Time-Resolved Electronic Phase Transitions in Manganites

T. Z. Ward,[1,2] X. G. Zhang,[3] L. F. Yin,[1] X. Q. Zhang,[4] Ming Liu,[5] P. C. Snijders,[1] S. Jesse,[1,3] E. W. Plummer,[2] Z. H. Cheng,[4] E. Dagotto,[1,2] and J. Shen[1,2,*]

[1]*Materials Sciences and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA*
[2]*Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA*
[3]*Center for Nanophase Materials Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA*
[4]*State Key Laboratory of Magnetism and Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
[5]*Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100080, China*
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The dynamics of first-order electronic phase transitions in complex transition metal oxides are not well understood but are crucial in understanding the emergent phenomena of electronic phase separation. We show that a manganite system reduced to the scale of its inherent electronic charge-ordered insulating and ferromagnetic metal phase domains allows for the direct observation of single electronic phase domain fluctuations within a critical regime of temperature and magnetic field at the metal-insulator transition.

Near the critical point of a first-order electronic phase transition, fluctuations between the competing phases are often a dominant phenomenon. The direct observation of these fluctuations in electronic phases is vital to revealing the details of the phase transition. This is especially true in strongly correlated transition metal oxides, in which a diversity of electronic phases coexist and are closely connected to several remarkable properties such as high-T_c superconductivity and colossal magnetoresistance [1,2]. It is well known that electronic phase separation exists even in chemically uniform, single crystalline samples [2,3]. Although the sizes of the phase-separated domains can vary from a few nanometers to micrometers depending on the materials, they are small enough that individual domain fluctuations at the critical point of the phase transition are unobservable when probed by spatially averaged techniques.

While this problem could potentially be solved by imaging a single domain, imaging techniques with high enough spatial resolution such as transmission electron microscopy [4], magnetic force microscopy [5,6], and scanning tunnelling spectroscopy [7] all lack the time resolution necessary to monitor the phase fluctuations found in complex oxides, as they require the probe to be fully scanned across the sample twice in order to find differences in the overall domain structures—producing data in a time scale of seconds.

To directly observe phase fluctuations in complex oxides with a high time resolution, we have developed an approach whereby individual phase fluctuations produce large changes in the experimental signal due to the small number of domains in the sample. This is accomplished by spatially confining a single crystal $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ thin film to a length scale on the order of the intrinsic ferromagnetic metal (FMM) and charge-ordered insulating

(COI) domains residing in the material [8,9]. The very limited number of phase domains that can be hosted effectively removes the problems associated with spatial averaging methods in conventional transport measurements [10,11] while allowing for a high temporal resolution. If this system is set at or very near the critical point of the metal-insulator transition (MIT), single domain fluctuations will show a clear signature in time-dependent resistivity measurements.

A single crystal thin film of $La_{5/16}Pr_{5/16}Ca_{3/8}MnO_3$ (LPCMO) was grown on $SrTiO_3$ (100) using laser molecular beam epitaxy. Film quality was verified by x-ray diffraction, Rutherford backscattering, and *in situ* atomic force microscopy. Films were confined to wire geometries using wet-etch optical lithography. Detailed growth and etching procedures are described elsewhere [10,12]. Transport measurements were conducted in a Quantum Design physical properties measurement system with a stable temperature precision of 0.01 K and a magnetic field precision of 0.1 Oe. The magnetic field was applied along the easy axis of magnetization. Resistivity vs time measurements were done using external electronics consisting of a Keithley 2400 power supply, National Instruments DAQ-card 6036E, and homebuilt LabView drivers for control and data collection. We made every effort to reduce external noise from the measurements through shielding and proper grounding. 2-probe and 4-probe transport measurements were compared and showed no difference in quality of data. All experimental data that we present were obtained using 2-probe dc measurements with a sourced constant current of 500 nA.

