PHYSICAL REVIEW B **76**, 014401 (2007)

# Non-Griffiths-like clustered phase above the Curie temperature of the doped perovskite cobaltite $La_{1-x}Sr_xCoO_3$

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(Received 22 February 2007; revised manuscript received 9 May 2007; published 3 July 2007)

The existence of preformed clusters above the Curie temperature of the doped perovskite manganites is well established and, in many cases, conforms to the expectations for a Griffiths phase. We show here that the canonical perovskite cobaltite ($La_{1-x}Sr_xCoO_3$) also exhibits a clustered state above the Curie point in the ferromagnetic phase. The formation of magnetic clusters at a well-defined temperature ($T^*$) is revealed in the small-angle neutron scattering and dc susceptibility. Remarkably, the characteristics of this clustered state appear quite unlike those of a Griffiths phase; the deviation from Curie-Weiss behavior is opposite to expectations and is field independent, while $T^*$ does not correspond to the undiluted Curie temperature. These results demonstrate that, although the Griffiths model may apply to many systems with quenched disorder, it is not universally applicable to randomly doped transition metal oxides.

DOI: 10.1103/PhysRevB.76.014401 PACS number(s): 75.25.+z, 75.40.−s, 75.47.Gk

The existence of electronic and magnetic inhomogeneity in many transition metal oxides is now well established.[1–3] Of the many forms of magnetoelectronic phase separation observed, the concept of "preformation" of ferromagnetically ordered clusters at some well-defined temperature ($T^*$) above the true long-range ferromagnetic (F) ordering temperature ($T_C$) seems to be particularly widely applicable.[1,2] This has been observed in Fs as varied as magnetic semiconductors,[4,5] oxides,[1–3,6–12] and magnetocalorics.[13] The explanation for colossal magnetoresistance in certain manganites in terms of field driven expansion of preformed F clusters[1–3,6,8] is an excellent example of the profound impact of this cluster formation.

Preformed clustering also emerges from theoretical descriptions of doped magnetic systems. This includes models developed specifically for the manganites,[1,2,14,15] as well as more general treatments of "random" Fs.[16,17] An example of the former is provided by the work of Dagotto *et al.*,[1,2] and Burgy *et al.*,[14] where it was shown that disorder at a first order phase transition [e.g., from an F metal to a charge and orbitally ordered antiferromagnetic (AF) insulator] leads to magnetic phase separation below a characteristic temperature $T^*$, in excess of the composition dependent $T_C$. The model of Griffiths, developed for randomly diluted Ising Fs,[16] is a more general treatment that has been found widely applicable to the perovskites.[8–11] Griffiths pointed out that a randomly diluted F will exhibit a suppressed long-range ordering temperature $T_C(x)$ ($x$ is the dilution), and in the region $T_C(x) < T < T_C^{\text{undiluted}}$, the thermodynamic properties (e.g., magnetization) will become nonanalytical due to formation of a low density of short-range ordered clusters. $T_C^{\text{undiluted}}$ is therefore the temperature at which this "Griffiths phase" forms and has been coined the Griffiths temperature $T_G$, analogous to $T^*$. The Griffiths model is viewed as applicable to the manganites as the quenched disorder induced by doping is analogous to random dilution. The original paper of Griffiths,[16] and subsequent work,[8–11,13,17] has shown that this phase has several characteristics: (i) the susceptibility ($\chi$) deviates from the Curie-Weiss (CW) predictions as $T \rightarrow T_C$ from above (at $T_G$), (ii) this deviation takes the form of an enhanced low field $\chi$ due to the contribution from the F clusters, (iii) the deviation is suppressed in large magnetic field ($H$) due to polarization of spins outside the clusters, and (iv) $T_G$ can be identified as $T_C^{\text{undiluted}}$, i.e., the maximum $T_C$ in the phase diagram. Numerous magnetic systems,[5,8–11,13] including manganites[8,9] and cobaltites,[10,11] exhibit these characteristics. In many cases (e.g., almost isotropic manganites), the properties of these Fs are quite different to those in the original Griffiths model (which was developed for Ising systems).

