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The evidence of the glassy behavior in the layered cobaltites

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In this letter, we demonstrate that the origin of the glassy behavior in the phase-separated layered cobaltites cannot be simply ascribed to intercluster interactions as the phase-separated manganites can. Instead, our result indicates that both the intercluster interactions and a spin glass phase contribute to the glassy behaviors. Thus, this study distinguishes the picture of phase separation between cobaltites and manganites. We also observe training effect of the exchange bias, which can be interpreted by a spin configurational relaxation model. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2913013]

Phase separation in perovskite manganites is attracting much attention due to its important role in understanding the abundant physical properties of these compounds.[1] Many phenomena are quite similar to those observed in classical spin glasses. There is a controversy on the question of whether the phase-separated state in manganites forms a classical spin glass phase or not. In a recent letter, Rivadulla *et al.* performed detailed magnetic analysis and demonstrated that the glassy behaviors in manganites can be understood, taking into account only the intercluster interactions.[2] Particularly, the authors proposed that this conclusion is general and should be applicable to the other phase-separated systems such as cobaltites. In this letter, we present a detailed study in a phase-separated layered cobaltite. However, contrary to the conclusion for manganites, our results demonstrate that the glassy behaviors in cobaltites cannot be simply ascribed to intercluster interactions.

In the layered cobaltites, the studies of magnetic properties and neutron diffraction for $Sr_{1+x}La_{1-x}CoO_4$ ($0 \leqslant x \leqslant 0.5$), $Sr_{1.4}La_{0.6}CoO_4$, and $SrPrCoO_4$ systems have been reported. These results have been proved to exhibit a clear picture of phase separation.[3–5] Nevertheless, these systems do not enter a low-temperature spin glass phase. Because of this, the origin of these glassy dynamic remains an open question. In this work, we solve this question by a detailed study of the field dependence of ac susceptibility in a layered $Sr_{1.5}Pr_{0.5}CoO_4$ sample. Our study indicates that both intercluster interaction and a spin glass phase contribute to the glassy magnetic behaviors in the phase-separated layered cobaltites.

The ceramic sample of $Sr_{1.5}Pr_{0.5}CoO_4$ is synthesized by a conventional solid-state reaction method. The x-ray diffraction pattern of $Sr_{1.5}Pr_{0.5}CoO_4$ shows that the sample has a tetragonal structure with the space group $I4/mmm$ similar to that of undoped Sr_2CoO_4 system.[6,7] The magnetic measurements are performed on a quantum design superconducting quantum interference device ($1.8\ \text{K} \leqslant T \leqslant 400\ \text{K}$ and $0\ \text{T} \leqslant H \leqslant 5\ \text{T}$).

Figure 1(a) shows the temperature dependence of magnetization $M(T)$ in a low magnetic field ($H=50$ Oe) under zero-field-cooled (ZFC) and field-cooled (FC) modes. Below 230 K, the ZFC and FC magnetizations display a bifurcation and a glassy behavior is observed. It indicates that the onset of ferromagnetic (FM) ordering within the clusters at $T_C = 230$ K. In the inset of Fig. 1(a), the ZFC magnetization exhibits a peak at the temperature T_f (=127 K) and a short shoulder near 170 K. The shoulder could be due to the intercluster interactions and the sharp peak around T_f implies a collective freezing of magnetic moments.[8] The result of measurement of the thermoremanent magnetization (TRM) is shown in Fig. 1(b). To obtain the TRM data, first, the sample is cooled in a field of 5000 Oe from the room temperature of 300 K down to 5 K. Then the field is removed. Lastly, the measurement is performed at zero field. The TRM decreases with increasing temperature until it vanishes at 230 K, as illustrated in the inset of Fig. 1(b), which further confirms the FM transition.

