Distinguishable reentrant spin-glass behavior induced by the frustration of exchange interaction in phase-separated $Sm_{0.5}(Ca,Sr)_{0.5}MnO_3$ systems

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In order to understand the relationship between the stability of the charge-ordered state and the low-temperature phase competition, the magnetic and electrical properties are systemically investigated for half-doped $Sm_{0.5}A_{0.5}MnO_3$ systems with a dissimilar average *A*-site cationic radius of Ca and Sr, which induces a complete different magnetic ordering and the complex coexistence of magnetic phases at the lower temperature. Some abnormal phenomena are observed in both systems. The frequency dependence of ac magnetization and the bifurcation between zero-field-cooled and field-cooled magnetization curves indicate the reentrant spin-glass behavior in both oxides, which may be induced by the frustration of the ferromagnetic double-exchange interaction and antiferromagnetic superexchange interaction. A long-time relaxation of magnetization is possibly due to the cluster-type and traditional reentrant spin-glass transition. The difference between the behaviors of these two series proves the existence of two types of reentrant spin glass.

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I. INTRODUCTION

The recent investigation of doped manganites has revealed their complex magnetic and transport behaviors far below the room temperature.[1–4] The magnetic and electronic properties are always correlated to each other due to the strong correlations between spin, orbital, and lattice degrees of freedom.[2,5] In this kind of material, the electronic phase separation has been generally observed,[6–8] which results from the competition between ferromagnetic (FM) metallic and charge-ordering (CO) antiferromagnetic (AFM) insulating states, and it is a characteristic that strongly influences the low-temperature properties. The half-doped $R_{0.5}A_{0.5}MnO_3$ (*R* is a trivalent rare-earth ion and *A* a divalent alkaline earth ion) is considered as a representative manganese oxide which presents CO state at low temperature,[5,9–12] generally with small radius $\langle r_A \rangle$,[12] and usually accompanied with a lot of novel phenomena, such as insulator-metal transition,[9] spin-glass (SG) transition,[13] etc. As a controversial issue, SG has been found in a wide variety of systems with the following common features: (1) frozen-in magnetic moments below some freezing temperature T_{SG} and hence a peak in the frequency-dependent susceptibility, (2) lack of periodic long-range magnetic order, and (3) remanence and magnetic relaxation on macroscopic time scales below T_{SG} when there are changes in the magnetic field.[14] Furthermore, a certain number of SG systems display reentrant behavior which shares the characteristics of both SG and magnetic orderings. These so-called reentrant spin-glass (RSG) systems undergo a magnetic ordering transition and have a spin freezing transition at lower temperature.[15,16] For $R_{0.5}Ca_{0.5}MnO_3$, it is proved that this long-range CO takes place in the Mn^{3+}/Mn^{4+} cations,[17] presenting not only in AFM regions but also in FM regions,[18] and it also shows highly insulting behavior which can be melted by several physical excitations. In bulk materials, the CO melting magnetic field, which is considered as a criterion of the stability of the CO state,[19–22] increases with the decrease of average *A*-site cationic radius $\langle r_A \rangle$.[12,23,24] However, at the lower temperature, the situation is not so simple because of the standing out of strong correlation and frustration of the interactions. Therefore, more punctilious and particular work is required for the further understanding of the lower-temperature behavior, such as SG behavior, and even the fundamentals of the strong-correlation mechanism. In this paper, we concentrate on ceramic $Sm_{0.5}Sr_{0.5}MnO_3$ and $Sm_{0.5}Ca_{0.5}MnO_3$ with a relatively large $\langle r_A \rangle$ (~1.22 Å) and small $\langle r_A \rangle$ (~1.16 Å), respectively. The existence of stable CO state in these two series has been testified and the complex coexistence of magnetic phases at the lower temperature is supposed.[25–27] In order to understand the relationship between the stability of the CO state and the low-temperature phase competition, we have studied the magnetic and transport behaviors of this two samples, especially at the lower temperature, and some abnormal phenomena are observed in both samples. All of these actually are associated with the magnetic relaxation of RSG state.[15] Our studies show that the RSG behaviors are different for $Sm_{0.5}Sr_{0.5}MnO_3$ and $Sm_{0.5}Ca_{0.5}MnO_3$, and these phenomena in both series originate from phase separation.

