples used in the aforecited investigations, thin films offer a natural constraint for growth of the percolation clusters in the direction perpendicular to the film plane. In this article we report observation of unconventional nonuniversal critical behavior of the magnetic susceptibility, $\chi(T)$, in thin $La_{0.7}Ca_{0.3}MnO_3$ films and discuss its connection to the phase separation effect.

The experiments were made on square-shaped LCMO films, prepared by pulsed laser deposition on a MgO (100) substrate (#1) and on a $SrTiO_3$ (100) substrate (#2aN), with the area of $S=11.7$ mm$^2$ and 6.7 mm$^2$, the rms roughness of 50 nm and 3 nm, respectively, and thickness $d\approx200$ nm. Sample #2aN was annealed in oxygen at 800 °C for $N=0$, 39, and 99 h to vary $T_C$. X-ray analysis showed that the films had the same cubic structure as ceramic LCMO.[11] The magnetization, $M(T)$, was measured with an rf-SQUID magnetometer under zero field cooled (ZFC) or field cooled (FC) conditions in fields of $B=80$ G, 0.5 kG or 1 kG, tilted to the film surface at an angle $\theta=0°$, 27° or 90°.

As evident from Fig. 1 (upper panel) #1 undergoes a PM–FM transition, identified by inflection of $M(T)$ at $T_C=227$ K. The irreversible magnetic behavior or deviation of $M_{ZFC}(T)$ from $M_{FC}(T)$ below $T_C$ in a low field (80 G), which is suppressed considerably when $B$ is increased to 1 kG, indicate a frustrated mixed (spin-glass or cluster-glass

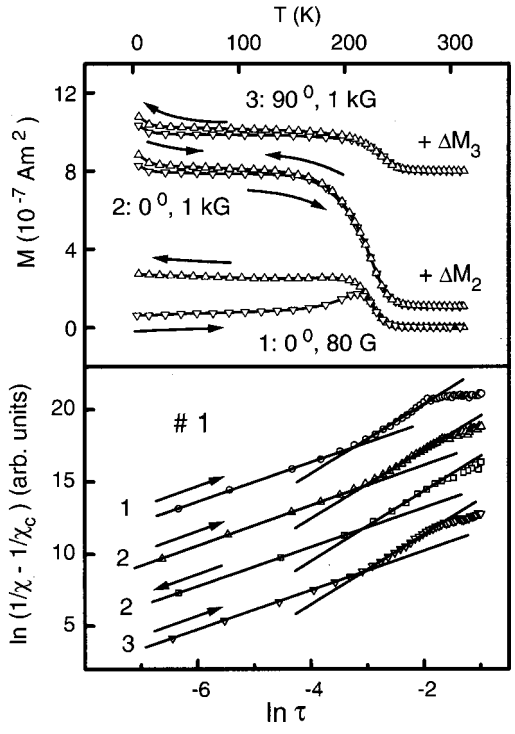


FIG. 1. Upper panel: values of $M(T)$ for #1 at different $\theta$ and $B$. The arrows mark ZFC and FC branches. For convenience the curves 2 and 3 are shifted along the $M$ axis by $\Delta M_2=1\times10^{-7}$ Am$^2$ and $\Delta M_3=8\times10^{-7}$ Am$^2$, respectively. Lower panel: critical behavior of $\chi(T)$ for the curves in the upper panel. The arrows show the direction of the temperature change.

 