Figure 1(a) shows the resistivity of a 10 μm $\times$ 50 μm $\times$ 70 nm wire as a function of temperature on warming under a 3.75 T magnetic field. This field is sufficient to align the ferromagnetic domains without melt-
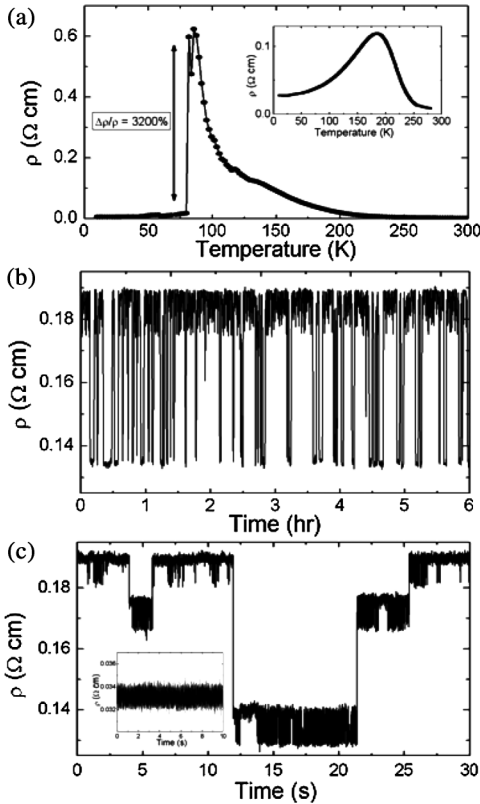
FIG. 1. Transport measurements. (a) Temperature-dependent resistivity plot for a 10 μm wide LPCMO wire under 0.5 μA constant current (inset: temperature vs resistivity plot of the same sample in a thin film form). (b) Long scale, low sample frequency resistivity vs time plot for wire held at 83 K. (c) Wire's resistivity vs time plot at the transition temperature taken at a sampling frequency of 45 kHz (inset: film's resistivity vs time plot under the same conditions).

ing the charge-ordered phase which allows us to probe only the electronic domains without interference from magnetic domains [11]. The metal-insulator transition is clearly visible across a 2 K window centered at 83 K as an ultrasharp peak in resistivity (ρ) with a $\Delta\rho/\rho$ of 3200%. This is contrasted with the same sample in a film geometry [Fig. 1(a), inset] which shows a smooth transition from metallic to insulating behavior across a 150 K window. The extremely large $\Delta\rho/\rho$ ratio results solely from the wire geometry's ability to remove the effects of spatial averaging in transport measurements. By setting the temperature of the LPCMO wire precisely in the middle of the 2 K window found in the temperature-dependent resistivity scan, it is possible to study the microscopic details of the transition in both space and time.

Figures 1(b) and 1(c) show the time-dependent resistivity while the wire is held at the transition temperature. Figure 1(b) has a relatively low time resolution of 10 s and is characterized by a stable competition between two states with resistivity jumps of 46%. By increasing the time resolution from 10 s to 22 μs, the true nature of this

volatility becomes clear [Fig. 1(c)]. The apparent two-state system is actually comprised of a much richer multistate system. There are three inherent resistivity levels, each containing a further two-state fluctuation. Stable fluctuations were also observed in thinner wires at the MIT but were never present in geometries wider than 20 μm (data not presented here). In unconfined structures, such as film [Fig. 1(c), inset] or bulk, this behavior is not observable under the same conditions, nor is it seen in the wire geometry outside of the metal-insulator transition 2 K window.

These data clearly show that fluctuations that change the electrical resistance exist in these phase-separated manganite wires. We observe that these fluctuations exist only near the transition temperature where electronic domains are fluctuating between FMM and COI and are not individually observable in films or bulk transport experiments. From this, we conclude that these fluctuations are a direct signal of the microscopic fluctuations in these phase domains at the transition temperature. The comparable dimensions of the inherent domains to the wire result in a large change in the total wire resistance when a single domain fluctuates from one phase to another.

Previous studies on $1/f$ noise in thin film La$_{1-x}$Ca$_x$MnO$_3$ systems have shown metastable two-state fluctuations in resistance over a wide temperature range [13,14]. In our studies, we find no evidence of two-state fluctuators in the film geometry and see stable fluctuations only within a very narrow temperature regime at the MIT. This difference could be due to the fact that the previous studies used much lower applied magnetic fields which may not have been high enough to completely align the FMM domains. Though the studies on $1/f$ noise tried to rule out magnetic domain fluctuations by performing measurements under applied fields near or slightly greater than the known demagnetization limit, it has been shown that higher fields may be needed to completely remove magnetic domain fluctuations in a system with inhomogeneous current densities [15,16].

