Electrical switching to probe complex phases in a frustrated manganite

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Electrical switching was used to investigate complex phases induced by Cr-substitution in $(Pr_{1/3}Sm_{2/3})_{2/3}Sr_{1/3}MnO_3$. This system was expected to transform from a Type I ($Mn^{4+}/Mn^{3+} \approx 3/7$) to Type II ($Mn^{4+}/Mn^{3+} \approx 1$) manganite at critical Cr content, satisfying a virtual Mn^{4+}/Mn^{3+} ratio close to unity. The phase diagram of $(Pr_{1/3}Sm_{2/3})_{2/3}Sr_{1/3}Mn_{0.8}Cr_{0.2}O_3$ including charge/spin ordered/disordered phases was probed by electrical switching. The ferromagnetic insulating phase at $< \sim 100$ K, located next to the charge-ordered antiferromagnetic phase, exhibited a sudden rise in conductivity upon electric-field biasing. This resulted from the melting of charge ordering, and demonstrated the presence of a crossover regime of two coexisting magnetic orderings.

Correlated electrons in transition metal oxides form a rich variety of electronic phases inside the solids. Owing to the electron's three degrees of freedom—charge, spin and orbital, complex combinations of their ordered and disordered states appear in the phase diagrams. These electronic phases often compete with each other, and phase changes may be induced upon applying external stimuli. Perovskite manganites (Ln_xAE_{1-x})MnO$_3$ (where Ln and AE are lanthanide and alkaline-earth metal cations in the A-site, respectively) have been widely investigated with respect to such phase changes. Manganites can be classified into two types, depending on their phase-change functions: Type I and II where x ~ 0.7 and 0.5, respectively.[1,2] Typical phase change behavior of Type I manganites is insulator-to-metal transition with decreasing temperature, accompanied by long-range ferromagnetic ordering.[3] The transition can also be induced by a magnetic field, which is known as the colossal magnetoresistance effect.[4–6] Type II manganites possess comparable Mn^{4+} and Mn^{3+} valence states, and exhibit charge ordering (CO) and magnetic (preferably antiferromagnetic) ordering.[4,7] The antiferromagnetic insulating (AFMI) state of CO can be transformed into a ferromagnetic metallic state, by applying an external magnetic field. This is known as CO-melting.[4,8,9] The CO state can also be destroyed by applying an electric field.[10,11] This electrical phase change gives rise to conductivity switching, and such materials' applications in switching and sensing devices have been studied extensively.

Engineering the B-site (Mn) of manganites can also induce interesting electronic phases.[12,13] One approach involves introducing magnetic frustration into a Type I compound, which naturally favors a ferromagnetic metallic ground state. (Pr$_{1/3}$Sm$_{2/3}$)$_{2/3}$Sr$_{1/3}$MnO$_3$ is a typical Type I system, exhibiting a ferromagnetic transition at a well-defined Curie temperature of ~150 K.[14] Incorporating Cr^{3+} ($t_{2g}^3e_g^0$) isoelectronic to Mn^{4+} ($t_{2g}^3e_g^0$) frustrates the magnetic lattice. The antiferromagnetic exchange interaction between Cr^{3+}–O^{2-}–Mn^{4+} and/or Cr^{3+}–O^{2-}–Cr^{3+} competes with the ferromagnetic exchange between Mn^{3+}–O^{2-}–Mn^{4+} and/or Mn^{3+}–O^{2-}–Cr^{3+}.[15] The decrease in Mn^{3+} content ($t_{2g}^3e_g^1$) [Mn^{4+}/Mn^{3+} $\approx$ 3/7 (3.33/6.67

in $(Pr_{1/3}Sm_{2/3})_{2/3}Sr_{1/3}MnO_3)$] causes the valence state to become more like those of Type II CO compounds [$Mn^{4+}/Mn^{3+} \approx 1$ (0.53/0.47 in the present system)]. Cr-substitution, where Mn^{4+} and Mn^{3+} are in comparable abundance, may give rise to an antiferromagnetic CO phase in the Type I manganite. Phase competition may lead to an inhomogeneous composition of both magnetic states, resulting in electronic phase separation.[16,17] In this study, electrical switching was used to characterize the frustration-induced CO phase and its phase-separated behavior.

The polycrystalline $(Pr_{1/3}Sm_{2/3})_{2/3}Sr_{1/3}Mn_{0.8}Cr_{0.2}O_3$ (PSSMCO) composition was investigated. Substitution was optimized at 20 at.% Cr, to ensure a Mn^{4+}/Mn^{3+} ratio of ~1. The composition was synthesized by the chemical citrate-gel route, using high purity precursors. The as-prepared powders were calcined at 1000 °C in air for 2 h. Powders were then formed in rectangular pellets, and sintered at 1200 °C in air. A single phase sample was confirmed by X-ray diffraction using Cu-Kα radiation (PW 3040/60 Philips, PANalytical). Magnetic measurements were recorded by vibrating sample magnetometry (Oxford, Maglab VSM), at a magnetic field (H) of 100 Oe and temperature (T) of 290-5 K. Electrical contacts for transport measurements were prepared on the sample surface using conducting silver paint. Resistivity (ρ) was measured from 300 to 5 K by the two-probe DC method[18,19] using a source-measure unit (Keithley 2612A). Temperature was controlled using a physical property measurement system (Quantum Design).

