Temperature memory and resistive glassy behaviors of a perovskite manganite

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I. INTRODUCTION

Glassy systems are well known for their nonequilibrium slow dynamics such as the long-time relaxation, aging, and memory behaviors. Although the dynamics of electrons is generally considered very rapid, glassy transport behaviors have been observed in various systems including electron glasses in Anderson-insulator film structures, a 2D electron system in Si and mesoporous Si ultrathin films, and a number of perovskite manganite and cobaltite polycrystalline bulks. Such a nongeneric electron dynamics is obviously not expected in conventional electronic systems and the underlying physics may not be unique considering the fact that it can be observed in a variety of materials. As for mixed-valence manganites, R$_1$-$\delta$A$_2$MnO$_3$ (R: trivalent rare earth, A: divalent alkaline elements), the slow resistance relaxation and aging phenomena were noticed quite early by Helmlot et al. after the discovery of the colossal magnetoresistance (CMR) effect. The observed glassy transport has been commonly attributed to the slow evolution of the phase conversions among competing phases coexisting in the material as a result of phase separation. Remarkably, using high-resolution transmission electron microscopy technique, Tao et al. observed a dynamic competition between charge-ordered and charge-disordered phases in La$_{0.77}$Ca$_{0.23}$MnO$_3$ and related it to the change in the time dependence of the resistivity. However, the authors also suggested that the resistivity relaxation could be a property of the charge-ordered (orthorhombic) phase itself and not related to the phase coexistence. Kimura et al. compared the transport and magnetic behaviors of Cr-doped Nd$_1$/2Ca$_1$/2MnO$_3$ with the dielectric phenomena in “relaxor ferroelectrics” and proposed that the system can be viewed as a “relaxor ferromagnet”. In addition, Wu et al. observed glassy transport in La$_{1-x}$Sr$_x$Co$_3$O$_7$ cobalites and specifically ascribed the phenomenon to the dynamics of the sample’s spin-glass component.

We report here the observations of long-time relaxation, aging, and memory behaviors of resistivity, which apparently very much resemble the characteristics of spin glasses, in the ferromagnetic (FM) state of a polycrystalline La$_{0.7}$Ca$_{0.3}$MnO$_3$ compound. The resistive glassy dynamics exists in zero magnetic field but is found to be magnetically originated. Strikingly, temperature memory behaviors of both resistivity and magnetization are revealed in the ferromagnetic state. We explain the results in terms of two competitive thermomagnetic processes: domain growth and magnetic freezing. We propose that glassy transport is a common behavior of mixed-valence perovskite compounds where phase separation occurs spontaneously and the interplay between magnetism and electrical property is strong; the materials therefore can be considered as “resistive glasses”.

II. EXPERIMENTS

The La$_{0.7}$Ca$_{0.3}$MnO$_3$ compound was prepared by a conventional solid-state reaction method. Pure (>99.99%) raw powders with appropriate amounts of La$_2$O$_3$, CaCO$_3$, MnO$_2$, and TiO$_2$ were thoroughly ground, mixed, pelletized and then calcined at several processing steps with increasing temperatures from 900 °C to 1200 °C and intermediate grindings and pelletizations. The product was then sintered at 1300 °C for 48 h in ambient atmosphere. The final sample was obtained after a very slow cooling process from the sintering to room temperature with an annealing step at 700 °C for 5 hours. Room-temperature x-ray diffraction measurements showed that the sample is single phase of a perovskite orthorhombic (space group Pnma) structure. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization and four-probe resistivity measurements were carried out in a Quantum Design PPMS-6000. The sample used for resistivity measurements was a 1.9×1.2×7.5 mm$^3$ rectangular bar that was firmly glued to the PPMS puck to have a good thermal contact but electrically separated from the puck by a sheet of cigarette paper. To
shows the reduced resistivity $\Delta \rho$ and cooling the sample to 50 K with a pause at 55 K for 2 h $\sim \rho_{\text{ref}}$. A low heating and cooling rate of 1 K/min was always chosen for all of the measurements. 

