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Phase separation versus spin glass behavior in $La_{0.85}Sr_{0.15}CoO_3$

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We present comprehensive studies of dc magnetization, ac susceptibility, and magnetotransport of two sets of $La_{0.85}Sr_{0.15}CoO_3$ samples, one exhibits phase separation and the other exhibits spin glass behavior. Our study reveals that the phase separation in $La_{0.85}Sr_{0.15}CoO_3$ is neither inherent nor ubiquitous; rather, it is a consequence of preparation condition. It is realized that the low temperature annealed sample exhibits phase separation while the high temperature annealed one shows the characteristic of spin glass behavior. This study shows that the most probable magnetic state of $La_{0.85}Sr_{0.15}CoO_3$ is spin glass. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3073939]

The extensive studies on transition metal oxides (TMOs) over decades has given rise to many new exciting complex phenomena such as colossal magnetoresistance in manganites, high temperature superconductivity in cuprates, metal insulator transition, etc. Such kind of complex phenomena has contributed to our understanding of highly correlated electron systems in the condensed matter physics. It appears that these materials are susceptible to intrinsic inhomogeneity (phase separation), which plays a crucial role in determining the magnetoelectronic properties of it. Recent theoretical[1] and experimental studies[2–5] (NMR, neutron diffraction, magnetic relaxation, etc.) on doped cobaltite system ($La_{1-x}Sr_xCoO_3$) are reported to exhibit microscopic inhomogeneity giving rise to phase separation. The essential concept behind such phenomenon is the spatial coexistence of ferromagnetic (F) metallic regions and non ferromagnetic insulating regions. This has enormously triggered the renewed interest in the doped cobaltite system and numerous works are being reported on this subject. Cobaltites also receive special attention owing to their extra degree of freedom of "spin state" at the cobalt site in addition to lattice, charge, and spin degree of freedom as found in many other TMOs. The rhombohedral $LaCoO_3$ undergoes a thermally induced spin state transition from low spin state ($(t_{2g}^6 e_g^0$; $S=2$, nonmagnetic) to intermediate spin state ($t_{2g}^5 e_g^1$; $S=1$) or high spin state ($t_{2g}^4 e_g^2$; $S=2$) with an increase in temperature.[6,7] The spin state transition in cobaltites is favorable due to comparable sizes (~10 mev) of crystal field energy (Δ_{cf}) and Hund's exchange (Δ_{ex}) energy. Further, hole doped $La_{1-x}Sr_xCoO_3$ has attracted great attention during past few decades because of their novel magnetic and electrical transport properties.[8–11] The parent compound $LaCoO_3$ is a charge transfer type insulator in which a charge gap is formed between the occupied oxygen $2p$ band and $3d$ e_g band.[12,13] When the parent compound is doped with Sr^{2+}, it introduces holes in Co–O network to maintain the charge neutrality, i.e., an equivalent number of Co^{3+} are converted to Co^{4+} ions. The competition between double-exchange F interaction (Co^{3+}–Co^{4+}) and superexchange antiferromagnetic interaction (Co^{3+}–Co^{3+}, Co^{4+}–Co^{4+}) results in different kinds of magnetic ordering with the change in doping concentrations. However, earlier report[11] shows that for $x<0.18$, the system behaves like a semiconductor with spin glass behavior and for $x>0.18$, it becomes metallic with long range magnetic ordering. Our present work here is aimed at investigating the "spin glass versus instability towards phase separation" in $La_{0.85}Sr_{0.15}CoO_3$ compound.

