Noise Probe of the Dynamic Phase Separation in $La_{2/3}Ca_{1/3}MnO_3$

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Giant random telegraph noise (RTN) in the resistance fluctuation of a macroscopic film of perovskite-type manganese oxide $La_{2/3}Ca_{1/3}MnO_3$ has been observed at various temperatures ranging from 4 to 170 K, well below the Curie temperature ($T_C \approx 210$ K). The amplitudes of the two-level fluctuations vary from 0.01% to 0.2%. We discuss the origin of the RTN to be a dynamic mixed-phase percolative conduction process, where manganese clusters switch back and forth between two phases that differ in their conductivity and magnetization.

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The current interest in the mixed valence perovskite manganites was originally fueled by the rediscovery of colossal magnetoresistance (CMR) in certain members of this group of materials [1]. The study of the physics of the manganites has, however, progressed far beyond CMR alone. Manganites have offered a fertile ground for the study of spin-charge interactions and transport-magnetism correlations. It is unusual that the same solid state system can exhibit so many ground states, ranging from ferromagnetic metallicity to charge ordering and orbital ordering [2,3]. This richness is due to competition between a variety of interactions of comparable strengths [4]. The energy balance can be so delicate that many have suggested that the ground state would not be homogeneous [5–7]. Indeed, a variety of experimental studies of the crystal and magnetic structures support the existence of both lattice [8] and magnetic polaronic [9–12] states near the ferromagnetic ordering temperature T_C. Furthermore, a multiphase description, where the insulator metal transition occurs via percolation has been put forward [13]. This picture of the coexistence of metallic and insulating phases, even in samples optimally doped to have the highest T_C, has recently been confirmed experimentally by scanning tunneling microscopy [14,15].

Random telegraph noise (RTN) results from transitions between two states of a switching entity called "fluctuator." The two states could be electrical or magnetic in origin. Each state has a different conductivity, and thus makes a different contribution to the overall conductivity; hence the switching results in discrete jumps in the overall sample resistance. Studying the temperature and field dependence of the RTN (switching behavior) provides insight into the electrical and magnetic nature of the fluctuators. Therefore, RTN is an effective tool for probing the dynamic behavior of an electrically inhomogeneous system, such as the manganites.

In this Letter, we report on the first observation of giant RTN in the resistance of a $La_{2/3}Ca_{1/3}MnO_3$ film. We have examined in detail the RTN as a function of temperature and magnetic field. We use a statistical analysis of the lifetimes of the two-level fluctuations (TLF) to gain insight into the microscopic electronic and magnetic state of this system. At low temperature (below 30 K) the TLF is well described by a thermally activated two-level model. At higher temperature (between 60 and 170 K) we observed critical effects of the temperature on the lifetimes of the TLF. Our results provide evidence for a dynamic phase separation in this system. More importantly, for the first time, we are able to give a quantitative estimate of the relative stability of these phases.

A 0.4 μm thick film was grown by pulsed laser deposition on a $LaAlO_3$ (100) substrate. It was patterned into a long four-probe geometry of 200 μm in length and 2 μm in width using a combination of optical lithography and wet chemical etching. The noise measurements were performed with a four probe dc technique as described in Ref. [16]. Care was taken to ensure that spurious noise does not contribute to our results.

We have observed RTN at various temperatures below T_C. From 4 to 170 K, the resistance fluctuations alternate between an anomalous non-Gaussian behavior to giant RTN as shown in Fig. 1. The fractional resistance steps of the RTN vary from 0.01% to greater than 0.2%, which is surprisingly high for an almost macroscopic sample.

The TLF process can be modeled as an asymmetrical two-state system with an energy barrier separating the two states [Fig. 2(a)]. Obviously, here the switching is thermally activated as indicated in Fig. 2(b). The average time τ_i spent in the ith state can then be described by the Arrhenius law,

$$\tau_i = \tau_{0,i} \exp\left(\frac{E_i}{k_B T}\right), \quad (1)$$

where E_i is the height of the barrier to escape from state i, k_B is the Boltzmann constant, and $\tau_{0,i}$ is a microscopic constant that depends on the details of the coupling between the thermal bath and the fluctuator.

