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Glassy transport phenomena in a phase-separated perovskite cobaltite

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We demonstrate that single-crystal $La_{1-x}Sr_xCoO_3$ in the semiconducting spin-glass phase ($x<0.18$) displays a strong interplay between electronic conduction and spin-glass freezing. The resistivity exhibits a bifurcation of zero-field cooled and field-cooled temperature dependences, glassy response to application and removal of magnetic fields, and, most remarkably, a waiting time or "aging" effect directly in the resistivity. This behavior has its origin in the magnetoelectronic phase separation into nanoscopic ferromagnetic clusters embedded in a nonferromagnetic matrix, analogous to relaxor ferroelectrics.

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There now exists a great deal of evidence that oxides such as cuprates and manganites exhibit a close competition among various magnetic and electronic ground states, and that this can result in magnetoelectronic inhomogeneity.[1,2] These systems exhibit spatial coexistence of multiple phases, even in the absence of chemical segregation. As an example, competition between a ferromagnetic (FM) metallic phase, and a charge and orbitally ordered insulating (COOI) phase is common in manganites.[1–4] This competition, and the ensuing phase separation, is found in many complex oxides and is thought to play a key role in some of their most intriguing properties.[1,2] This point is reinforced by the global manganite phase diagram in the plane of disorder versus one-electron bandwidth, which reveals that the colossal magnetoresistance (CMR) is maximized when COOI and FM phases compete.[5]

The doped perovskite cobaltite $La_{1-x}Sr_xCoO_3$ (LSCO) has been advanced as a model system for the investigation of magnetic phase separation.[6–9] At low doping, metallic FM clusters form in a non-FM insulating matrix, as proven by Co (Ref. 7) and La (Ref. 8) NMR, and small-angle neutron scattering.[9] With increasing x the clusters become more populous, eventually coalescing at $x=0.18$, leading to long-range FM order and a coincident percolation transition.[10,11] The non-FM matrix has a spin and/or cluster glass (SG) component and the system behaves like a SG semiconductor at $x<0.18$, and as a FM metal at $x>0.18$.[11] Recently we have begun to elucidate the *consequences* of this phase separation by demonstrating that the formation of FM clusters in a non-FM matrix leads to an intergranular giant magnetoresistance (GMR) effect analogous to that seen in artificial heterostructures.[9] Such a situation was envisioned in the theoretical work of Dagotto *et al.*[1] In this paper we describe a second consequence of the magnetoelectronic phase separation—the existence of glassy transport phenomena. We find that in the semiconducting SG phase of single-crystal LSCO ($x<0.17$) the resistivity shows bifurcation of field-cooled and zero-field cooled resistivity curves at the SG freezing temperature (T_{SG}), slow response to removal of applied fields after field cooling, slow response to application of applied fields and, most remarkably, a "waiting time" or "aging" effect directly in the resistivity. The latter effect is analogous to that seen in the magnetization relaxation rate of typical spin glasses.[12] and has been detected here by transport.

A strong dependence of electrical resistivity on SG freezing is rare in manganites, with a few notable exceptions.[13–15] In fact, the strong interplay between magnetic interactions and electronic conduction in magnetic semiconductors in general leads to large MR,[3,16–22] field-tuned metal-insulator transitions (MITs),[23,24] magnetic polaron scattering,[18] and hard gaps in the density of states,[25] but rarely any form of interplay between transport and SG freezing. The only effects observed to date involve a subtle freezing of the bound magnetic polaron binding energy in some dilute magnetic semiconductors.[18,21,25] We demonstrate here that LSCO is remarkably different in that it displays a strong interplay between SG freezing and electronic conduction, a direct result of the phase separation.

Single-phase LSCO single crystals with $x\leqslant 0.20$ were grown by a floating zone method and characterized by x-ray and neutron diffraction.[9] Magnetometry and magnetotransport measurements were performed in a commercial superconducting quantum interference device (SQUID) magnetometer and a flow cryostat with a 90-kOe superconducting magnet, respectively. Indium contacts were used in a van der Pauw configuration and the measurements were made with both dc and ac (13.7 Hz) excitations. Rigorous checks were made to ensure ohmic behavior of the contacts down to 4 K.