Polycrystalline samples of $La_{0.85}Sr_{0.15}CoO_3$ are synthesized by conventional solid state reaction method using stoichiometric mixture of La_2O_3, CO_3O_4, and $SrCO_3$ powders. We have prepared two different sets of samples from the same mixture depending on the heat treatment that they have undergone. In both the cases the mixture was first calcined at 900 °C in air with several intermediate grinding for homogenization and to form the single phase. Then, for one set of samples, some amount of the calcined mixture is pressed into pellet and then the pellets were sintered at 1150 °C for 24 h in air. For the other set of samples, the remaining calcined mixture was further annealed at 1300 °C with intermediate grinding and finally it was pressed into pellets and sintered at 1300 °C for 24 h. X-ray diffraction patterns for both set of samples show that they are single phase and structurally identical. The oxygen content of both set of samples was determined by iodometric titration and it was found to be 3 ± 0.02. Henceforth, two set of samples are termed as low temperature annealed (S1) and high temperature annealed (S2) respectively. Magnetization measurements are made using commercial Quantum Design superconducting quantum interference device and ac susceptibility measurement units. Electrical and magnetotransport properties are measured using a standard four probe configuration in a magnetic field up to 11 T using a superconducting magnet.

Figure 1 shows the temperature dependence of dc magnetization for S1 and the inset shows the same for S2. Both field cooled (FC) and zero field cooled (ZFC) magnetizations

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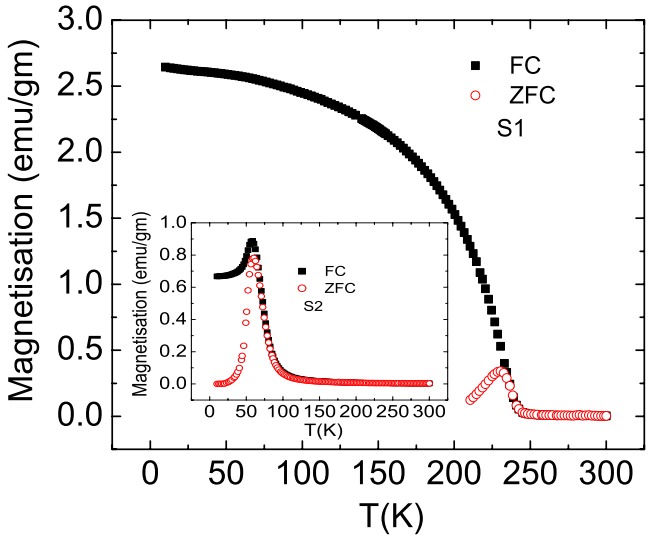

FIG. 1. (Color online) Temperature dependence of FC and ZFC dc magnetizations for S1. The inset shows the same for S2.

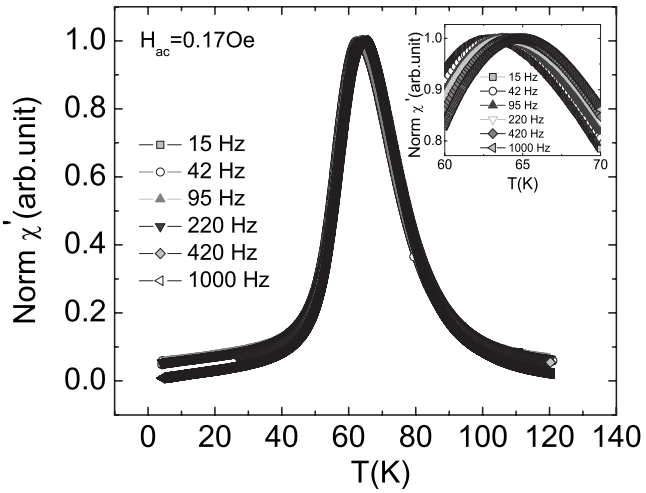

FIG. 2. Temperature dependence of normalized (norm) in-phase component $\chi'(T)$ of ac susceptibility for S2 in an ac field of $H_{ac}=0.17$ Oe with frequencies of 15, 42, 95, 220, 420, and 1000 Hz, respectively. The inset shows a close up view of frequency dependent peak shifts.