In order to get an insight into the variation of glassy behavior, we carry out the measurements of $M(T)$ in differ-

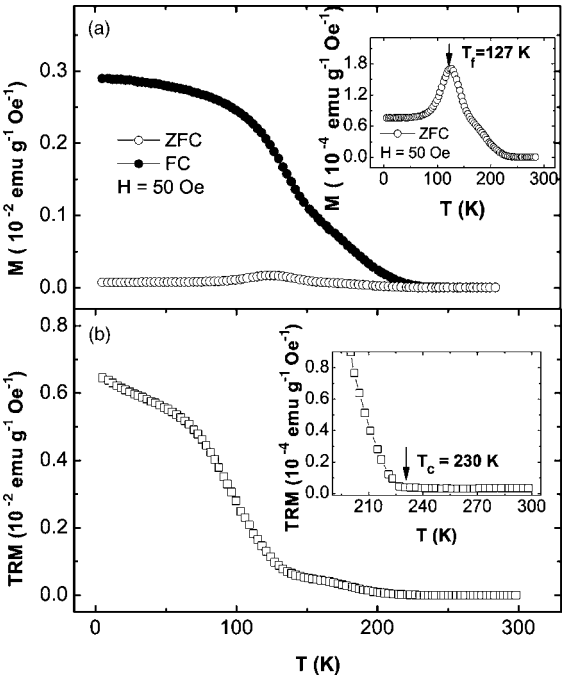

FIG. 1. (a) The temperature dependence of magnetization $M(T)$ under ZFC and FC modes at $H=50$ Oe. (b) The TRM as a function of temperature is obtained on warming at zero field after the sample is cooled from 300 to 5 K at 5000 Oe. Inset: enlargement of (a) $M \sim T$ under ZFC mode and (b) TRM $\sim T$ curve near T_C.

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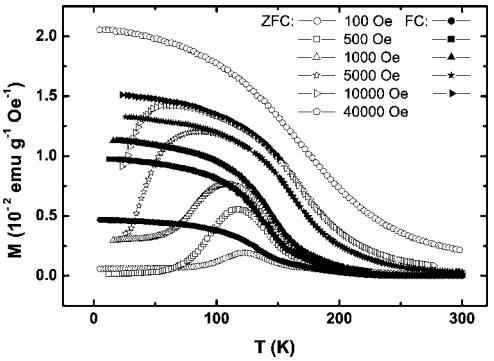

FIG. 2. The $M(T)$ curves under ZFC and FC modes at different magnetic fields.

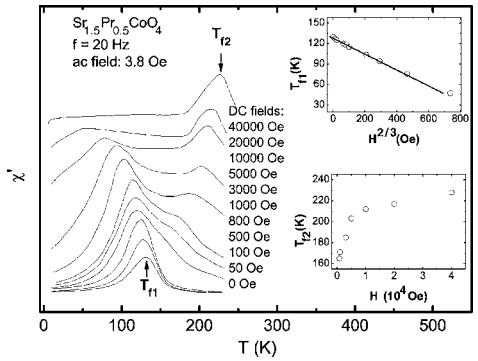

FIG. 4. The temperature dependence of the ZFC ac susceptibility with different superimposed dc fields. Upper inset: T_{f1} vs H. The solid line is the best fit according to the AT line. Lower inset: T_{f2} vs H.

ent applied magnetic fields ($100\ \text{Oe} \leqslant H \leqslant 40\,000\ \text{Oe}$), as shown in Fig. 2. The magnitude of M increases with increasing H. Moreover, both the freezing temperature T_f and the irreversibility temperature T_{irr} (defined from the corresponding temperature of $M_{\text{FC}}=M_{\text{ZFC}}$) shift to the low temperatures. The frozen spin glasslike state is gradually destroyed under the larger H. When H is up to 40 000 Oe, the spin glasslike completely disappears and $M(T)$ displays a pure FM behavior at low temperatures.

We have also performed ac susceptibility measurement. Figure 3 shows the temperature dependence of in-phase component $\chi\prime(T)$ of ac susceptibility in an ac field of 3.8 Oe for the frequencies of 10, 100, and 997 Hz. $\chi'(T)$ presents a peak around $T_f=126$ K at $f=10$ Hz, which is close to the freezing temperature. The peak shifts to a higher temperature with increasing measuring frequency. Such behavior is a typical glass state. The frequency dependence of the shift of the peak in $\chi'(T)$, i.e., $p=\delta T_f/(T_f \delta \log_{10} f) \sim 0.008$. The value is typical for the canonical spin glass system where p ranges from 0.0045 to 0.28.[9] Therefore, the result suggests that the $Sr_{1.5}Pr_{0.5}CoO_4$ system is a spin glass state rather than a cluster glass state.