Figure 1 shows the temperature dependence of the resis-

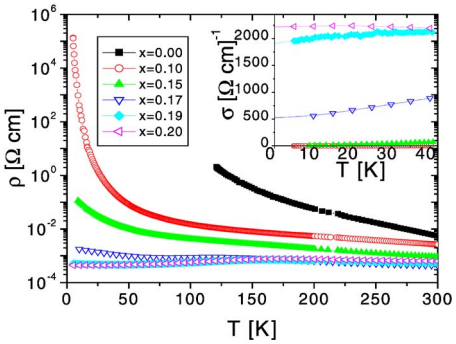

FIG. 1. (Color online) Temperature dependence of the resistivity of six single crystals of $La_{1-x}Sr_xCoO_3$ ($0<x<0.20$), in the vicinity of the metal-insulator transition. Inset: Temperature dependence of the low T conductivity of the same samples.

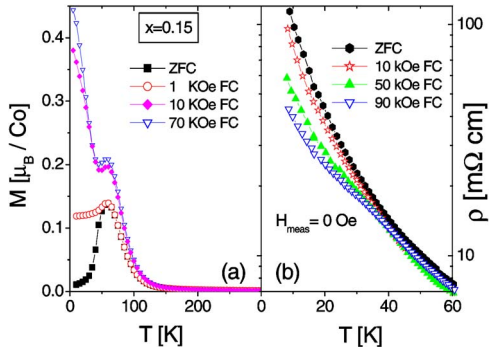

FIG. 2. (Color online) Temperature dependence of (a) the dc magnetization (measured in 1 kOe) after field cooling in 1, 10, and 70 kOe, and after zero-field cooling, and (b) the resistivity measured in zero field after cooling in 0, 10, 50, and 90 kOe. The magnetization data were taken on warming at 1.25 K/min after cooling at 10 K/min. The resistivity data were taken on warming at 2 K/min after cooling at 3 K/min.

tivity (ρ) of six samples of LSCO with $0.00 \leqslant x \leqslant 0.20$. $\rho(T)$ evolves from strongly insulating at low doping to a weak temperature dependence with positive $d\rho/dT$ at high temperatures for $x \geqslant 0.17$. The inset to Fig. 1 displays the low T conductivity showing that the system crosses over from a $T=0$ extrapolation of the conductivity that is zero at $x \leqslant 0.15$ to a situation at $x \geqslant 0.17$ where $\sigma(T \to 0)$ is clearly finite, indicating a MIT at $x \approx 0.17$. On the semiconducting side of the MIT we observe the intergranular GMR-type effect previously reported,[9] as well as the glassy transport phenomena that are the subject of this paper. Figure 2 shows the T dependence of the magnetization, M (left panel), and ρ (right panel) taken on warming after field cooling (FC) and zero-field cooling (ZFC) from 300 K. The $x=0.15$ sample is shown as representative of all of the semiconducting compositions, as all samples with $x \leqslant 0.16$ exhibit qualitatively similar behavior. (Note that these effects are *not* present at $x \geqslant 0.17$ when the isolated FM clusters coalesce into a long-range ordered FM network.) As expected, the ZFC $M(T)$ exhibits a sharp peak at $T_{SG} \approx 50$ K, accompanied by a clear bifurcation of ZFC and FC $M(T)$ curves even in small cooling fields (1000 Oe). The peak in $M(T)$ is preserved even for high cooling fields (up to 70 kOe). What is remarkable about this system is the sensitivity of the *zero field measured* $\rho(T)$ to this SG freezing, as shown in Fig. 2(b). The FC $\rho(T)$ splits from the ZFC curve at a temperature just below T_{SG}, the extent of the splitting increasing monotonically with reducing T and increasing cooling field. It is important to note that the ZFC–FC split in $M(T)$ is clear even in small magnetic fields (10 Oe), whereas $\rho(T)$ is sensitive only to larger cooling fields (10–100 kOe). We will return to this point later. Note that very small splitting between ZFC–FC $\rho(T)$ curves have been observed in Pr_2CuGe_6 (Ref. 26) and some heavy fermion systems,[27] while much larger effects have been observed in a small number of manganites.[13–15] To the best of our knowledge simple metallic SG materials do not display this effect.