While the interpretations given in the studies on $1/f$ resistivity noise [13,14] imply the presence of a percolating network of electrical transport channels, none actually substantiated this assertion with an actual model. To better understand the observed resistance jumps in an electronic phase-separated system, we employ a random resistor model, which is widely used in modeling low-frequency resistance fluctuations [17,18]. Our LPCMO system can be understood using only a few fluctuating resistors in the theoretical model because only a small number of phase domains reside in the wire [19] [Fig. 2(a)]. In the simulation, nodal coordinates are randomly placed in a simulated wire and randomly linked by conductive connections. Subsequently, each of these nodes is assigned a random probability of switching between the open and closed states to simulate the attempt frequency of individual
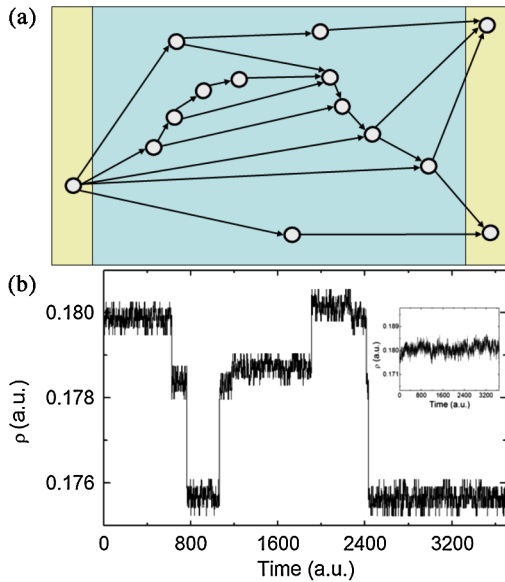
FIG. 2 (color online).   Modeling using a random resistor network. (a) Diagram of the model using a few node switches to simulate the random transition flippings of phase domains in a wire geometry. (b) Modeled data for the wire geometry showing discrete fluctuations that closely resemble the experimental data (inset: modeled network containing 1000 nodes that closely matches the experimental results corresponding to films). Note: Arbitrary units are used.

domains with slightly different characteristic energies held in a degenerate state within $k_B T$ at the metal-insulator transition. Figure 2(b) shows one such simulation in time-dependent resistivity. There is a clear three-level fluctuation with a nested two-level fluctuation in each level which is very similar to our experimental observations. Because of the random generation of nodes, running this simulation for a much longer time would produce an even closer match to experimental data. This method was also used to simulate a 2D film by increasing the number of nodes to 1000 and setting a periodic boundary condition in one direction perpendicular to the current to simulate an infinite film; it closely resembles our experimental data for the film [Fig. 2(b), inset]. The simulation confirms that the fluctuating resistance of the wires is a direct result of individual domains fluctuating between the metallic FMM phase and the insulating COI phase. These results also raise questions about previous experiments on $1/f$ noise in manganites that claimed to see two-state fluctuations arising from electronic phase fluctuations in the context of a percolating network; since the size of the electronic phase-separated domains in LCMO are on the order of 10 nm, which should be modeled as many thousand switching sites in the relatively large geometries that they study, no two-state fluctuators would be independently observable in those experiments. However, in our model these systems would show individual fluctuators if the fluctuating domains were on the order of several mi-

crons, which is the size of magnetic domains in LCMO [20]. Therefore, the $1/f$ noise in Refs. [13,14] could possibly be due to magnetic fluctuations instead of metal-insulator domain fluctuations.

The robust nature of the domains in the LPCMO wires is illustrated in Fig. 3(a), which shows two 10 s scans with a resolution of 22 μs, taken 5 h apart. The perfect consistency of these resistance traces show that even after >5 h at the transition temperature, the exact same microscopic parts of the material are still fluctuating between the COI and FMM phases—intermittently blocking and opening local conductivity paths. Moreover, the very same two-level fluctuator still randomly switches between its two states that are apparently degenerate within $k_B T$. Thus, both the global configuration of COI and FMM domains and their microscopic configuration are in (thermal) equilibrium.

