Glassy magnetic behavior in the phase-separated perovskite cobaltites

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In this paper we demonstrate that the origin of the glassy behaviors (memory, aging, etc.) in the phase-separated perovskite cobaltites cannot be simply ascribed to intercluster interactions as the phase-separated manganites can. Instead, our study indicates that both the intercluster interactions and a spin glasslike phase contribute to the glassy behaviors. Thus, this study distinguishes the picture of phase separation between manganites and cobaltites.

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Spontaneously phase separation (PS) in perovskite oxides is attracting much attention because of its important role in understanding the unique physical properties of these compounds, e.g., colossal magnetoresistance effect in manganites and high-temperature superconductivity in cuprates. In the past several years, there have been plenty of reports on the unusual nonequilibrium dynamics and time dependent phenomena in the PS state of perovskite manganites. For example, irreversibilities in the magnetization, frequency-dependent peaks in the real or imaginary parts of the AC susceptibility, and aging and memory effects on the resistivity and magnetization were observed in manganites. These phenomena are quite similar in appearance to those observed in classical spin glasses. Therefore, there is a controversy on the question of whether the PS state in manganites constitutes a classical spin glass phase or not. In a recent letter, Rivadulla et al. performed detailed analysis on the magnetic relaxation and demonstrated that the glassy behaviors in manganites can be understood taking into account only the intercluster interactions. Moreover, the authors proposed that this conclusion is general and should be applicable to other phase-separated systems such as cobaltites. In this paper, we present a detailed study in a phase-separated cobaltite sample. Nevertheless, contrary to the conclusion for manganites, our results demonstrate that the glassy behaviors in cobaltites cannot be simply ascribed to intercluster interactions.

The experiments were performed on a ceramic sample of La$_{0.82}$Sr$_{0.18}$CoO$_3$ which was prepared by solid state reaction method. A stoichiometric mixture of SrCO$_3$, Co$_3$O$_4$, and La$_2$O$_3$ powders was well ground and calcined twice at 800 and 950 °C for 24 h. Then, the resulting powder was pressed into pellets and sintered at 1100 and 1150 °C respectively, for 24 h. The proximity of this composition to the percolation threshold makes it an optimal choice for studies of magnetic relaxation phenomena. X-ray diffraction shows that the sample is single phase with rhombohedral structure. DC magnetization measurements were performed using a Superconducting quantum interference device (SQUID) magnetometer. AC susceptibility was measured in a quantum design, physical property measurement system (PPMS). In order to obtain a low field, the superconducting magnets of two apparatuses were demagnetized before measurements.

First, we demonstrate the characteristic behaviors of glassiness, i.e., the memory and aging effects, in phase-separated cobaltites. The memory effect was studied by employing a DC magnetization method that was originally developed for the study of spin glasses. The sample was first zero-field-cooled (ZFC) from 360 K to 5 K continuously at a cooling rate of 2 K/min. After reaching the bottom temperature, a 10 Oe field was applied and the magnetization was measured on heating at the same rate up to 120 K. This $M$-$T$ curve was referred as the reference curve, shown as a solid line in Fig. 1. Then, the sample was cooled again from 360 K to 5 K at the same rate in zero field but with a temporary stop at 50 K for a time $t_m = 10,000$ s. Finally, the magnetization in a 10 Oe field was recorded again during heating. The obtained results are shown in Fig. 1. It is clear that the magnetization with a stop (open circle) shows a dip around 50 K. The difference between two $M(T)$ curves, $\Delta M = M(T) - M_{ref}(T)$, is also shown in Fig. 1. A minimum is
observed at the stop temperature 50 K, reflecting the memory effect.

We then demonstrate aging effect in magnetic relaxation. The sample was cooled from 360 K to a measurement temperature 60 K in zero field. After a waiting time $t_w$, a small field $H = 10$ Oe was applied and the magnetization $M$ was recorded vs time $t$. The magnetic relaxation curves $M(t)$ (not shown) can be perfectly described by the stretched exponential function

$$M(t) = M_0 - M_r \exp \left[ -\left( \frac{t}{\tau_r} \right)^{1-n} \right],$$

where $M_0$ relates to an intrinsic FM component. The glassy component $M_r$ and the time constant $\tau_r$ depend on $T$ and $t_w$. $n$ is only a function of $T$. The obtained value of $\tau_r$ increases with increasing $t_w$, indicating a stiffening of the spin relaxation. To illustrate a waiting time dependence of the magnetic relaxation it is convenient to use the relaxation rate $S$, defined as $S = -(1/H)(\partial M/\partial \ln t)$. $S$ vs $\log_{10}(t)$ is plotted in Fig. 2 for different waiting times. It is clear that the magnetic relaxation depends on the waiting time. A maximum in $S$ occurs at a time which is approximately equal to $t_w$, implying an aging effect. The effect was predicted early by the droplet model\(^{19}\) in which the maximum of the relaxation rate can be interpreted to be associated with a crossover from quasiequilibrium dynamics at short observation times ($t \leq t_w$) to nonequilibrium dynamics at long observation times ($t \geq t_w$).