The glassy behavior below T_{SG} is illustrated further in Fig. 3, which shows $M(t)$ and $\rho(t)$ after field cooling to

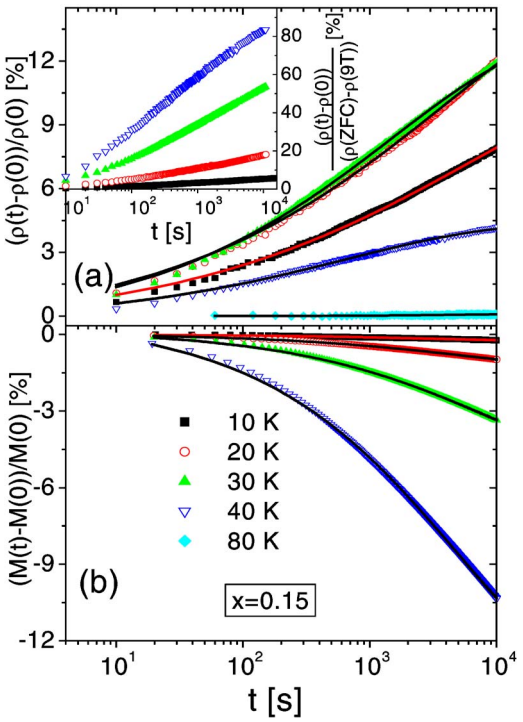

FIG. 3. (Color online) (a) Time dependence of the resistivity (plotted as % change in resistivity vs time on a $\log_{10}$ scale) after cooling from 100 to 10 K at >1 K/s in 90 kOe, then removing the field in 760 s. The solid lines are fits to the stretched exponential form given in the text (fitting parameters: 10 K: $\tau=6600$ s, $\gamma=0.31$; 20 K: $\tau=3811$ s, $\gamma=0.34$; 30 K: $\tau=1480$ s, $\gamma=0.38$; 40 K: $\tau=650$ s, $\gamma=0.38$). (b) Time dependence of the dc magnetization (plotted as % change in magnetization vs time on a $\log_{10}$ scale) after cooling from 100 to 10 K at 0.08 K/s in 10 Oe, then removing the field in 100 s. In both cases $t=0$ corresponds to the point where the field reaches zero. The solid lines are fits to the stretched exponential form (Fitting parameters: 10 K: $\tau=7840$ s, $\gamma=0.39$; 20 K: $\tau=7200$ s, $\gamma=0.44$; 30 K: $\tau=5800$ s, $\gamma=0.47$; 40 K: $\tau=4900$ s, $\gamma=0.47$) Inset: The data of (a) scaled by the difference between zero-field cooled and 90 kOe field-cooled resistivity at that particular temperature [from Fig. 2(b)].

$T < T_{SG}$ and removing the cooling field. Consistent with Fig. 2, ρ is found to increase with t while M slowly decreases after removal of the cooling field. The time scale of the resistivity relaxation is very long ($>10^5$ s), indicating glassy behavior. Note that the magnitude of resistivity relaxation in 10^4 s is nonmonotonic with temperature. This can be simply understood on the basis of Fig. 2. As the freezing temperature is approached from below, the splitting between ZFC and FC curves decreases, eventually reaching zero at ~40 K. It is therefore clear that with increasing T, the total extent of the resistivity relaxation shown in Fig. 3 is reduced as the resistivity difference between the initial state and the ZFC value $[\rho_{ZFC}(T) - \rho_{FC}(T)]$ becomes small. In order to take this into account the data of Fig. 3(a) are replotted in the inset, where $\rho(t)$ is normalized to $\rho_{ZFC}(T) - \rho_{FC}(T)$, as determined from Fig. 2, and a monotonic temperature dependence of the relaxation rate is recovered for $T < T_{SG}$. At 40 K almost 90% of the full relaxation is achieved in 10^4 s, and indeed $\rho(t)$ begins to saturate at long times. $\rho(t)$ can be described by the