II. EXPERIMENTAL PROCEDURE

The experimental samples were prepared by a conventional solid-state reaction method. The quality of the samples was checked by x-ray diffraction (18 kW D/max-2500 diffractometer, Cu $K\alpha$ radiation), indicating that both samples are in good single phase of orthorhombic structure (see Fig. 1). Magnetic measurements were carried out using PPMS-9 (physical property measurement system, Q/D Inc., USA) with the precision of 20 nV for voltage and 0.2 Oe for the magnetic field. All the *M-H* curves were recorded after the sample was cooled down under zero-field-cooled (ZFC) condition from the paramagnetic state at room temperature. Resistivity measurements were carried out using the conventional four-probe technique, under applied dc magnetic fields ranging from 0 to 7.0 T, with a temperature precision of

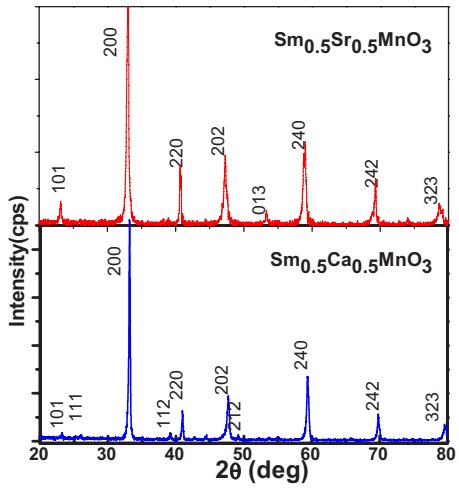

FIG. 1. (Color online) Room-temperature x-ray diffraction patterns of $Sm_{0.5}Sr_{0.5}MnO_3$ and $Sm_{0.5}Ca_{0.5}MnO_3$ samples.

0.01 K. The temperature range of these measurements is 2.5–300 K. All of the results are repeatable.

III. RESULTS AND DISCUSSION

The previous experiments showed that $Sm_{0.5}Ca_{0.5}MnO_3$ is a COAFM insulator and no metallic state can be detected below room temperature.[25] From the present ac susceptibility $M'(T)$ curve, an obvious peak is observed at lower temperature (~41 K), as shown in Fig. 2, while the temperature dependence of electrical resistivity evidences a normal behavior of insulator under dc fields of 0, 0.3, and 6 T, attributed to the establishment of stable COAFM state (the upper inset of Fig. 2). This is a strange result for $Sm_{0.5}Ca_{0.5}MnO_3$, which is generally considered as a stable COAFM insulator below $T_{CO} \approx 270$ K,[25] and it is easy to have visions of RSG

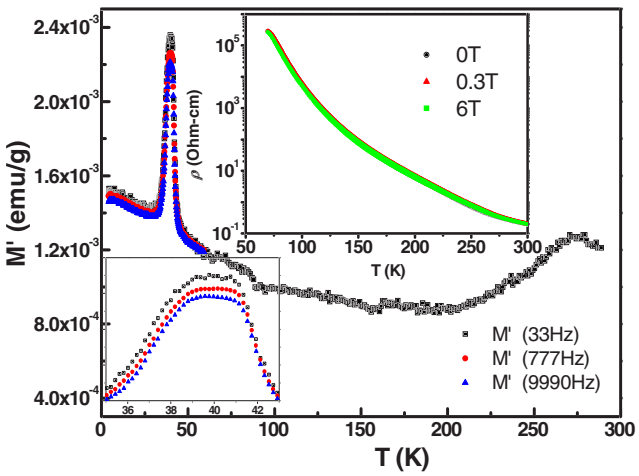

FIG. 2. (Color online) Temperature dependence of ac magnetization at 10 Oe with different frequencies, 33, 777, and 9990 Hz, for $Sm_{0.5}Ca_{0.5}MnO_3$ sample and the lower inset is the enlargement of the peak. The upper inset shows the temperature dependence of electrical resistivity for $Sm_{0.5}Ca_{0.5}MnO_3$ sample at different dc fields.