However, the origin of these glassy magnetic behaviors is still unclear because both classical spin glasses and assemblies of interacting magnetic clusters could give rise to such glassy behaviors. One way is 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.[10] In contrast, for assemblies of interacting FM clusters whose sizes depend on applied dc magnetic field, the peak in ac susceptibility shifts to higher

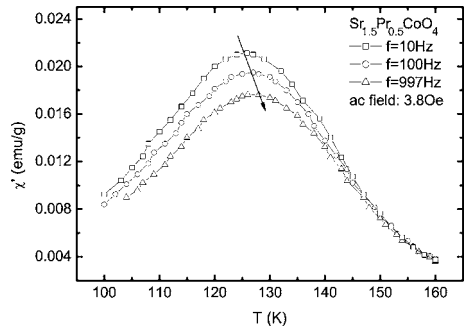

FIG. 3. The temperature dependence of in-phase component of ac susceptibility in an ac field of 3.8 Oe for the frequencies of 10, 100, and 997 Hz, respectively.

temperatures with increasing field due to the growth of the clusters.[2]

In Fig. 4, we show the temperature dependence of ZFC ac susceptibility with different superposed dc fields. The ac field and frequency are fixed as 3.8 Oe and 20 Hz. For clarity, the value of χ' for high dc fields has been correspondingly multiplied by a factor. Surprisingly, the peak in ac susceptibility shows a very peculiar dependence on the applied dc fields. In 50 Oe dc field, the ac susceptibility exhibits a pronounced peak at 127 K defined as T_{f1}, consistent with T_f in the ZFC dc $M(T)$. With the increase of the dc field, the peak broadens and shifts to lower temperature. When the dc field reaches 800 Oe, another peak at high temperature (defined as T_{f2}) becomes clear, which causes the coexistence of two peaks in the ac susceptibility. With further increase of dc field up to 40 000 Oe, the peak of T_{f2} becomes more pronounced and shifts to higher temperature while the peak of T_{f1} becomes invisible.

The unusual field dependence of the peaks in ac susceptibility is totally different from that in manganites.[2] It indicates that there is a more complex picture in the phase separated state for cobaltites than manganites. The T_{f1} shifts to lower temperature at higher dc fields in many classical spin glasses and can be described by the well known de Almeida–Thouless (AT) line,[10–13] i.e.,

$$H_{\text{AT}} = H_0[1 - T_f(H)/T_0]^{3/2}. \tag{1}$$

The solid line in the upper inset of Fig. 4 shows the best fitting result using Eq. (1). The fitted values are obtained with $H_0=1098$ Oe and $T_0=130$ K. In general, the AT line is experimentally identified from the onset of magnetic irreversibility.[11] For the present system, the existence of the spin glass phase is evidenced by the AT irreversibility line.

The dc field dependence of T_{f2} is displayed in the lower inset of Fig. 4. With the increase of the dc field, T_{f2} shifts to higher temperature and gradually approaches the Curie temperature ($T_C \sim 230$ K) of FM clusters. This behavior is similar to that in the phase separated manganites, indicating that the size of magnetic clusters can be tuned by a magnetic field. The growth of magnetic clusters can accompany with the magnetic-field-induced spin state transition of Co^{3+} ions. Because only the intermediate or high spin-state Co^{3+} ions can take part in the Co^{3+}–O–Co^{4+} FM exchange interaction leading to the formation of FM clusters, 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 glass phase in addition to the FM

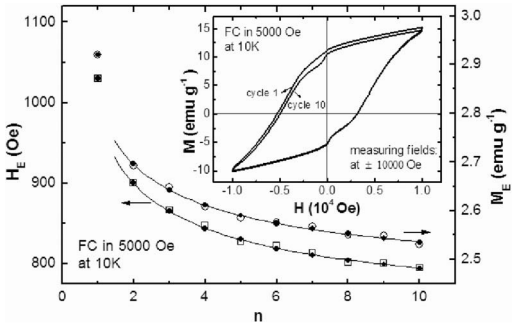

FIG. 5. The number of field cycles n dependence of H_E and M_E (open symbols) at 10 K after FC in 5000 Oe magnetic field. The solid lines show the best fitting with Eq. (2) to the data for $n \geqslant 2$. The solid symbols show the data originated from the Eq. (3) (see the text). The inset: the training effect of exchange bias. The first and the tenth loops at 10 K after FC in 5000 Oe magnetic field.

clusters in the present $Sr_{1.5}Pr_{0.5}CoO_4$ system. It seems that cobaltites 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.