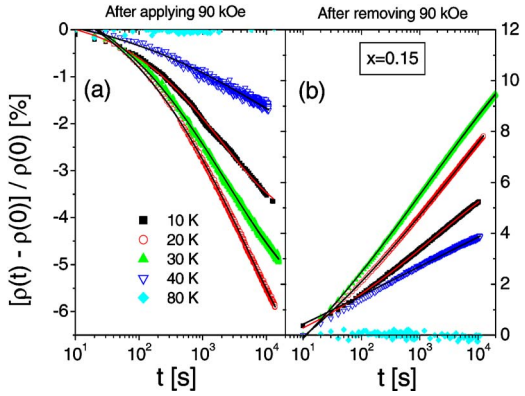

FIG. 4. (Color online) Time dependence of the resistivity after zero-field cooling from 100 K to the measuring temperature at >60 K/min, then (a) applying a 90-kOe field, and (b) removing the 90-kOe field. In case (a) the field reached 90 kOe after 1140 s (defined as $t=0$). In case (b) the field reached zero in 760 s (defined as $t=0$). The solid lines are fits to the stretched exponential form given in the text. The fitting parameters are (a) 10 K: $\tau=2060$ s, $\gamma=0.45$; 20 K: $\tau=5510$ s, $\gamma=0.35$; 30 K: $\tau=2505$ s, $\gamma=0.36$; 40 K: $\tau=919$ s, $\gamma=0.27$, (b) 10 K: $\tau=1730$ s, $\gamma=0.24$; 20 K: $\tau=6400$ s, $\gamma=0.16$; 30 K: $\tau=1470$ s, $\gamma=0.17$; 40 K: $\tau=1890$ s, $\gamma=0.15$. At 80 K the fitted τ values diverge, reflecting the fact that no time-dependent relaxation is occurring.

general stretched exponential form, $\rho(t)=A+B\exp(-t/\tau)^{\gamma}$, where A and B are constants, τ is the relaxation time, and γ is an exponent. This stretched exponential form can be used to describe many quantities in glassy systems, with $0<\gamma<1$. As shown by the solid lines in Fig. 3 this provides a good description of the data with an almost constant exponent ($0.31<\gamma<0.38$), and a relaxation time that decreases monotonically with T, from 7000 s at 10 K to 700 s at 40 K. The decrease in τ with increasing T is consistent with the above discussion and also explains the observation that the apparent freezing temperature from $\rho(T)$ is slightly lower than that from $M(T)$ (see Fig. 2). This is due to the relatively rapid increase in the resistivity relaxation rate with increasing temperature, resulting in a warming rate dependent merging of the ZFC and FC $\rho(T)$ curves. The $M(t)$ data shown in Fig. 3(b) can also be fit with a stretched exponential function. These fits are shown as the solid lines in the figure and the corresponding parameters are given in the caption. The values of τ (7800–4900 s) and γ (0.39–0.47) are comparable to those obtained from $\rho(t)$ in Fig. 3(a). As a final comment on the data of Fig. 3, note that the time-dependent effects disappear at 80 K, i.e., for $T>T_{SG}$, as expected.

The data of Fig. 4 demonstrate that the response to application or removal of magnetic fields after ZFC to $T<T_{SG}$ is also glassy. In this measurement mode the sample is cooled from 300 K to the measuring T, a 90-kOe field is applied, and $\rho(t)$ recorded. A large negative MR response is observed instantaneously, followed by a slow residual decrease out to 10^4 s. After this measurements is completed, removal of the magnetic field in 760 s results in a corresponding instantaneous increase in ρ followed by a slow increase at large t [Fig. 4(b)]. Clearly, the response of the system to field application or removal is time dependent, on a similar scale to that seen in the other measurements (Fig. 2). As expected, the glassy effects disappear at 80 K, which is above T_{SG}. Note that the data of Fig. 4 can also be fitted with a stretched exponential form with exponents in the range $0.15<\gamma<0.45$ and relaxation times of several thousand seconds (see caption for exact values).

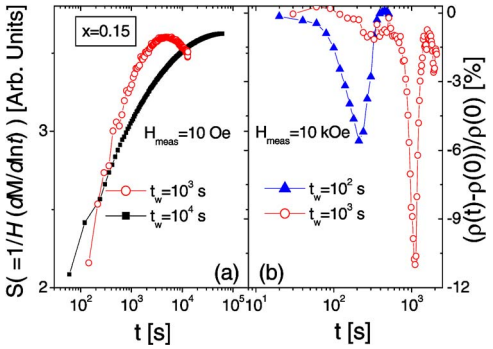

FIG. 5. (Color online) Time dependence of (a) the magnetization relaxation rate $[S=1/H(dM/d\ln t)]$ after zero-field cooling from 300 to 10 K, waiting t_w seconds, then applying a probe field and measuring, and (b) the resistivity (plotted as a % change). For (a) the probe field is 10 Oe and took 100 s to apply and for (b) the probe field is 10 kOe and took 700 s to apply. The error on S is of the order of 0.1 to 0.01, while the error on ρ is about 5% (absolute) and 1 in 10^3 (relative). Most of the fluctuation appearing in (b) is due to small temperature variations.