are performed at 100 Oe. It is clear from Fig. 1 that the FC curve for S1 exhibits a Brilliouin-like temperature dependence of the magnetization and the ZFC exhibits a cusp around 230 K. The Brilliouin-like behavior of FC curve and the presence of cusp in ZFC curve indicates that the sample possesses long range ferromagnetic order owing to the presence of different hole rich ferromagnetic regions embedded in a nonferromagnetic matrix ($LaCoO_3$). However, the magnetic behavior of S2 as shown in the inset of Fig. 1 is contrary to what is observed for S1. The FC curve for S2 no longer shows a Brillouin-like behavior, rather it exhibits a kink in magnetization at ~60 K and this phenomenon is well ascribed to the typical characteristic feature of various spin glass systems. So it is pertinent to say that the physical properties of the same stoichiometric samples are greatly influenced by the process of heat treatment. The ZFC curve for S2 shows a cusp around (60K) spin freezing temperature (T_f) as usually observed in spin glass systems.[11] It is important to note here that FC and ZFC curves for S2 start deviating from each other at around T_f, where both FC and ZFC curves exhibit a maximum. However there are many reports[14,15] from different groups which show that the bifurcation between ZFC and FC curve occurs at irreversibility temperature (T_{irr}) and generally it is $>T_f$. The existence of T_{irr} line in cobaltite phase diagram is believed to arise when the material evolves into a magnetically phase separated state, i.e., there coexist different hole rich metallic ferromagnetic regions separated by hole poor matrix similar to $LaCoO_3$. However our experimental result finds that no such T_{irr} is found above T_f and thus it suggests that S2 does not show any indication of phase separation in it.

Figure 2 shows the temperature dependence of in-phase component $\chi'(T)$ for S2 in an ac field of 0.17 Oe and with frequencies of 15, 42, 95, 220, 420, and 1000 Hz. It is observed that $\chi'(T)$ shows a peak around 63 K at $f=15$ Hz and the peak shifts to higher temperature with increasing measuring frequency. The inset in Fig. 2 shows the magnified view of these peaks corresponding to different frequencies and such kind of behavior is the typical characteristic of spin glass. The frequency dependent peak shifts in $\chi'(T)$ can be quantified, i.e., $s=\Delta T_f/T_f\Delta \log_{10} f=0.0149$, where $\Delta T_f=(T_{f1}-T_{f2})$, $\Delta \log_{10} f=(\log_{10} f_1-\log_{10} f_2)$ with $f_1=1000$ Hz and $f_2=15$ Hz. This calculated value is typical for the canonical spin glass system where s ranges from 0.0045 to 0.08.[16] It has to be mentioned here that no indication of any other peak for S2 was observed when the measurement was performed in a range from 120 to 300 K, ruling out the possibilities of any of the high temperature phases. However, the ac susceptibility measurement for S1 shows a complete different behavior compared to S2. Figure 3 shows the temperature dependence of $\chi'(T)$ for S1 in an ac field of 0.17 Oe and with frequencies of 15 and 420 Hz and a temperature up to 280 K. It is clearly observed that the sample shows a sharp peak around 230 K and the peak position is almost independent of measuring frequencies. This ensures that the sample possess long range ferromagnetic order originating from ferromagnetic clusters present in it. In addition, the sample also exhibits a feeble shoulder in $\chi'(T)$ with lowering temperature around 60 K, which gives a signature of glassy behavior present in it. This suggests that the

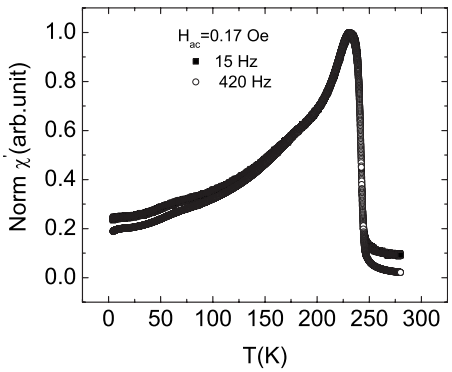

FIG. 3. Temperature dependence of normalized (norm) in-phase component $\chi'(T)$ of ac susceptibility for S1 in an ac field of $H_{ac}=0.17$ Oe with frequencies of 15 and 420 Hz.