The above results confirm that phase-separated cobaltites exhibit glassy behaviors. However, the origin of these glassy magnetic behaviors remains unclear because both classical spin glasses and assemblies of interacting magnetic clusters could give rise to such glassy behaviors. One way to clarify this question is to study the field dependence of ac susceptibility. For a classical spin glass, the peak in ac susceptibility, corresponding to the freezing temperature $T_f$, usually shifts to lower temperature with increasing applied dc field.\(^{20}\) In contrast, for assemblies of interacting FM clusters whose sizes depend on applied dc magnetic field, the peak in ac susceptibility shifts to higher temperatures with increasing field due to the growth of the clusters.\(^{6}\)

In Fig. 3 we show the temperature dependence of ZFC ac susceptibility with different superposed dc fields. The ac field and frequency are fixed as 5 Oe and 20 Hz. For clarity, the value of $\chi'$ for high dc fields have been multiplied by a factor correspondingly. Surprisingly, the peak in ac susceptibility shows a very peculiar dependence on the applied dc fields. In zero dc field the ac susceptibility exhibits a pronounced peak at 134 K defined as $T_{f1}$, consistent with $T_f$ in

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**FIG. 1.** Temperature dependence of the reference magnetization $M_{\text{ref}}$ (solid line), the magnetization $M$ (open circle), and $\Delta M = M - M_{\text{ref}}$ (close circle).

**FIG. 2.** (Color online) $S$ vs $\log_{10}(t)$ at 60 K for different waiting times.

**FIG. 3.** Temperature dependence of the ZFC ac susceptibility with different superimposed dc fields. Upper inset: $T_{f1}$ vs $H$. The solid line is the best fit to Eq. (2). Lower inset: $T_{f2}$ vs $H$. 

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the ZFC dc $M(T)$. With increase of the dc field, the peak broadens and shifts to lower temperature. When the dc field reaches 3000 Oe another peak at high temperature (defined as $T_f$) becomes clear, which causes the coexistence of two peaks in the ac susceptibility. It is possible that this secondary peak is already present at low dc fields, but cannot be discerned due to the weak signal and the broadness of these peaks. With further increase of dc field up to 80 kOe, the peak at high temperature becomes more pronounced and shifts to higher temperature while the peak at low temperature becomes invisible. We note that the coexistence of two peaks in ac susceptibility has been reported in similar cobaltites by Mira et al.,\textsuperscript{21} although the evolution of these peaks with dc magnetic field had not been studied. Those authors interpreted this behavior as evidence of two different interaction processes in hole-doped cobaltites. It also should be mentioned that a shoulder above 200 K is seen in the ac susceptibility curves with dc field below 100 Oe. Through the out-of-phase component of the ac susceptibility, the same information is obtained. This shoulder is also observed in other La$_{1-x}$Sr$_x$CoO$_3$ samples,\textsuperscript{21} and it corresponds to the Curie temperature of ferromagnetic clusters.

The unusual field dependence of the peaks in ac susceptibility is totally different from that in manganites.\textsuperscript{6} It indicates that there is a more complex picture in the PS state for the Co 3+-O-Co$^{4+}$ FM exchange interaction that causes the formation of FM clusters, it is likely that there are more intermediate or high spin-state Co$^{3+}$ ions as the FM clusters grow with increasing magnetic field. The above results suggest that there is a spin glasslike phase in addition to the FM clusters in La$_{0.82}$Sr$_{0.18}$CoO$_3$. In fact, the existence of a spin glass phase has been confirmed by NMR measurements.\textsuperscript{16} It seems that coherbilities tend to intrinsically separate into FM regions, low spin non-FM regions, and spin glass regions that surround the FM regions as interface layers between FM regions and low spin non-FM regions.

To further examine the nature of the glassy behaviors in cobaltites, we also analyzed the magnetic relaxation using the method for manganites.\textsuperscript{6} Ulrich et al.\textsuperscript{23} proposed a model for interacting magnetic particles and demonstrated that for all particle densities the relaxation rate, $W(t) = -(dl/dt) \ln M(t)$, decays by a powder law, with a density-dependent exponent $n$.

$$W(t) = Ae^{-nt}.$$  \hspace{1cm} (3)

The theoretical prediction was recently corroborated by magnetic relaxation measurements in superferromagnetic granular multilayer\textsuperscript{24} and PS manganites.\textsuperscript{5} We measured the relaxation for our sample with the following procedure, cooling the sample in 10 Oe field from 360 K to $T_m$ (25 K, 60 K, 110 K) after 10 000 s waiting. The solid lines are the best fits to Eq. (3).

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure4.png}
\caption{(Color online) $W$ vs log$_{10}t$ after FC in 10 Oe from 360 K to $T_m$ (25 K, 60 K, 110 K) after 10 000 s waiting. The solid lines are the best fits to Eq. (3).}
\end{figure}

In conclusion, our study of a phase-separated La$_{0.82}$Sr$_{0.18}$CoO$_3$ sample demonstrates that the observed glassy magnetic behaviors cannot be explained only taking into account the intercluster interactions, which is contrary to the situation in manganites. Instead, both a spin glasslike phase and intercluster interactions contribute to the glassy magnetic behaviors. Therefore, it is concluded that the PS...
state in cobaltites consists of FM clusters, non-FM matrix, and spin glasslike regions. It is likely that the spin glasslike regions are the interface layers between the FM clusters and the non-FM matrix. This picture of phase separation in cobaltites is different from that in manganites where the phase separation is in the form of FM clusters embedded in an antiferromagnetic matrix and the glassy behaviors are solely due to intercluster interactions.

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