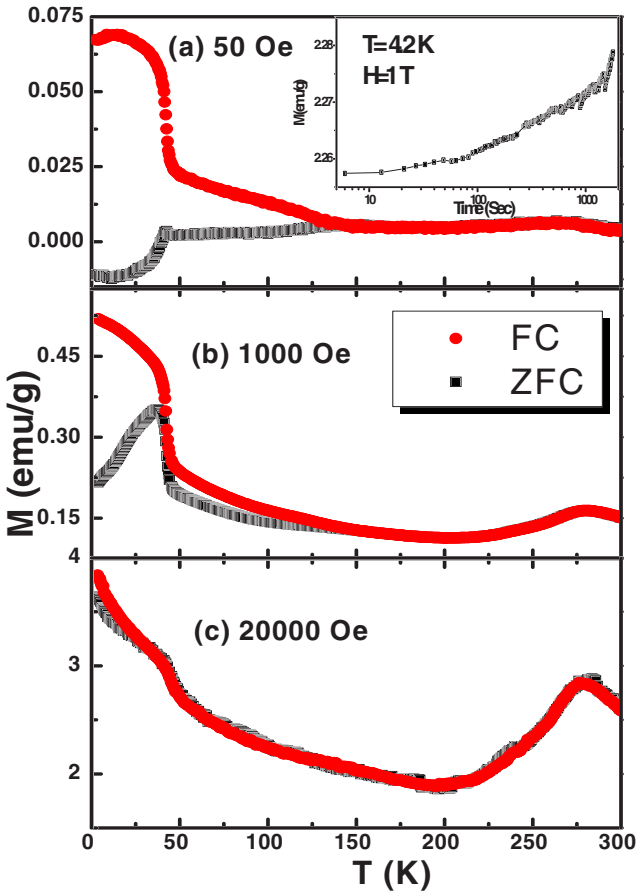

FIG. 3. (Color online) Temperature dependence of dc magnetization for $Sm_{0.5}Ca_{0.5}MnO_3$ sample at (a) 50 Oe, (b) 1000 Oe, and (c) 20000 Oe in the zero-field-cooled (ZFC) and field-cooled (FC) modes. Inset: Time dependence of ZFC magnetization of $Sm_{0.5}Ca_{0.5}MnO_3$, with $H=1$ T at 4.2 K.

transition,[15] which shares the characteristics of both SG and magnetic ordering such as FM or AFM ordering. In order to understand this intriguing phenomenon, a series of experiments at the lower temperature were taken. Figure 2 also gives the $M'(T)$ curves with various frequencies, 33, 777, and 9990 Hz, around the temperature of 41 K. The peak of $M'(T)$ is frequency dependent (see the enlargement of the peak shown as the lower inset of Fig. 2). It should be noticed that the height of these peaks descends with increasing frequency from 33 to 9990 Hz. These are the intuitionistic behavior of the classical SG transition[14] and it is necessary to combine other experimental results to clarify it.

Magnetization data of $Sm_{0.5}Ca_{0.5}MnO_3$ as a function of temperature collected at 50, 1000, and 20 000 Oe under the field-cooled (FC) and ZFC conditions are shown in Fig. 3. In 50 Oe field, for both conditions, although the magnetization is very small in the temperature range from 140 to 300 K, it can be observed that there is a peak linked to the CO transition at 270 K, even in the higher magnetic field. At 140 K, the remarkable noncoincidence in (a) and (b) of Fig. 3 may be attributed to the nonhomogeneous magnetic clusters.[28,29] Below 41 K, the irreversible behavior becomes more obvious: the FC curve heightens drastically from 41 down to

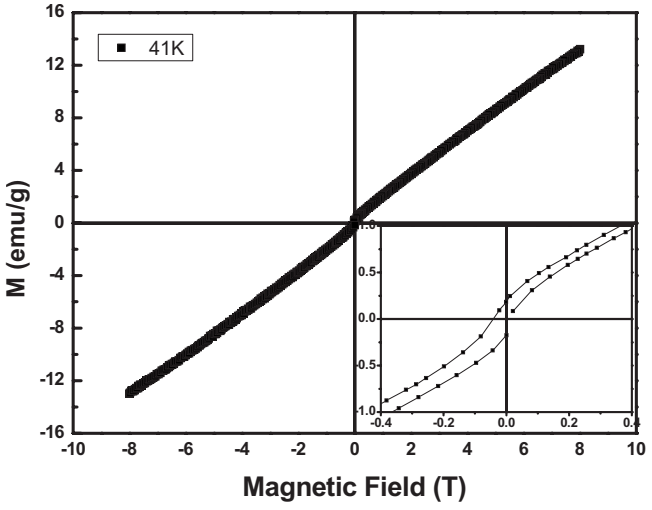

FIG. 4. Magnetization curves of $Sm_{0.5}Ca_{0.5}MnO_3$ measured at 41 K. The inset is the enlargement of the low field condition.