A more detailed look at the resistivity fluctuations shows that the jumps can be characterized by an inverse exponential transition in time between states [Fig. 3(b)]. This is true for all observed phase fluctuations—the three large shifts and the two level fluctuations nested within them. The lifetimes of all transitions are between 1 and 2 ms. It should be pointed out that these transition times are far longer than the response time of the electronics used to collect the data. Capacitive charging within the system can also be ruled out since these measurements are done using constant current which would result in a linear charging characteristic [$V(t)$] in a RC system. Clearly, the intrinsic switching speed of individual domains between the two respective phases is accessible in this experiment.

By binning all recorded resistivity values taken over a 6 h period, a more precise view of the three distinct fluctuation levels and the nested two-state fluctuations can be obtained [Fig. 3(a), inset]. The nested two-state fluctuation is created by a single domain that is actively fluctuating with a higher frequency throughout the measurement process than those that cause the larger changes in resistivity. Further, the data show that the nested two-state fluctuations have a changing asymmetric preference that is dependent on the state of the other domains in the wire. The microscopic fraction of material that fluctuates in the two-level system spends a greater amount of time in the high resistance COI phase when other domains are also in the charge-ordered insulating phase. This correlation between domains is most likely mediated by field changes associated with the FMM-COI transition; whether this is from changes in the E field or strain field is unclear, but deviations in the strain field are known to cause changes in the transition temperature [4,10,12] in manganites. Indeed, the change in observed asymmetry is consistent with what would be expected if a single domain's transition temperature were to change very slightly while the system was held at a constant temperature. The symmetry breaking of the structure of the unit cell associated with the transition from
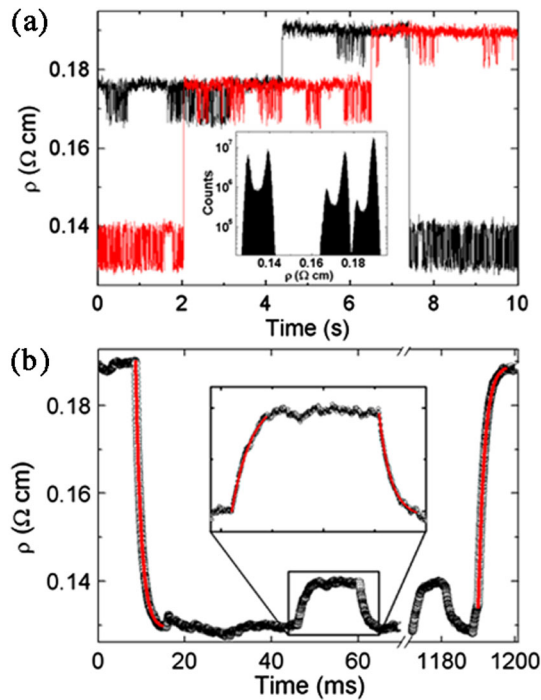
FIG. 3 (color online).   High sampling frequency transport measurements on a 10 μm wire held at the critical point. (a) Comparison of 10 s worth of data taken 1 h after the critical temperature was reached (black) and 6 h after the critical temperature was reached [gray (red online)] (inset: histogram of all data points taken over a 7 h period). (b) Examples of transition behaviors for both large and small fluctuations. Gray (red online) lines indicate inverse exponential fits.

one phase to another could explain the observed asymmetry in occupancy of the two-level fluctuators. As one domain fluctuates to a different phase, it induces a change in the local field that either modifies the total energy of a nearby phase domain or produces asymmetric energy barriers associated with a fluctuation in the nearby domain. This resembles the behavior of nanoscale metallic systems in which a single or a few correlated atomic defects acting as fluctuators can generate abrupt changes in resistance [21,22].

These experimental findings shed new light on the nature and the dynamics of phase formation and behavior during phase transitions. All of the reported dynamical behaviors are seen only within a narrow window balanced at the transition temperature in thin wires containing a small number of phase domains. It appears that the metal-insulator transition is not a smooth process in which all domains undergo a universal and smooth transition; instead, finite regions individually flip from the metallic to the insulating phase. The asymmetric occupancy of the nested fluctuations shows that there are correlations between domains which could be mediated by asymmetries induced in the local fields created by phase fluctuations in

neighboring domains. These observations should help us further understand the underpinnings of phase separation and first-order phase transitions in complex oxides. Finally, the generic quality of our spatial confinement technique means that it is not limited to the model system presented here; it should be equally useful in studying other systems where phase separation plays a role in influencing unusual electronic properties.

*To whom correspondence should be addressed.
shenj@ornl.gov

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