A typical $\rho(T)$ curve recorded during this cooling procedure with $T_a = 55$ K and $t_a = 2$ h are plotted as $\rho_c(T)$ in Fig. 1b, which shows a step at $T_a$ caused by the aging. Right after reaching 50 K, the temperature was swept back and $\rho_h(T)$ data were collected. Intuitively, curves $\rho_{\text{ref}}(T)$ and $\rho_h(T)$ are not the same, indicating a cooling history dependence. By subtracting $\rho_h(T)$ from $\rho_{\text{ref}}(T)$ we obtained a temperature dependence of the reduced resistivity, $\Delta \rho(T)$, that shows a maximum at $\sim 58$ K [the inset of Fig. 1(b)], which is very close to the temperature where the pause was made. This feature seems to imply that the pause at $T_a$ during cooling was imprinted into the system and can be retrieved on reheating, signaling the presence of a temperature memory effect that was previously observed in magnetic glassy systems. Henceforth, we refer the measurement of a heating curve following a paused cooling as "memory measurement" (or "memory curve"). In the case where one pause is made, the memory characterized by a maximum of $\Delta \rho(T)$ is then called "single temperature memory" (SME) and $\Delta \rho$ is denoted as $\Delta \rho_{\text{SME}}$. Observations of magnetic glassy behaviors similar to

FIG. 1: (color online). (a) $M_{\text{ZFC}}(T)$, $M_{\text{FC}}(T)$ (left axis, $H = 100$ Oe) and $\rho(T)$ (right axis, $H = 0$ and 6 T) of La$_{0.7}$Ca$_{0.3}$Mn$_{0.925}$Ti$_{0.075}$O$_3$. (b) $\rho(T)$ measured by different protocols: $\rho_{\text{ref}}(T)$ was measured on heating following a continuous cooling from 300 K to 50 K, $\rho_c(T)$ was recorded during cooling the sample to 50 K with a pause at 55 K for 2 h and $\rho_h(T)$ was then measured on reheating. The inset of (b) shows the reduced resistivity $\Delta \rho(T) = \rho_{\text{ref}}(T) - \rho_h(T)$ that exhibits a maximum at $\sim 58$ K.

reduce Joule heating and current induced effects, a very small dc current $I = 100$ nA (corresponding to a current density of 4.4 $\mu$A/cm$^2$) driven in AC mode was used. A low heating and cooling rate of 1 K/min was always chosen for all of the measurements.

III. RESULTS AND DISCUSSION

A. Magnetic and transport characterizations

According to the double-exchange (DE) mechanism for mixed-valence manganites, the transfer of an $e_g$ electron between two adjacent Mn ions occurs only when their localized $t_{2g}$ magnetic moments are aligned in parallel, implying that metallic conducting behavior should come along with a FM state. Nevertheless, manganites are strongly separated systems, so that the ideal DE correlation between magnetism and electrical transport may not be always obtained. While La$_{0.7}$Ca$_{0.3}$MnO$_3$ is a typical DE ferromagnet that has a metallic conducting behavior in the FM phase below $T_c \approx 250$ K, since Ti$^{4+}$ ions do not take part in magnetic couplings, substitution of Mn by Ti destabilizes the network of Mn ions, leading to a deterioration of both DE ferromagnetism and conductivity. Temperature dependent magnetizations, $M_{\text{ZFC}}(T)$ and $M_{\text{FC}}(T)$, and resistivity, $\rho(T)$, in Fig. 1(a) show that the La$_{0.7}$Ca$_{0.3}$Mn$_{0.925}$Ti$_{0.075}$O$_3$ compound is an insulator ferromagnet with $T_c \approx 108$ K. The insulating behavior in the FM state would suggest that the sample is segregated into metallic conducting FM regions separated by non-FM insulating boundaries. With decreasing temperature, the resistance increases continuously and goes beyond the limit of our measurement system below 50 K. Under the influence of a magnetic field $H = 6$ T, the transport behavior remains that of an insulator but the resistance is strongly suppressed leading to a negative magnetoresistance, $-\Delta MR = (R_{H=0} - R_{H=6T})/R_{H=6T}$, which increases with lowering temperature and reaches up to $\sim 9000\%$ at 50 K. The negative magnetoresistance is probably due to an expansion of the DE FM metallic conducting regions that is more favored at lower temperatures.

B. Temperature memory and resistive glassy behavior

The $\rho(T)$ data in Fig. 1(a) were measured on reheating the sample from 50 K following a continuous cooling from 300 K. The $\rho(T)$ curve in zero field is replotted in Fig. 1(b) as a reference heating curve, denoted as $\rho_{\text{ref}}(T)$. In other measurements, instead of cooling down the sample continuously directly to 50 K, the cooling was paused at a constant temperature $T_a < T_c$ for a duration time $t_a$. Interestingly, we observed a clear resistance relaxation that had no tendency to stop even after several hours during the pause, showing a signature of an aging process. The cooling was then resumed to cool the sample to 50 K. A typical $\rho(T)$ curve recorded during this cooling procedure with $T_a = 55$ K and $t_a = 2$ h are plotted as $\rho_c(T)$ in Fig. 1b, which shows a step at $T_a$ caused by the aging.
and 75 K, but appears less and less defined with further cooling.