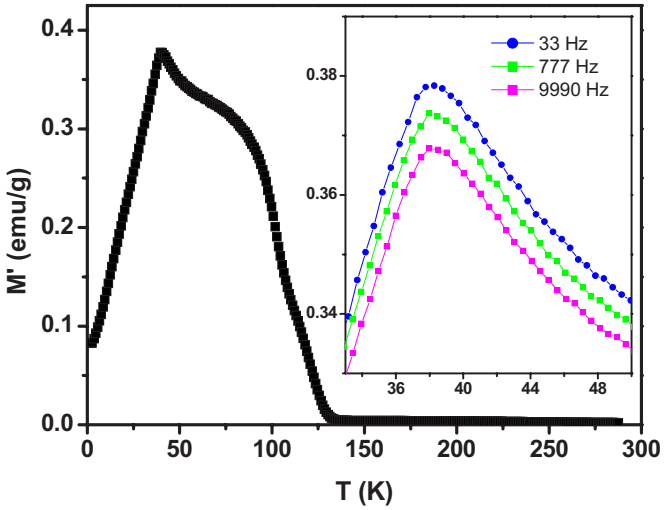

FIG. 5. (Color online) The temperature dependence of ac magnetization of the $Sm_{0.5}Sr_{0.5}MnO_3$ sample at an ac field of 10 Oe. The inset shows the maximum of the $M'(T)$ at various frequencies.

2 K; meanwhile, the ZFC curve falls off after a tiny tine. This kind of bifurcation is a magnetic characteristic of the SG state and the tiny tine argues that a short-range FM order is established, which is much more similar to those found in cluster-glass systems.[30] As shown in Fig. 3, the higher magnetic field is, the less inconspicuous the difference between ZFC and FC curves becomes and the lower bifurcation temperature is. This behavior indicates that the high magnetic field suppresses the relaxation behavior of SG. Thus, it is suitable to term this behavior cluster-type RSG. The inset of Fig. 3 shows the time dependence of M, measured after ZFC process to 4.2 K and applying the field $H=1$ T. After the field is applied (Time=0 s), the magnetization exhibits a slow nonexponential increase, indicative of a nonequilibrium nature. This long-time relaxation of magnetization is another signature of glassiness.[14] Unexpectedly, negative magnetization is detected below 40 K under ZFC condition until up to 140 Oe, which probably originates from an antiparallel orientation of Mn weak ferromagnetic moment and the Sm moment induced by Sm-Mn exchange interaction.[31] These complex interactions, such as COAFM, short-range FM, and Sm-Mn exchange interactions, lead to cluster-type phase separation[32] and frustration at lower temperature, which may be the origination of cluster-type RSG.

In order to detect the existence of short-range FM order in the magnetic disorder environment at 41 K, the temperature of cluster-type RSG transition, M-H curve is given in the Fig. 4. At higher temperature, the M-H curves show a linear behavior which is attributed to the AFM state, without any evidence of the FM state, for which the magnetization is strongly influenced by the applied field until magnetic saturation. As shown in the Fig. 4, at 41 K, the situation is changed subtilely. Although from −8 to 8 T it also shows linear behavior in the whole range, magnetic hysteresis loop is observed at the low field and the coercive force is about 0.04 T, which is the characteristic of the short-range FM order that we mentioned above despite the fact that the proportion is so small that the electrical transport behavior cannot be influenced and the disorder localizes e_g electrons at this temperature. The nonlinear behavior is seen in the data taken under both increasing and decreasing fields. It is the characteristic of the weak FM order. In previous investigation,[33] it has been considered that with the decrease of $\langle r_A \rangle$, the magnetic ordering changes from AFM (e.g., $Pr_{0.7}Ca_{0.3}MnO_3$ with $\langle r_A \rangle$ of 1.179 Å) to spin-glass-like (e.g., $Y_{0.5}Sr_{0.5}MnO_3$ with $\langle r_A \rangle$ of 1.03 Å). The $\langle r_A \rangle$ of $Sm_{0.5}Ca_{0.5}MnO_3$ is intermediate between them, so the cluster-type RSG transition appears at 41 K. This lower temperature around 40 K is very special not only for $Sm_{0.5}Ca_{0.5}MnO_3$ but for $Sm_{0.5}Sr_{0.5}MnO_3$. $Sm_{0.5}Sr_{0.5}MnO_3$ and $Sm_{0.5}Ca_{0.5}MnO_3$ are so different in chemical factors that magnetic and electrical transport properties, which have been systematically studied,[25] such as double-exchange (FM), superexchange (AFM), and Sm-Mn exchange interactions, are competing with each other for both series at the lower temperature, and their corresponding phenomena are shown in different ground states.