We emphasize that in the temperature range 4 to 180 K the noise has a strong non-Gaussian character, i.e., the resistance fluctuations are dominated by "few" fluctuators. The features observed in the traces in this temperature range are reminiscent of a superposition of few TLF processes with different characteristic lifetimes (traces recorded at 38 and 156 K, Fig. 1). In our experiment,

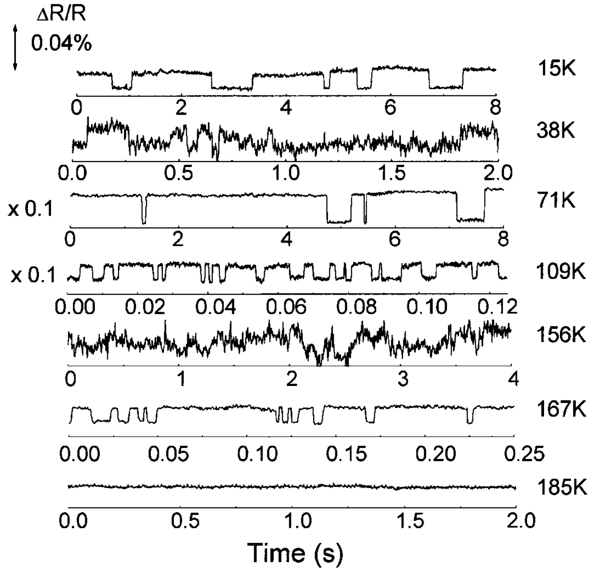

FIG. 1. Resistance vs time at different temperatures. The noise alternates from a strongly non-Gaussian fluctuation-type to a random telegraph noise (RTN) with $\Delta R/R$ ranging from 0.01% to 0.2%. The features observed in the traces recorded at 38 and 156 K are reminiscent of a superposition of "few" two level fluctuations processes with different characteristic lifetimes. At certain temperatures only a single fluctuator dominates, giving rise to the RTN at 15, 71, 109, and 167 K. There is no evidence for the RTN above 180 K (the Curie temperature $T_C \approx 210$ K).

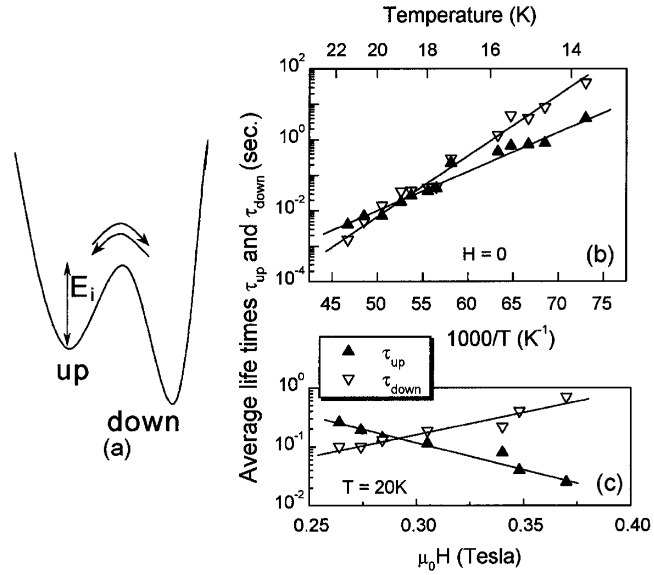

FIG. 2. (a) Schematic representation of an asymmetric double-well model used to describe the fluctuation process. (b) The measured average lifetimes for the high-resistance state ($\tau_{\rm up}$) and the low-resistance state ($\tau_{\rm down}$) are plotted versus the reciprocal temperature; (c) $\tau_{\rm up}$ and $\tau_{\rm down}$ versus magnetic field. In this temperature range, increasing the temperature decreases the lifetime of both states while an applied magnetic field increasingly favors the low-resistance state to the detriment of the high-resistance one. The solid lines are fits to $\tau_i = \tau_{0,i} \exp(\frac{E_i(H=0)+\Delta\mathbf{m}_i\cdot\mathbf{H}}{k_B T})$ (see text).

the accessible time window ranges from 10 ms to a few minutes. If the average lifetime of a fluctuator [Eq. (1)] falls outside of the experimental window, then it is not directly observable. The observable fluctuators are thus selected by setting the working temperature. In fact, at certain temperatures only a single fluctuator dominates, giving rise to the RTN (Fig. 1). For some of these TLF processes we were able to study the temperature and magnetic field dependence of the average lifetime (τ_i). It is this study that constitutes the focus of this Letter.