Another noticeable feature is the tendency for the observation of this memory effect, these results indicate a combination of the corresponding single temperature memories, $\Delta \rho_{\text{SME}}(T_a)$, $\Delta \rho_{\text{SME}}(T_b)$, and $\Delta \rho_{\text{SME}}(T_c)$; i.e., the summation of the two SME curves with $T_a = 60 K$ and 70 K, $\Delta \rho_{\text{SME}}(60K,70K)$, and $\Delta \rho_{\text{SME}}(60K,2h)$ in Fig. 2(a) clearly show a very strong downward relaxation at 60 K, a weaker upward relaxation at 100 K, and no relaxation at all at 160 K. Qualitatively, the changes in both amplitude and sign of $\rho(t)$ are consistent with the variation of the $\Delta \rho_{\text{SME}}$ curves. Although the underlying physics is probably different, this behavior is reminiscent of the change in relaxation direction of the field-cooled magnetization in the vicinity of the glass phase transition in spin glasses and random magnets.

The results in Fig. 2 clearly demonstrate that the system memorizes the temperature where an event was made during cooling and recalls it on reheating. To figure out whether the system can memorize separately more than one event in a single cooling (thus yielding a "multiple temperature memory") we made two pauses with the same $t_a = 2 h$ sequentially at $T_a = 70 K$ and $T_a = 60 K$ in the same cooling process. The corresponding $\rho(t)$ curve (Fig. 3) shows a large maximum near 60 K and a small shoulder around 70 K, indicating a "double temperature memory" (DME) behavior. Moreover, this DME is in fact a combination of the two SME’s at the corresponding $T_a$’s; i.e., the summation of the two SME curves with $T_a = 60 K$ and 70 K, $\Delta \rho_{\text{SME}}(60K,70K)$ and $\Delta \rho_{\text{SME}}(60K,2h)$ respectively, matches very well the DME curve $\Delta \rho_{\text{DME}}(60K,70K,2h)$, as illustrated in Fig. 3. Just for another example, we reduced $t_a$ of the pause at 60 K to 0.5 h in both the SME and DME experiments and again observed that the superposition of two SME’s gives the corresponding DME. Unambiguously, the system can memorize multi-

\[ \Delta \rho_{\text{SME}}(T_a) = \Delta \rho_{\text{SME}}(T_b) + \Delta \rho_{\text{SME}}(T_c) \]

\[ \Delta \rho_{\text{DME}}(T_a, T_b) = \Delta \rho_{\text{SME}}(T_a) + \Delta \rho_{\text{SME}}(T_b) \]
ple events separately created on a single cooling and store them without interference – a behavior that has been well observed in magnetic glasses.\textsuperscript{24,25,28,29}

The use of temperature as the only parameter to vary the dynamics of the system allows probing the system by its original dynamics. The observed nonequilibrium behaviors of resistance bear striking resemblances with the dynamic characteristics of magnetic glasses. The resistance keeps relaxing towards equilibrium in such a long period of time that could go beyond the laboratory time scale even in a constantly stabilized condition. After being ”aged” at the pauses during cooling, the system responds differently on reheating, demonstrating a clear age-dependent behavior. Furthermore, the temperature memory effect, an inherent characteristics of magnetic glasses, is also observed. Since the resistive glassy behaviors are observed only in the FM state, they must have a magnetic origin. The insulating behavior in FM state suggests that the sample is not a pure DE ferromagnet, but probably a separated system consisting of two competing phases: DE FM metallic-conducting domains separated by a non-FM insulating matrix. Low temperatures or high magnetic fields both favor the DE interaction and expand the FM domains at the expense of the non-FM insulating matrix. During the pause below \( T_c \), the FM domains would evolve with time by polarizing the spins surrounding to expand the conducting regions. On the other hand, thermal activation helps the domain moments relax towards directions which are energetically favored by their randomly distributed local anisotropy, therefore increasing the spin scattering of electrons traveling between domains. The domain growth seems to be dominant at low temperatures, resulting in a downward resistivity relaxation (Fig. 2). In contrast, magnetic moments relax faster at higher temperatures, overcoming the domain growth process at temperatures close to \( T_c \) and therefore producing an upward resistivity relaxation.