As is well known, a spin-disordered interface/surface layer is usually formed when a FM particle is embedded in a non-FM matrix.[14] It is possible that the spin glass regions could exist at the interfaces between the FM clusters and the non-FM matrix. Thus, the exchange bias could be explored based on the fact that there exists a coupling between the FM clusters and spin glass regions in the layered cobaltites. One of the important characteristics in exchange bias system is the training effect, which describes the reduction of exchange bias field H_E and exchange bias magnetization M_E when the sample is continuously field cycled.[15] The shift of magnetic field is defined as $H_E=-(H_{C1}+H_{C2})/2$, where H_{C1} and H_{C2} are the negative and positive coercive fields, respectively. The vertical magnetization shift is defined as $M_E=(M_{r1}+M_{r2})/2$, where M_{r1} and M_{r2} are the positive and negative remanent magnetization. For $Sr_{1.5}Pr_{0.5}CoO_4$ sample, the continuous hysteresis loops are measured at 10 K after FC at 5000 Oe and the measuring field range is from −10 000 to 10 000 Oe. The first and the tenth loops are shown in the inset of Fig. 5. The exchange bias field H_E and the shift of magnetization M_E decrease with the field cycling. The number of field cycles n dependence of H_E (open squares) and M_E (open circles) is shown in Fig. 5.

The usual experimentally observed relationship between H_E (M_E) and n is given by a simple power law

$$H_E - H_{E\infty} \propto 1/\sqrt{n}, \tag{2}$$

where $H_{E\infty}$ is the exchange bias field in the limit of infinite loops.[15,16] The solid lines in Fig. 5 show the best fitting results by H_E and M_E data with the field cycle number $n>1$. The fitting curves show satisfactory agreement with the experimental data with $n>1$. The fitting parameters $H_{E\infty}=710$ Oe and $M_{E\infty}=2.41$ emu/g are obtained, respectively. However, the Eq. (2) holds only for loop cycles $n \geqslant 2$ and can not explain the steep relaxation for $n=1$. Recently, Binek has used a discretized relaxation model deducing a recursive formula with the n dependence of H_E (M_E).[17] The relation is expressed by

$$H_E(n+1) - H_E(n) = -\gamma[H_E(n) - H_{E\infty}]^3, \tag{3}$$

where γ is a sample-dependent constant. Using $\gamma=1.46\times10^{-6}$ Oe^{-2} and $H_{E\infty}=583$ Oe, the theoretical values of H_E (solid circles in Fig. 5) are calculated by the Eq. (3). Likewise, the theoretical values of M_E (solid circles in Fig. 5) are obtained with $\gamma=1.17$ emu/g^{-2} and $M_{E\infty}=2.34$ emu/g. Interestingly, it is found that the theoretical data are well accordant with experimental results not only for $n>1$ but also for $n=1$. Thus, the spin configurational relaxation model can describe our experimental results well. When the applied magnetic field continuously cycles, some of the frozen spin glass spins along with the cooling field direction and may alter their directions and fall into the metastable configurations, which decrease the strength of exchange coupling at the interfaces. The continuous reversion of the FM cluster magnetization triggers the configurational relaxation of the interfacial spin glass spins towards equilibrium and causes the training effect.

In summary, our result of the phase-separated $Sr_{1.5}Pr_{0.5}CoO_4$ sample demonstrates that the observed glassy magnetic behaviors cannot be explained by only taking into account the intercluster interactions, which is contrary to the situation in manganites. Instead, both a spin glass phase and intercluster interactions contribute to the glassy magnetic behaviors. Additionally, the exchange bias exhibits a training effect, which can be explained by a spin configurational relaxation model.

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