In Fig. 2(b), the temperature dependence of the mean lifetimes for a TLF system active between 10 and 20 K is presented. Although very limited in temperature range, a fit to Eq. (1) for the average lifetime of the low-resistance state $\tau_{\rm down}$ (the high-resistance state $\tau_{\rm up}$) yields a measure of the energy barrier height, $E_{\rm down}/k_B = 380 \pm 30$ K ($E_{\rm up}/k_B = 270 \pm 20$ K). The attempt time is found to be $\tau_{0,\rm down} = 3 \times 10^{-11}$ s ($\tau_{0,\rm up} = 2 \times 10^{-8}$ s). Since the phonon spectrum is *a priori* the same for the two states, the discrepancy between the attempt times $\tau_{0,\rm down}$ and $\tau_{0,\rm up}$ is likely due to a slight temperature dependence of the energy barrier heights. This point will be discussed in more detail below.

The magnetic field dependence of the noise reveals the magnetic nature of the switching entities [Fig. 2(c)]. The effect of the field is to systematically stabilize the low-resistance state to the detriment of the high-resistance state. Within the framework of the TLF model, the effect of the magnetic field can be accounted for by including a field-dependent energy barrier in Eq. (1), $E_i(\mathbf{H}) = E_i(0) + \Delta\mathbf{m}_i \cdot \mathbf{H}$, where $\Delta\mathbf{m}_i = \mathbf{m}_i - \mathbf{m}_v$, with $\mathbf{m}_i$ being the magnetic moment associated with the fluctuator in the state i, $\mathbf{m}_v$ being the magnetic moment of the virtual state (at the top of the energy barrier), and $\mathbf{H}$ being the applied field. From Fig. 2(c), we infer $\Delta m_{\rm down} \approx -\Delta m_{\rm up} \approx 550\mu_{\rm B}$, where $\mu_{\rm B}$ is the Bohr magneton.

Magnetic noise has been reported in various systems [17,18], and has most commonly been attributed to magnetic domain fluctuations. In our case, however, this scenario can be readily ruled out: (1) We have observed RTN in fields higher than the demagnetization field (0.6 T). Such fields tend to suppress any magnetic domains and therefore any magnetic domain fluctuations. (2) If we assume the magnetic entity responsible for the resistance change to be a magnetic domain, its volume derived from the known Δm_i values would be of the order of (2 nm)^3, many orders of magnitude too small to account for a relative variation of the resistance of 0.2% [19,20].

As the temperature rises above ~60 K, we observed a striking change in the temperature dependence of the lifetimes of the TLF. As shown in Fig. 3(a), for a fluctuator active around 109 K, we typically observe that over a narrow temperature range of ~1 K, the lifetimes of the low-resistance and the high-resistance states change by more than an order of magnitude. Nevertheless, in contrast to the low temperature case, where both lifetimes decrease with increasing T, here the lifetime of the high-resistance state actually increases with rising T. In fact, we observe