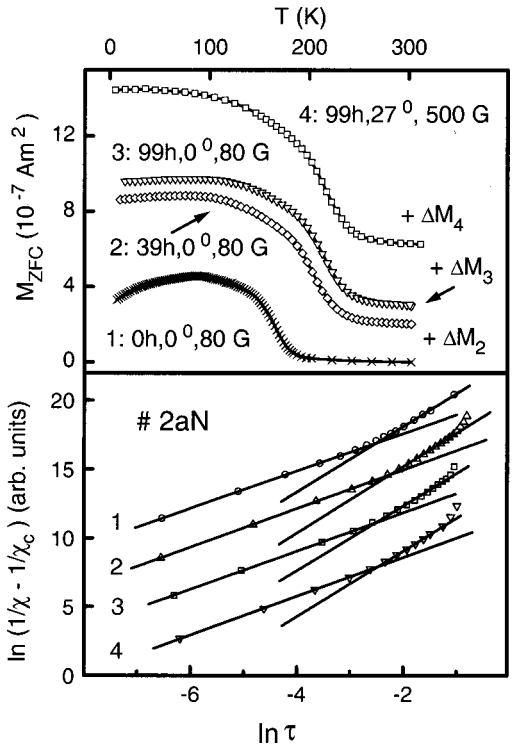


FIG. 2. Upper panel: values of $M_{ZFC}(T)$ for #2aN at different $N$, $\theta$, and $B$. The shifts of the curves 2, 3, and 4 are $\Delta M_2=2\times10^{-7}$ Am$^2$, $\Delta M_3=3\times10^{-7}$ Am$^2$, and $\Delta M_4=6\times10^{-7}$ Am$^2$, respectively. Lower panel: critical behavior of $\chi(T)$ for the curves shown in the upper panel.

$+$FM) phase similar to bulk LCMO samples.[14,15] In addition, a large difference between the values of $M$ measured at $\theta=0°$ and 90° is observed, demonstrating, as typical for thin films, a strong angular dependence of the demagnetizing factor $D$. The same features are also well observable in #2aN. As shown in Fig. 2 (upper panel) the value of $T_C$ depends strongly on the annealing time, $T_C=165$, 203, and 217 K for $N=0$, 39, and 99 h, respectively. The shift of $T_C$ to higher temperatures when $N$ is increased can be explained by increase of $c$.[16]

When analyzing the critical behavior of the apparent susceptibility $\chi(T)=M(T)/B$, it is convenient to use the difference $\chi^{-1}(T)-\chi^{-1}(T_C)$ to exclude the influence of $D$. Because the width of the films is much larger than their thickness, the inhomogeneity of $M$ is unimportant at large $\theta$ and the dependence of $D$ on the true susceptibility $\chi_t$ can be neglected. This may not be valid for small $\theta$, but in this case $D$ is small anyhow. Therefore, using the conventional equation $1+4\pi\chi=(1+4\pi\chi_t)/(1+D\chi_t)$ we obtain in all cases $\chi^{-1}(T)-\chi^{-1}(T_C)\sim\chi_t{}^{-1}(T)-\chi_t{}^{-1}(T_C)$. At $T\to T_C$ we have $\chi_t{}^{-1}(T)-\chi_t{}^{-1}(T_C)\sim(T/T_C-1)^{\gamma}\equiv\tau^{\gamma}$, leading to the relation

$$\chi^{-1}(T)-\chi^{-1}(T_C)\sim\tau^{\gamma}. \tag{1}$$

The plots of $\ln[\chi^{-1}(T)-\chi^{-1}(T_C)]$ vs $\ln\tau$ are shown for #1 and #2aN in the lower panels of Fig. 1 and Fig. 2, respectively. They contain two linear parts with slopes $\gamma_{lt}=1.37\pm0.02$ and $1.38\pm0.02$ when $0<\tau<\tau_1$ with $\tau_1\approx0.05$ for #1 and $\approx0.09$ for #2aN, and $\gamma_{ht}=2.41\pm0.05$ and $2.40\pm0.05$ when $\tau_1<\tau<\tau_2$ with $\tau_2\approx0.2$ for #1 and $\approx0.3$ for #2aN. The values of $\gamma_{lt}$ are close to $\gamma=1.39-1.43$ in $La_{1-x}Sr_xCoO_3$,[7] $\gamma=1.39\pm0.05$ in $La_{0.95}Mg_{0.05}MnO_3$[10] and $\gamma=1.45$ in LCMO single crystal with $\chi=0.2$,[17] corresponding to the 3D Heisenberg spin system. On the other hand, $\gamma_{ht}$ is in a good agreement with predictions for a two-dimensional (2D) percolation system: $\gamma=2.38\pm0.03$[12] and $2.43\pm0.03$.[18]