Figure 5 shows the temperature dependence of ac magnetization of the $Sm_{0.5}Sr_{0.5}MnO_3$ sample, comprising four regions: a rapid increase from 2.5 to 40 K at which a remarkable peak appears, a plateau from 40 to 80 K, a drastic decrease from 80 to 130 K, and a plain from 130 to 300 K. This temperature dependence is quite similar to that of $Sm_{0.7}Sr_{0.3}MnO_3$ (Ref. 32) except the numerical value of transition temperature. It is unambiguous that the Curie temperature (T_C) is 110 K, which conforms to the phase diagram given by Martin *et al.*[25] What we are interest in is the lower-temperature behavior below T_C, such as the maximum of M' around 40 K, which is very similar to that of $Sm_{0.5}Ca_{0.5}MnO_3$. Although FM state is dominant below T_C, AFM component partly remains and coexists with the FM component toward phase separation. The inset of Fig. 5 gives the frequency dependence of the $Sm_{0.5}Sr_{0.5}MnO_3$ sample at the temperature around 40 K. The frequency dependence of the maximum is so analogous with that of $Sm_{0.5}Ca_{0.5}MnO_3$ sample which should be associated with the glassy state. At the lower temperature, the drastic decrease of M' while the

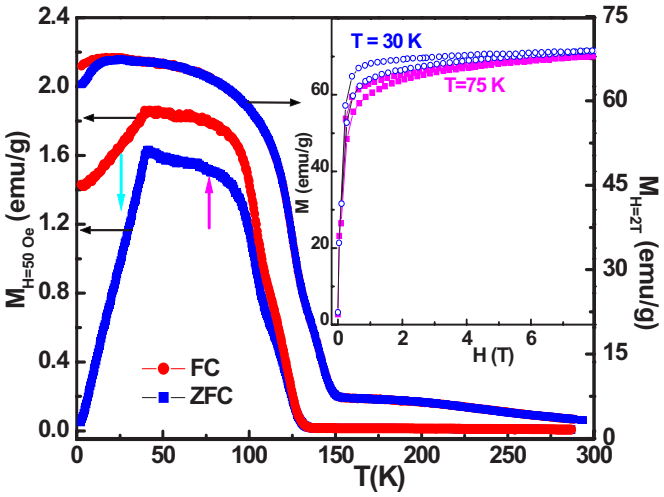

FIG. 6. (Color online) The ZFC and FC magnetization vs temperature $M(T)$ curves at 50 Oe and 2 T dc field. The inset shows the magnetic hysteresis loops at 30 and 75 K [marked in the ZFC $M(T)$ curve at the corresponding temperature], respectively.

temperature goes down in this figure evidently displays the intrinsic frustration of FM exchange interaction and the buildup of the disordered magnetic component.

For more information about the lower-temperature behavior, we give the ZFC and FC magnetization vs temperature $M(T)$ curves, under dc field 50 Oe and 2 T, in Fig. 6 and the magnetic hysteresis loops at 30 and 75 K [marked in the 50 Oe ZFC $M(T)$ curve at the corresponding temperature], respectively (see the inset of Fig. 6). Below T_C, the FM exchange interaction is dominant but not absolute. As the result of the previous study,[25] paramagnetic phase to COAFM phase transition occurs at $T_N \sim 170$ K for the polycrystalline $Sm_{0.5}Sr_{0.5}MnO_3$ sample, which is difficult to be detected on the $M(T)$ curve but it is evidenced by microscopy observations. The establishment of COAFM state can also be detected by the electrical transport behavior study shown in Fig. 7. It always displays an abrupt increase of the resistivity, which is hardly influenced by the applied field. Below T_C, it is more reasonable that FM state coexists with the residual canted AFM state rather than a pure FM state in the material, because the ZFC and FC curves bifurcate and