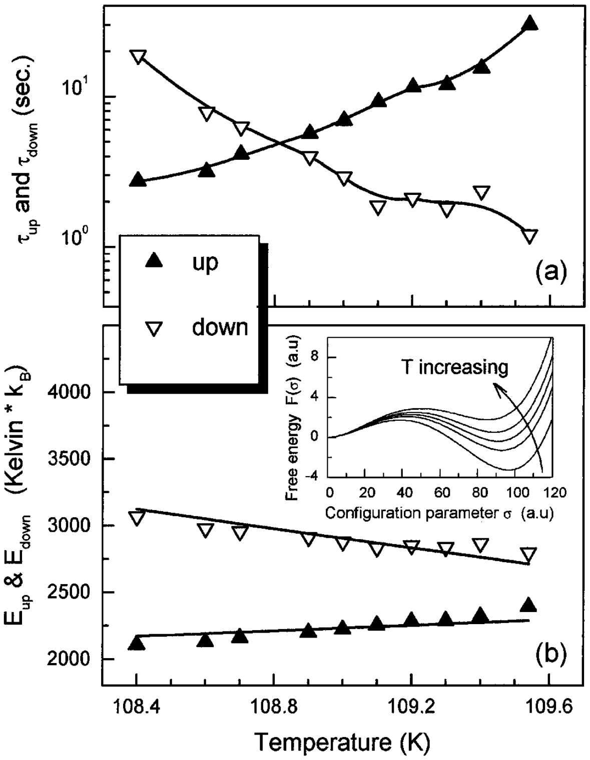

FIG. 3. (a) Temperature dependence of the average lifetimes for a fluctuator activated around 109 K. Note that by increasing the temperature the high-resistance state is stabilized and the low-resistance state becomes less probable. The solid lines are a guide to the eye. (b) Temperature dependence of the deduced activation energies for both states (we used for $\tau_{0,i}$ the values found at low temperature; see text). Inset: Free energy functional $F(\sigma, T) = a(T - T_0)\sigma^2 + b\sigma^3 + c\sigma^4$ versus configuration parameters σ at different temperatures ($\sigma = 0$ corresponding to the high-resistance state). a, b, c, and T_0 are fitting parameters chosen to describe simultaneously the temperature dependence of the activation energies E_{up} and E_{down} [solid lines in panel (b)]. Detailed description of the fitting procedure will be published elsewhere.

a dramatic inversion of the occupation probability between the two states over this temperature range. A fraction of a K above the equiprobability temperature, the occupation probability of the low-resistance state becomes negligible compared to that for the now much more stable high-resistance state. In the analysis of the low temperature data in Eq. (1), the heights of the energy barriers are assumed to be temperature independent, and the temperature dependence of τ_i results purely from thermal activation. Namely, there is no change in the energy configuration with varying T. This is clearly not the case any longer at high T, although we still expect the dynamics to be dominated by thermal activation and Eq. (1) remains valid for a given energy configuration (i.e., at a given temperature). We thus extend the TLF model by introducing a temperature dependent energy barrier $E_i(T,H)$. By inverting Eq. (1) we can estimate the temperature dependence of the energy barrier from the measured lifetime τ_i.

$$E_i(T,H) = k_B T \ln\left(\frac{\tau_i(T,H)}{\tau_{0,i}}\right). \quad (2)$$

Over the studied temperature range (~1 K), we can neglect the temperature dependence of $\tau_{0,i}$. Moreover, the value of $\tau_{0,i}$ is mainly a logarithmic offset in Eq. (2).

Figure 3(b) displays the temperature dependence of the activation energies deduced from Fig. 3(a). We assume that in this narrow temperature range, the temperature dependence of the free energy can be described by a functional, $F(\sigma)$, dependent on a dimensionless configuration parameter σ. In analogy to the Landau-Ginzburg model for first order phase transitions [21], we write $F(\sigma)$ as a polynomial expansion in σ. The simplest possible form, putting aside any symmetry argument, is a fourth order polynomial. The fit of the local extrema of $F(\sigma)$ reproduce well the temperature dependence for the energy barriers of both the low- and high-resistance states (Fig. 3 caption). Similar to the low temperature case, the effect of a magnetic field, at high temperature, is to stabilize the low-resistance state. The corresponding net magnetization difference is $\Delta m_{\mathrm{down}} \approx -\Delta m_{\mathrm{up}} \approx 2500\mu_B$.