In this paper, we examine the possibility of preformed clusters above $T_C$ in the F part of the phase diagram of the best understood perovskite cobaltite, $La_{1-x}Sr_xCoO_3$ (LSCO). The existence of magnetic phase separation at low $T$ in LSCO has been demonstrated using transmission electron microscopy (TEM),[18,19] nuclear magnetic resonance (NMR),[20,21] small-angle neutron scattering (SANS),[22] neutron diffraction,[18,23] and other indirect techniques.[18,24,25] At low doping, the system forms nanoscopic (~3 nm) F metallic droplets in a non-F semiconducting matrix.[22,23] As $x$ is increased, these clusters increase in density, eventually achieving percolation and subsequent entry into a long-range ordered F state at $x=0.18$.[22–25] Although the phase separation is clear as a function of $x$ at low $T$, the region above $T_C$ has not been investigated in detail. Caciuffo *et al.*[26] observed a deviation from CW around 305 K in $x=0.3$ powder, which they interpreted as entry into a "cluster-fluctuation regime." SANS data were dominated by chemical scattering but revealed a weak magnetic Guinier component, which was ascribed to magnetic polarons.[26] The correlation length peaked at 14 Å near $T_C$ (the magnetic intensity also reaches a peak in this region), and the authors concluded that a transition from itinerant to polaronic conduction took place near the Curie point. This was backed up by diffraction data indicating an anomalous thermal expansion in this temperature region. Unfortunately, the SANS data were not acquired to

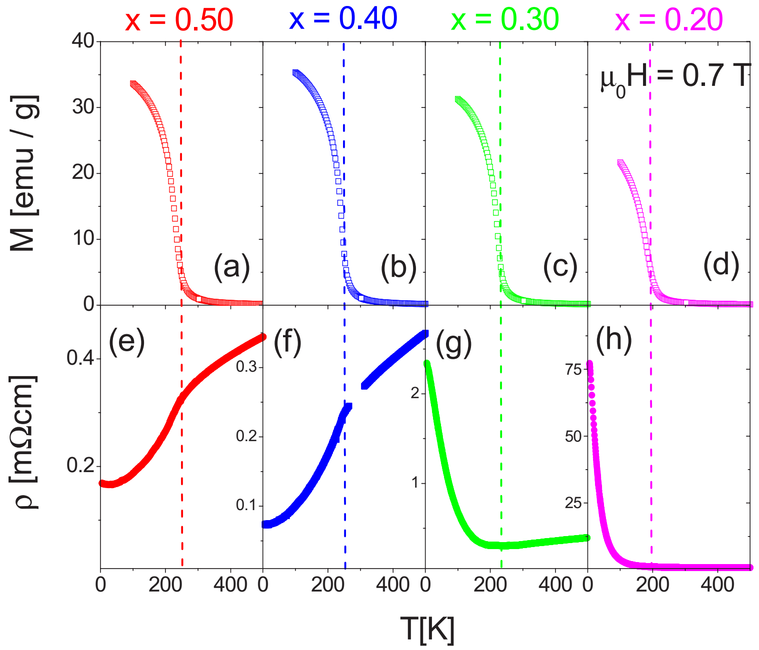

FIG. 1. (Color online) Temperature dependence of the 0.7 T dc magnetization (top panel) and zero field resistivity (bottom panel) of [(a) and (e)] $x=0.50$, [(b) and (f)] 0.40, [(c) and (g)] 0.30, and [(d) and (h)] 0.20 polycrystals. The vertical dashed lines mark $T_C$.

sufficiently high $T$ to observe any possible $T^*$. In this paper, we provide a full (high $T$) investigation of the behavior above $T_C$ at multiple $x$ ($0.20 \leqslant x \leqslant 0.50$) in the F part of the phase diagram on both polycrystals and single crystals. The magnetic SANS intensity, magnetic correlation length, and dc susceptibility all show signatures of a well-defined temperature $T^*$ ($\approx 360$ K), below which a clustered state is entered as a precursor to full F ordering.

Polycrystals and single crystals were fabricated by solid-state reaction and floating zone methods, respectively.[20–22,25] These samples have been characterized by x-ray and neutron diffraction, scanning TEM with energy dispersive spectroscopy, thermogravimetric analysis, and multiple electronic and magnetic probes.[20–22,25] The onset of significant oxygen deficiency at $x > 0.50$ limited our study to the range $x \leqslant 0.50$. SANS measurements were made at a wavelength of 5 Å over the range $0.02 < q < 0.35$ Å$^{-1}$ at the National Institute of Standards and Technology. Use of large grain size ($\sim 10$ $\mu$m) polycrystals minimized the contribution from structural scattering. Magnetometry was performed in a commercial superconducting quantum interference device, while zero field resistivity was measured using indium contacts in a van der Pauw configuration at 13.7 Hz. Measurements were performed in the range 5 K $< T <$ 500 K in order to probe the regime well above $T_C$. Checks were made to ensure that the electronic and magnetic properties did not suffer irreversible changes after heating to 500 K due to oxygen loss.