We attribute the nonuniversal critical behavior to the phase separation effect being responsible for creation of small FM particles in the PM host matrix at $T$ well above $T_C$.[2–4] When $T$ is decreased both the radius $r$ and the volume fraction $\eta(r)$ of these particles are increased, joining them into strongly correlated FM clusters.[3,4] The cluster correlation length can be expressed as $\lambda(\tau)=\lambda_0\tau^{-\upsilon}$ where $\lambda_0\approx2(4\pi n/3)^{-1/3}$ is the mean distance between the FM particles and $\upsilon\approx1$ is the critical exponent.[19] The condition of the onset of the 2D critical behavior is $\lambda(\tau_2)\approx d$, giving $n\approx6/[\pi(d\tau_2)^3]\approx4\times10^{16}$ cm$^{-3}$ and $7\times10^{15}$ cm$^{-3}$ for #1 and #2aN, respectively. Down to $\tau_2$ the clusters are 3D objects, so the volume fraction of the FM phase is $\eta=1-\exp(-4\pi nr^3/3)$.[19] Assuming that at $T$ well above $T_C$ the radius of a FM particle attains the smallest value, $r_{\min}\approx a\sqrt{3}/2\approx0.67$ nm, where $a\approx0.77$ nm is the lattice parameter of cubic LCMO, we estimate $\eta_{\min}=\eta(r_{\min})\approx5\times10^{-5}$ and $9\times10^{-6}$ for #1 and #2aN, respectively.[11] FM droplets with similar $r\approx0.85$ nm have been observed by neutron scattering investigations in LCMO single crystals with $x=0.05$ and 0.08,[2] and close value of $\eta\approx5.2\times10^{-5}$ was estimated from critical behavior of the resistivity near $T_C$ in the same film #1.[20]

The average moment of the FM particles, $\mu$, at $\tau_2$ can be estimated from the equation $M(T_2)\approx\mu nL(\mu B/kT_2)$, where $L(\xi)$ is the Langevin function and $T_2$ is the temperature corresponding to $\tau_2$. Then the volume fraction at $\tau_2$ is $\eta(\tau_2)\approx n\mu/M_s$, where $M_s\approx860$ emu/cm$^3$ is the saturation magnetization. Finally, the value of $r(\tau_2)$ can be found from the relation between $\eta$ and $r$. We obtain $\mu\approx1\times10^4\mu_B$ and $1\times10^5\mu_B$, $\eta(\tau_2)\approx5\times10^{-3}$ and $1\times10^{-2}$ and $r(\tau_2)\approx3$ and 7 nm for #1 and #2aN, respectively. A similar value of $r\approx5$ nm has been obtained by Mössbauer investigations at $T$ just below $T_C$ in bulk LCMO with $x=0.2$.[4]

The estimates made above are consistent with the rapid increase of $\eta$ when $T$ is decreased. However, even at $\tau_2$ the value of $\eta$ is still very small in comparison with the 3D percolation threshold, $\eta_c=0.29$.[19] Because the clusters behave below $\tau_2$ as 2D objects, in our case $\eta_c$ would be even higher. The critical behavior of $\chi$ below $\tau_2$ demonstrates that $\eta_c$ is not reached, and near $\tau_1$ the contribution of the FM clusters to the net magnetization becomes smaller than that of the PM host phase. On the other hand, due to $a\ll d$ this phase represents essentially a 3D spin system, which explains the 3D Heisenberg behavior for $0<\tau<\tau_1$.

To summarize, nonuniversal critical behavior of the magnetic susceptibility of $La_{0.7}Ca_{0.3}MnO_3$ films is observed, including crossover from a 2D percolation spin system to the 3D Heisenberg spin system. This behavior is independent of the surface quality of the films, the direction and strength of

the applied field, the way of cooling (ZFC or FC), and the value of $T_C$, giving strong evidence that it is an intrinsic property of the material. It can be explained by phase separation or presence of FM clusters with temperature dependent correlation length in the PM matrix of the films.

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