Except when a single fluctuator dominates, the power spectral density of the resistance fluctuation has mainly a $1/f$ dependence, in good agreement with previous studies [19,22,23]. The normalized noise level shows a 4 orders of magnitude increase when the sample temperature is increased from 4 to 100 K and then decreases sharply at higher temperature to the background level, whereas the resistivity maximum occurs at 210 K, well above the noise maximum (Fig. 4). It is worth mentioning that above 180 K we have seen no evidence for the RTN, and the non-Gaussian character of the resistance fluctuations is much weaker.

Obviously the large noise level below 180 K is due to the presence of two-level fluctuators with large $\Delta R/R$ values. We have established, however, that those fluctuators, even though they have a strong magnetic character, cannot originate from magnetic domains. Instead, we believe that the rapid variation of the energy configuration with temperature, as inferred from the RTN at high temperature (Fig. 3), suggest the dynamic coexistence of two phases: a ferromagnetic metallic phase and a phase with relatively depressed magnetic and electrical properties. The RTN occurs when a cluster, the fluctuator, switched back and forth between the two phases. The magnetic field will always stabilize the ferromagnetic state, which is the low-resistance one. At low temperature the conductivity is dominated by the ferromagnetic metallic phase; by increasing the temperature, some clusters will switch to the depressed state, increasing the total resistance of the sample by the RTN quanta. We surmise, therefore, that the conduction is a mixed-phase percolation process, consistent with the phenomenological model of Jaime *et al.* [24]. These authors developed a model of coexisting metallic and thermally activated (polaronic) transport. Conduction near T_C is activated, whereas the metallic character dominates at low temperature (far from T_C). In this picture, the location of the noise level peak well below T_C and its surprising

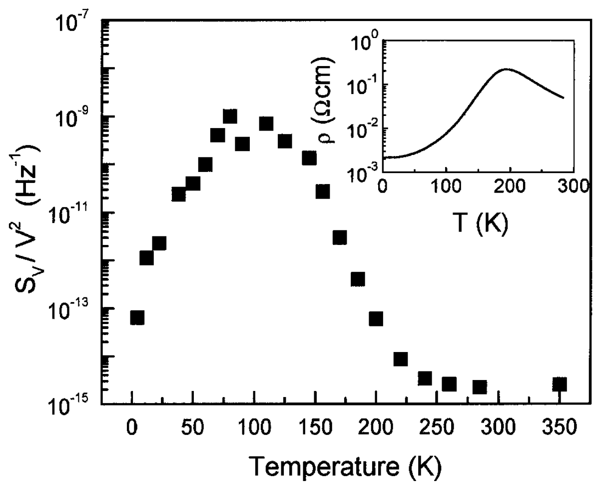

FIG. 4. Temperature dependence of the power spectral density at 10 Hz normalized to the applied voltage. Inset: The resistivity versus temperature is presented. Note the 4 orders of magnitude increase of the noise level between 4 and 100 K, and different locations of the peaks of noise level and resistivity.

amplitude is a direct consequence of the mixed phase: near the percolation threshold for the metallic state, the conduction is dominated by the narrowest current paths. A few switching clusters located in these critical bonds will have dramatic effect on the overall connectivity of the metallic network, which results in a large increase of the noise level [25,26].

Finally, to address the issue of the intrinsic or extrinsic nature of the observed phase separation, we emphasize that the final state was never exactly the same upon thermal cycling: the RTN could disappear altogether and, if present, displays different characteristics, i.e., different $\tau_{0,i}$, E_i. This leads us to conclude that the mixed phase is not related to any chemical inhomogeneity or physical disorder but rather to a statistical probability to have the sample in a given state out of many possible configurations with comparable energies.

In conclusion, we have shown for the first time direct evidence of phase separation in $La_{2/3}Ca_{1/3}MnO_3$ by a transport measurement. The present study gives a rough estimate of $\sim$100 K for the energy difference between the two states at low temperature. A typical size of the switching clusters can be estimated from the net magnetization difference Δm. A simple model [27] yields an order of magnitude volume of (20 nm)^3 at 20 K which involves 10^5 Mn atoms.

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Note added.—After submission of this paper we became aware that R. D. Merithew *et al.* [28] have also observed giant RTN noise in the same system.

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