Figure 1 provides a global view of the magnetization ($M$) and resistivity ($\rho$) for four F polycrystals ($x=0.20-0.50$) in the extended range up to 500 K. The data at $T < 300$ K are in agreement with prior reports.[24,25] These compositions show F behavior with a $T_C$ that increases gradually with $x$. The $T \to 0$, extrapolation of the conductivity of all four compositions is finite, indicating metallic conductivity.[27] The sign of $d\rho/dT$ at high $T$ (i.e., $T > T_C$) changes between $x=0.30$ and 0.20, and the compositions with "metalliclike" $d\rho/dT$ show a distinct slope change in the vicinity of $T_C$, as expected.[24,25]

Figure 2 focuses on the regime between 200 and 500 K (i.e., close to and above $T_C$), showing the magnetic part of the absolute SANS intensity ($q=0.1$ Å$^{-1}$) and the magnetic correlation length ($\xi$) extracted from the SANS for polycrystals. The magnetic contribution was obtained by subtracting the intensity at the highest temperatures (400–500 K), a procedure which is validated by the fact that the magnetic intensity is negligible until $T$ is decreased down to $\approx 360$ K. Below this temperature, which is independent of doping, the

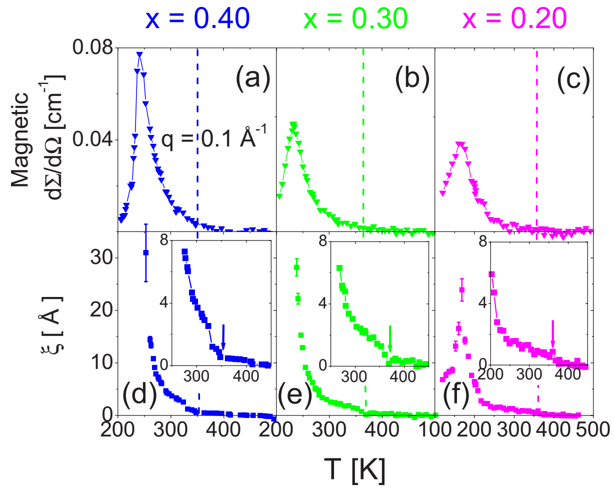

FIG. 2. (Color online) Temperature dependence of the magnetic part of the absolute small-angle neutron scattering intensity (zero field) at $q=0.1$ Å$^{-1}$ (top panel) and the correlation length extracted from this scattering (bottom panel). Error bars are included but in some cases are smaller than the points. The insets show the same data in a "close-up" near 360 K. The data are for $x=0.40$ (left panel), 0.30 (middle panel), and 0.20 (right panel). The vertical dashed lines (and arrows) mark the sharp turn on in correlation length ($T^*$). The small anomaly at 325 K in (d) was not repeatable in other temperature sweeps.

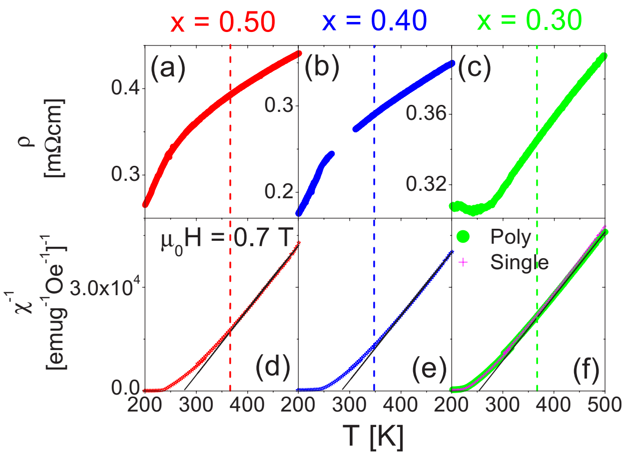

FIG. 3. (Color online) Temperature dependence of the zero field resistivity (top panel) and the inverse dc susceptibility ($H/M$) at 0.7 T (bottom panel). The data are for $x=0.50$ (left panel), 0.40 (middle panel), and 0.30 (right panel). For the $x=0.30$ case, the (almost indistinguishable) susceptibility data are shown for both polycrystals and single crystals. Solid lines in (d), (e), and (f) are Curie-Weiss fits to the high temperature behavior. The vertical dashed lines mark the sharp turn on in correlation length ($T^*$).