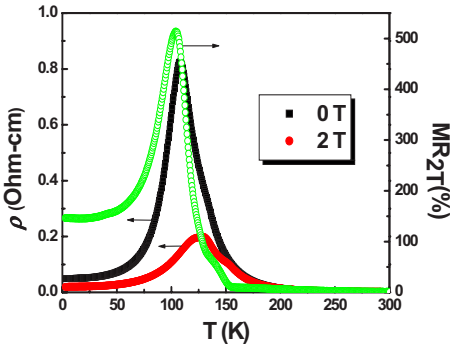

FIG. 7. (Color online) The temperature dependence of the resistivity measured in 0 and 2 T and the magnetoresistance defined as $MR_{2\ T}=100\% \times [R(0)-R(2\ T)]/R(2\ T)$.

the magnetization curve at 75 K continuously increases without saturation up to 8 T. The further forfication, at 40 K, is an evidence for the RSG, which is associated with the competing frustration among the FM double-exchange interaction and AFM superexchange interaction, originating from the phase-separation state. When the field is increased up to 2 T, the irreversibility still remains between ZFC and FC magnetizations but the bifurcate temperature becomes lower, which actually is the property of SG phase. This RSG phase is more susceptive to the applied field than the AFM phase, though with a long spin relaxation time, and it is also easy to be ordered to the FM state with an irreversible magnetizable process at the lower temperature, such as 30 K shown in the inset of Fig. 6. The different magnetizable process results in the dissimilar slope of these two curves shown as the magnetic hysteresis loops at 30 and 75 K with the approximative magnetization at 8 T. These $M(T)$ curves and hysteresis loops of $Sm_{0.5}Sr_{0.5}MnO_3$ indicate the reduction of canted AFM phase, which is attributed to the frustration of competition between double-exchange and superexchange at lower temperature. Focusing on the dc magnetization results of these two series, while in $Sm_{0.5}Ca_{0.5}MnO_3$ the M_{FC} below $T_{RSG} \sim 41$ K drastically increases with the lowering of T, in $Sm_{0.5}Sr_{0.5}MnO_3$ sample it monotonically descends. Compared to the former system, which is considered as cluster-type RSG, the difference between M_{FC} and M_{ZFC} is more inconspicuous in $Sm_{0.5}Sr_{0.5}MnO_3$ at sufficiently low temperature, indicating the presence of isolated atomic magnetic moments glassy disorder phase, i.e., traditional RSG phase.[15,16]

The temperature dependence of the resistivity and the magnetoresistance ($MR_{2\ T}=100\% \times [R(0)-R(2\ T)]/R(2\ T)$) are shown in the Fig. 7. Above the temperature of 150 K, the $R(T)$ curves under magnetic fields of 2 and 0 T match together without the influence of applied field on the resistivity. It shows that the CO phase stabilizes electrical transport effectively until the FM domain, which should take charge of the colossal magnetoresistance behavior, is generated. From the zero-field $R(T)$ curve, a maximum is found at $T_C \approx 110$ K, around which the MR reaches the maximum. However, the maximum of 2.0 T field $R(T)$ curve moves to higher temperature, indicating that the applied field is helpful in establishing the FM state. What should be noticed is the kink of the MR(T) curve around 40 K and a platform below 40 K, which should also be associated with the presence of the RSG disorder phase. At this temperature, the disorder phase is easy to be ordered under the applied field, so the intensity of spin scattering is reduced with the increase of applied field. It is shown that the CO phase and the disordered phase can markedly influence the electrical transport, which can be presented by the contrast between the resistivity characteristics with and without applied field.

IV. CONCLUSIONS

We studied ac and dc magnetization and transport properties of $Sm_{0.5}Ca_{0.5}MnO_3$ and $Sm_{0.5}Sr_{0.5}MnO_3$ systems with a dissimilar average A-site cationic radius of Ca and Sr. The peaks of $M'(T)$ curves for both samples show the frequency-

dependent behavior far below the magnetic ordered temperature. At the RSG transition temperature T_{RSG}, the magnetizations have different kinds of bifurcation between ZFC and FC data, indicating a long-time relaxation of magnetization. These are presumably due to the cluster-type and traditional RSG transition, respectively. At and even above T_{RSG}, the $Sm_{0.5}Ca_{0.5}MnO_3$ appears COAFM long-range ordered accompanied with FM cluster. Correspondingly, in the $Sm_{0.5}Sr_{0.5}MnO_3$ sample, FM order is dominant after the collapse of COAFM and shows the colossal magnetoresistance behavior, though there is coexisting residual canted AFM phase. This phase-separation behavior at the lower temperature in both systems leads to the frustration, which should be the origin of the RSG phase.

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