Canonical SG systems also exhibit a phenomenon known as aging.[12] In aging experiments the sample is cooled rapidly to some $T(<T_{SG})$ and the temperature is equilibrated. After a period of time t_w, the "waiting time," a probe field is then applied and $M(t)$ recorded. The relaxation rate of the magnetization, $S=1/H(dM/d\ln t)$, is found to reach a maximum at a time $t=t_w$, i.e., the system retains memory of the incubation time.[12] As shown in Fig. 5 LSCO not only displays this behavior in $S(t)$ (as expected) but it is also present in $\rho(t)$. This is shown in Fig. 5(b) where it can be seen that $\rho(t)$ reaches a sharp minimum after a period of time roughly equal to the waiting time t_w before the probe field was applied.[28] Quite remarkably, *the effect is observed directly in the resistivity not the resistivity relaxation rate*. This is in stark contrast to the magnetization and is currently unexplained.

We believe that the glassy transport phenomena have their origin in the spontaneous phase separation into isolated FM clusters embedded in a non-FM matrix.[6–11] Rivadulla *et al.* recently analyzed the magnetic behavior of oxides with a phase-separated cluster state, concluding that intercluster interactions alone could be responsible for the glassy behavior.[29] In fact, glassy magnetism is observed in several manganites[30–35] with systems such as $Nd_{0.5}Ca_{0.5}Mn_{1-y}Cr_yO_3$,[13] where the random Cr doping induces a quenched random field leading to magnetic frustration, being particularly relevant to this work. In this material a phase-segregated state composed of nanoscopic FM clusters in a non-FM matrix is also observed. Kimura *et al.*[13] pointed out that this is analogous to the relaxor

ferroelectrics[36–38] such as $PbMg_{0.33}Nb_{0.67}O_3$, which form nanoscopic ferroelectric domains in a nonferroelectric matrix leading to glassy behavior of the electric polarization.[36] This is thought to be due to quenched random electric fields and can be interpreted within the random field interaction model of Imry and Ma.[39] The similarity to the phenomenology seen in the phase-separated state of $Nd_{0.5}Ca_{0.5}Mn_{1-y}Cr_yO_3$ led Kimura *et al.* to label these systems as "relaxor ferromagnets."[13]

Although it is clear that the situation in LSCO is similar to those discussed above, and that the formation of a clustered state is responsible for the glassy transport[40] it must be explicitly recognized that the LSCO system may have a glassy component in the non-FM matrix. Previous NMR data[7,8] revealed that the matrix is composed of two phases, one being paramagnetic, the other exhibiting disordered glassy behavior. This allows us to offer a specific explanation for the glassy transport phenomena observed in this material, where the long time scale relaxation effects [in both $M(t)$ and $\rho(t)$], after field cooling and application or removal of magnetic fields, arise due to the SG component in the matrix. We propose that on field cooling the ferromagnetic clusters align with the cooling field (and hence dominate the magnetic response) while a much smaller component of the magnetization arises from partial alignment of the glassy phase. When the cooling field is removed the glassy component relaxes on long time scales giving rise to the effects shown in Fig. 3. Note that the $M(T)$ shown in Fig. 2 responds even to low cooling fields, as M is dominated by the ferromagnetic clusters. The resistivity is sensitive to both the alignment of the ferromagnetic clusters *and* the polarization of the glassy component. In Fig. 4(a) for example, the application of the 90-kOe field results in the large instantaneous negative MR effect previously reported,[9] due to alignment of the FM clusters and the corresponding increase in spin-dependent transport probability. The residual time-dependent effects that follow this come from the slow polarization of the glassy phase. Fast removal of the 90 kOe field [Fig. 4(b)] results in the inverse effect where the spin alignment in the glassy phase gradually relaxes. Although this model provides a qualitative explanation for the data shown in Figs. 2–4, the waiting time phenomenon observed directly in the resistivity, perhaps the most remarkable result presented here, remains unexplained.

In summary, we have presented data showing that semiconducting $La_{1-x}Sr_xCoO_3$ single crystals exhibit glassy transport phenomena that have their origin in the phase separation into nanoscopic ferromagnetic clusters embedded in a nonferromagnetic matrix. Direct analogies between this system, relaxor ferroelectrics, relaxor ferromagnets, and phase-separated manganites (where intercluster interactions could be responsible for the glassy magnetism) have been made. Several aspects of the data can be simply explained by ascribing the long time scale response to a glassy component in the nonferromagnetic matrix.

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