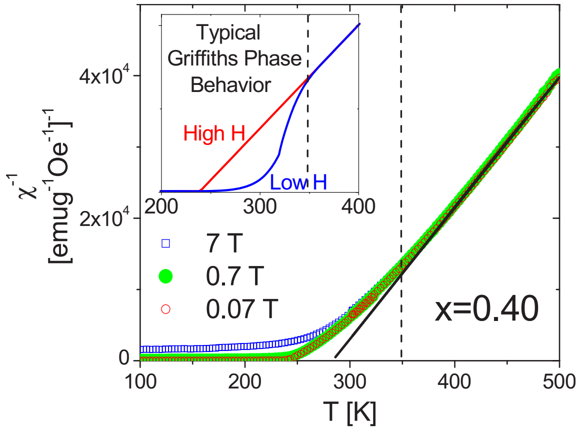

FIG. 4. (Color online) Temperature dependence of the inverse dc susceptibility ($H/M$) of an $x=0.40$ polycrystal for applied fields of 7, 0.7, and 0.07 T. The vertical dotted line denotes $T^*$. The inset shows the expected behavior in the Griffiths phase.

magnetic intensity rises, reaching a peak at the (doping dependent) $T_C$. Such "critical scattering" would typically be ascribed to quasielastic scattering from the short-range spin correlations that increase in prominence as $T_C$ is approached. The $q$ dependence follows the Lorentzian form $I=I_0/[q^2+(1/\xi)^2]$, where $I_0$ is a constant. At a conventional F transition, $\xi$ is expected to show a smooth increase from zero at high $T$, diverging as $T\rightarrow T_C$. $\xi(T)$ extracted from fitting to the Lorentzian form is shown in Figs. 2(d)–2(f). The data depart from simple expectations. $\xi(T)$ shows a distinct, sharp onset in the range 346 K (for $x=0.40$) $<T<369$ K (for $x=0.20$), as opposed to a gradual increase, indicating the sharp onset of spin correlations at a well-defined temperature $T^*$ (dotted lines and arrows in Fig. 2). In agreement with prior work on other materials, we interpret this temperature at which a sharp increase in $\xi$ occurs as the point at which F clusters emerge. [Note that prior La NMR data at $x=0.30$ (Ref. 21) showed an F signal extending above $T_C$ (the highest temperature measured was 280 K), further evidence for preformation of F clusters.] It is worth pointing out that we attempted to fit our data to a Guinier form (following Ref. 26), but it was clear that the Lorentzian form provided a far better description of the data.

Figures 3(d)–3(f) show that the inverse susceptibility also reflects this cluster formation at $T^*$; $\chi^{-1}$ is CW-like at high $T$ but shows departures from CW at $T\gg T_C$. The solid lines are fits to CW between 400 and 500 K, and extrapolation to lower $T$ yields temperatures at which deviations occur of ~360 K, very close to the $T^*$ values determined from $\xi(T)$. Note that the data deviate *upward* from the CW prediction on a $\chi^{-1}$ vs $T$ plot, i.e., toward lower $\chi$. It should be pointed out that such upward deviations are common in conventional Fs. However, in this case, the close agreement between the temperature at which a discontinuity in $\xi(T)$ occurs and the one at which we observe deviations from CW suggests that the two are related.[26] As shown in Figs. 3(a)–3(c), the zero field $\rho(T)$ does not show a large anomaly near 360 K (there may be evidence for a subtle change in slope), which is consistent with the very small F cluster size at these temperatures. $T^*$ is also present in crystals. Figure 3(f) displays $\chi^{-1}(T)$ for an $x=0.30$ single crystal, which is practically indistinguishable from the corresponding polycrystal.

From the data presented thus far, the existence of $T^*$ in LSCO is clear. In terms of determining whether the clustered state has the characteristics of a Griffiths phase, $\chi(T)$ is of particular interest. As already mentioned, the upward deviation from CW [Figs. 3(d)–3(f)] is at odds with the Griffiths model[16,17] as well as multiple experimental observations.[7–11,13] $\chi$ is expected to increase over CW, at least at low $H$, where the susceptibility of the clusters is dominant, as shown in the inset to Fig. 4. The $H$ dependence of $\chi^{-1}(T)$ is therefore important and is examined in detail in Fig. 4 for a representative polycrystalline sample ($x=0.40$). The data at applied fields of 0.07, 0.7, and 7 T overlap down to $T\approx T_C$, showing the same upward deviation from CW at the same $T^*$ of 350 K. Data were acquired at fields down to only 1 mT, showing no change in form, no change in $T^*$, and no evidence for any downward deviation from CW in $\chi^{-1}$ vs $T$. These data are in stark contrast to the predictions of the Griffiths model (Fig. 4, inset), a point that will be returned to later.