We adopt the Néel’s relaxation law\textsuperscript{22} to qualitatively describe the freezing of FM domains, \( \tau = \tau_0 \exp(E_a/k_B T) \), where \( E_a \) is the anisotropy energy that is proportional to the domain size, \( k_B \) is the Boltzmann’s constant, and \( \tau \) and \( \tau_0 \) are the relaxation and microscopic relaxation times, respectively. Lowering temperature leads to an exponential increase of \( \tau \), causing the domains to become deeper frozen. One of the key ingredients of the temperature memory effect is the freezing of magnetic moments in random directions that preserves the ”aged” magnetic configuration when cooling is resumed after the pause. The frozen moments would still relax but with very much smaller rates at lower temperatures. Upon reheating, the melting of the aged configuration returns the system to the state without aging above \( T_a \), exhibiting the observed memory effect. Since after the pause the magnetic moments relaxed into directions with higher energy barriers \( [k_B T_a \ln(t_a/\tau_0)] \), according to the Néel’s law, higher temperatures are then required to remove them from the freezing directions. This explains why the maximum of \( \Delta \rho(T) \) is always at a higher temperature than \( T_a \). In a real system, there always exist wide distributions of \( \tau_0 \) and \( E_a \). Magnetic moments of domains with \( E_a \leq k_B T_a \) rotate freely under the thermal excitation, those with \( E_a > k_B T_a \) are effectively frozen, and only those with \( E_a \geq k_B T_a \) contribute to the relaxation at \( T_a \). This explains why we could observe a multiple temperature memory. Ideally, if \( T_s 2 \ln(t_s/\tau_0) < T_s 1 \), there could be no interference between the two aged configurations. \( \Delta \rho(T) \) approaches zero only at sufficiently high temperature far above \( T_a \) where there is effectively no difference in domain sizes between the memory and the reference configurations.

In order to examine the influence of magnetic field on the memory effect, a magnetic field \( H_a \) was turned on during the pause. Right after the aging time \( t_a \), \( H_a \) was removed and the cooling was immediately resumed. The SME \( \Delta \rho(T) \) curves measured with different \( H_a \)’s are presented in Fig. 4. The field is expected to favor the domain growth and therefore to increase the \( \Delta \rho(T) \)’s near \( T_a \). However, the freezing of magnetic moments are also strongly affected. Instead of relaxing towards random directions, the magnetic moments are polarized and relax preferentially towards the external field direction, establishing a configuration that is advantageous for the unfrozen domains to grow such that the domain growth during further cooling could effectively overwhelm the aged configuration previously established at \( T_a \). We can see clearly in Fig. 4 that, while the maximum of \( \Delta \rho(T) \) curves is indeed raised with increasing \( H_a \), it is significantly broadened and spreads towards lower temperatures. Apparently, higher \( H_a \) applied at \( T_a \) causes a stronger development of magnetic domains upon further cooling, which may interfere with the aged configuration pre-established at \( T_a \). With \( H_a = 3 \) kOe, the maximum of \( \Delta \rho(T) \) is no longer defined, suggesting that the development of magnetic domains with decreas-

![FIG. 4: The influence of magnetic field on the nonequilibrium resistance dynamics. A magnetic field \( H_a \) is turned on during the pause at \( T_a = 65 \) K on cooling. The application of \( H_a \) causes a ”crosstalk” between the memory established at \( T_a \) and the domain configurations developed during further cooling. The memory maximum in the \( \Delta \rho_{\text{SME}}(T) \) curve is unresolvable at \( H_a = 3 \) kOe.](image-url)
FIG. 5: (color online). The temperature memory behavior observed on $M_{\text{ZFC}}(T)$. For the memory curves (symbols), the sample was zero-field-cooled from 300 K to 5 K with a pause at $T_a = 65$ K for $t_a = 2$ h. For the reference curves (lines), the sample was cooled directly to 5 K. After the temperature had reached 5 K, a probing field $H$ was immediately applied and $M_{\text{ZFC}}(T)$ was recorded on reheating. Main figure: $H = 10$ Oe, insets (a), (b), and (c): $H = 30$, 70, and 150 Oe, respectively. Sufficiently high probing fields can align the moments of the aged domains toward its direction, turning the memory ”dip” lying below into a ”cusp” lying above the reference curve.

IV. CONCLUSION

Nonequilibrium dynamic behaviors such as long-time relaxation, aging, and temperature memory of both resistivity and magnetization have been revealed in the insulator ferromagnet La$_{0.7}$Ca$_{0.3}$Mn$_{0.925}$Ti$_{0.075}$O$_3$. The glassy transport has a very close association with the magnetic glassiness and appears to be magnetically originated. These results can be qualitatively explained in terms of two competing thermodynamic processes: domain growth and magnetic freezing. The results of our dynamical study evidence the presence of phase separation and strong correlation between magnetism and electrical transport in the CMR perovskite manganite. We propose that resistive glassiness is a common character of mixed-valence perovskite manganites as a direct result of both electronic and magnetic phase separation. This nonequilibrium dynamics may be found profound in systems where there exists a strong competition between conducting and insulating phases, most likely near the metal-insulator transition with doping. Since the temperature memory behavior of resistance is associated with the freezing of magnetic domains, it is expected to be observable in the manganite insulators where FM metallic domains are embedded in the non-FM insulating matrix.

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