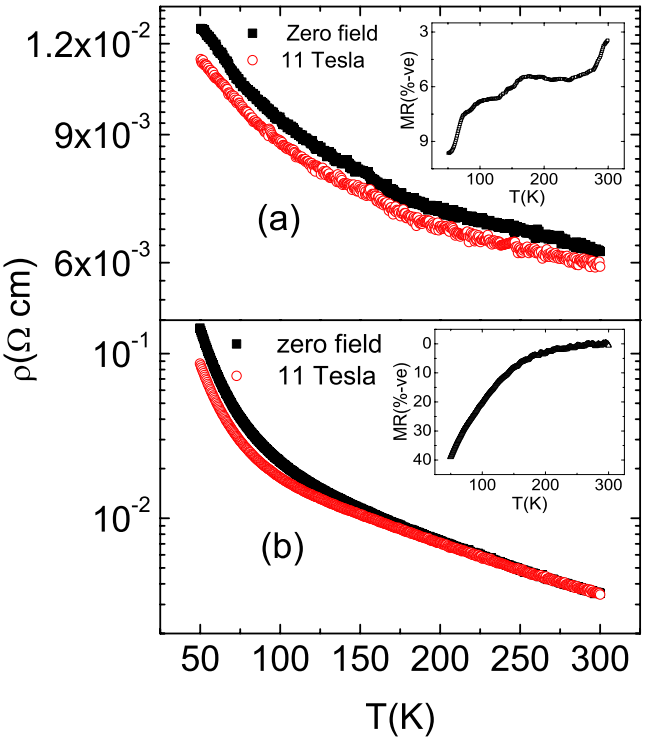

FIG. 4. (Color online) Temperature dependence of resistivity for (a) S1 and (b) S2 in $H=0$ T and $H=11$ T. The insets in both the figures display the calculated MR as a function of temperature.

sample exhibits both ferromagnetic as well as feeble glassy behavior.

Figure 4 shows temperature dependence of resistivity in zero field and at an applied field of 11 T for both S1 and S2 down to a temperature of 50 K. Both the samples exhibit semiconducting behavior $[(d\rho/dT)<0]$ and more interestingly S2 is found to be strongly semiconducting in nature as compared to S1. The different trends in electrical conduction for two samples could be understood on the basis of phase separation. We believe that in case of S1 there exists predominantly hole rich ferromagnetic regions of different concentration $(x>0.18)$ and they get interconnected with each other forming ferromagnetic metallic clusters. So the electrical conduction in S1 is carried out by both metallic clusters as well as semiconducting matrix $(LaCoO_3)$ such as two channel conduction. However in case of S2, the electronic and magnetic inhomogeneity (i.e., ferromagnetic clusters) disappears and it gives rise to spin glass state. The spin glass state is responsible for such high resistance in S2. The application of magnetic field in both the cases reduces the resistance as shown in Fig. 4 and thus it results in a negative MR effect. The MR calculated as $[(\rho(H)-\rho(0))/\rho(0)]$, are clearly shown as the insets in Fig. 4. It is observed that S2 exhibits a high negative MR of ~40% at 50 K and then it monotonically decreases with an increase in temperature. It is important to observe that no anomaly in MR is found near T_f, which suggests that T_f has no effect either in resistance or MR. The origin of such high MR in S2 is not clearly understood, however it is strongly believed to be due to spin dependent part of random potential distribution which gets suppressed largely when the spins get aligned in the presence of magnetic field.[14,17] However, the MR in case of S1 is very low (~9%) as compared to that of S2 at 50 K and it goes on decreasing with increase in temperature. This could be due to the presence of interconnected ferromagnetic clusters in S1 which could reduce the spin dependent scattering and increases the hopping probability of charge carriers. In order to completely rule out the possibility of phase separation in this system, one needs to undertake studies such as Co nuclear magnetic resonance,[18] neutron scattering,[19] resistivity relaxation, and magnetic relaxation on both samples.

In the present study, we find that the high temperature annealed sample (S2) exhibits the characteristic of spin glass behavior where as the low temperature annealed sample (S1) exhibits ferromagneticlike behavior. Here, we attribute this phenomenon to be a consequence of preparation method. In summary, we have tried to resolve the issue related to "spin glass versus phase separation" in $La_{0.85}Sr_{0.15}CoO_3$ and find that with the same stoichiometric ratio one can have either presence or absence of phase separation depending on the preparation method. We believe that the magnetic state of $La_{0.85}Sr_{0.15}CoO_3$ is like a spin glass system.

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