Taking the $T^*$ determined from our most sensitive probe [i.e., $\xi(T)$] and adding them to our previously determined magnetic phase diagram,[25] we obtain Fig. 5. This figure highlights the doping independence of $T^*$, in addition to the fact that $T^*$ does not correspond to the maximum $T_C$. Although precise determination of $T_C^{\max}$ is hindered by the difficulty in preparing fully oxygenated specimens at $x>0.5-0.7$, the maximum values reported [280–320 K (Refs. 28–30)] are far below our observed $T^*$ of ~360 K. From the data of Figs. 2–4, we can draw two firm conclusions: (i) a clustered state occurs below a well-defined temperature in the F portion of the phase diagram, with a clear signature in SANS, $\chi(T)$, and NMR and (ii) the characteris-

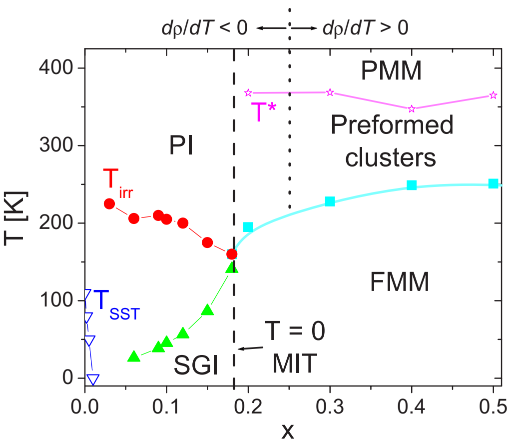

FIG. 5. (Color online) Revised magnetic phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ showing the new regime between $T^*$ and $T_C$ where preformed magnetic clusters exist. $T_{irr}$ and $T_{SST}$ (see Ref. 25) are the irreversibility temperature and spin-state transition temperature, respectively. PMM, FMM, PI, SGI, and MIT denote paramagnetic metal, ferromagnetic metal, paramagnetic insulator, spin-cluster–glass insulator, and metal-insulator transition.

tics of this state differ significantly from the Griffiths predictions. We therefore conclude that although the Griffiths model seems to apply to many doped magnetic systems,[5,8–11,13] it is not universally applicable to the doped oxides. One puzzling aspect of this observation is the fact that the cobaltites (which have large magnetocrystalline anisotropy) might be considered better candidates than the manganites for direct comparisons to the Griffiths model (which was originally developed for Ising systems). Although we cannot provide definitive explanations for all aspects of this clustered state (we hope this paper will stimulate further theoretical work), the existence of $T^*$ is certainly in agreement with many phase separation scenarios, and we can speculate on the origin of some of the observed features. For instance, the upward deviation from CW in the $\chi^{-1}(T)$ data (which is also seen in other work[6,26]) could be due to AF interactions, which would favor antiparallel alignment of neighboring clusters, suppressing $\chi$. In fact, recent muon spin relaxation measurements on $\text{LaCoO}_3$ (Ref. 31) indicate AF coupling between magnetic excitons (which are thought to be the precursors to F clusters in LSCO) and the surrounding matrix. In addition, the possible dynamic nature of this regime[26] may have to be taken into account to understand $\chi(T)$. In terms of a proposed origin for the phase separation that occurs on cooling below $T^*$, the stochastic fluctuations in local composition that must occur in any randomly doped system at such short length scales [see Figs. 2(d)–2(f)] should not be ignored. We believe that it is possible that the local ordering temperature in Sr rich clusters at global compositions of order $x=0.5$ (which are fully oxygenated) could exceed that seen in much higher doped samples (which are difficult to fully oxygenate), leading to a $T^*$ in excess of the apparent $T_C^{\max}$, as observed.

In summary, we have presented neutron scattering and magnetometry data on the canonical doped perovskite cobaltite $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, revealing the formation of short-range ordered ferromagnetic clusters at a well-defined temperature of 360 K. Although not fully understood, this phase separated state exhibits behavior quite distinct from that of a Griffiths phase, demonstrating that the Griffiths model is not universally applicable to complex oxides exhibiting preformed ferromagnetic clusters, despite its success in describing the behavior of many randomly doped oxides.

We acknowledge support from DOE (DE-FG02-06ER46275), NSF (DMR-0509666), and the ACS PRF, as well as neutron facilities at NIST. Argonne, a US DOE Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357.

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