The variations of resistivity, zero-field cooled (ZFC) and field cooled (FC) magnetization (M) with T are shown in Fig. 1. Insulating/semiconducting-like behavior was observed across the entire sampled T range. However, a weak CO signature was observed at ~100 K (Fig. 1, inset shows derivative plot).[14] This suggested the possibility of manganite Type I to II transition induced by isoelectronic Cr^{3+}-substitution. The thermo-magnetic irreversibility between the ZFC and FC magnetization curves, rounding off of the ZFC curve, and deviation from Curie-Weiss behavior indicated the presence of magnetic inhomogeneities, which are indicative of electronic phase separation.[20,21] The experimentally deduced magnetic moment

at 50 kOe and 5 K was 2.4 μ_B/fu, which was less than the theoretical magnetic moment of ~3.3 μ_B/fu estimated by considering only spin moments. This discrepancy was likely caused by the reduced ferromagnetic exchange interaction by Cr^{3+}-substitution, and the resulting relatively stable ferromagnetic and antiferromagnetic ordering. To explain these observations, the formation of AFMI-CO clusters was assumed within the ferromagnetic insulator (FMI) matrix. A phase diagram consistent with these observations and assumption is:

Region I: $150 < T < 300$ K, paramagnetic insulator (PMI),

Region II: $50 < T < 150$ K, predominately FMI with crossover regime where the AFMI-CO phase may locally evolve in the FMI matrix, and

Region III: $T < 50$ K, AFMI with CO and insignificant FMI phases.

Conventional characterization techniques make it difficult to identify AFMI-CO domains in Region III and its evolution in Region II prior to the macroscopic antiferromagnetic transition at ~50 K.
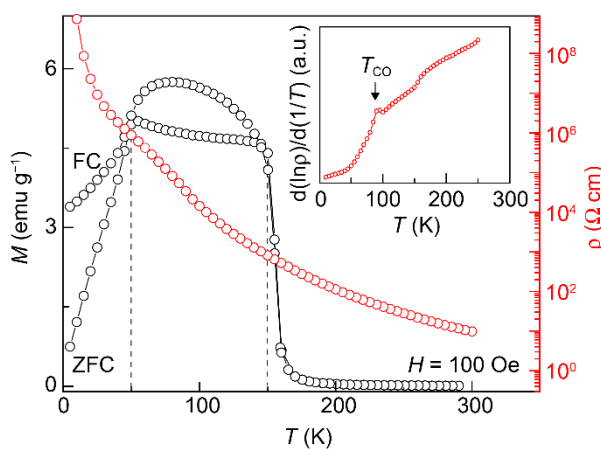

Fig. 1. Variation of ZFC and FC M (left axis) and ρ (right axis) with T. Inset shows the first derivative of the ρ curve, in which a weak CO signature is apparent.

CO phases in Region III were detected by electrical switching measurements. A 1 kΩ load resistor (R_L) was inserted in series to protect the sample from a sudden burst of current upon conductivity switching (Fig. 2, inset). The electric field applied to the sample (E_{sample}) was obtained according to $E_{sample} = (V - R_L I) / d$, where V, I and d are the bias voltage

supplied from the source-measure unit to the whole circuit, measured current and separation between the two electrodes (d = 0.4 mm), respectively. Figure 2 shows an E_{sample} versus current density (j) plot obtained at 20 K, where the AFMI phase was dominant. The threshold electric field (E_{th}) was defined as the maximum field in the j versus E curve. At the E_{th} of ~2050 V cm^{-1}, the curve exhibited a discontinuous rise in j. The associated decrease in E_{sample} was caused by the drop in the voltage applied to the PSSMCO, by voltage redistribution in the measurement circuit upon switching. E_{th} was of the order of kV cm^{-1}, and was 2–3 orders of magnitude smaller than those of dielectric breakdown fields of oxide band insulators (typically of the order of MV cm^{-1}).[22] Unlike the permanent breakdown observed for the latter oxides, the field-induced conducting state in PSSMCO recovered its insulating state upon decreasing E_{sample}. This conductivity switching behavior was consistent with that reported for CO manganites.[10,11] It has been reported in related Cu Mott insulators[18] that Joule heating does not play a major role in the huge increase in conductivity by electric-field biasing, which would also apply to the present system. These results demonstrate the presence of the AFMI-CO phase, and the partial melting of CO at high electric fields.
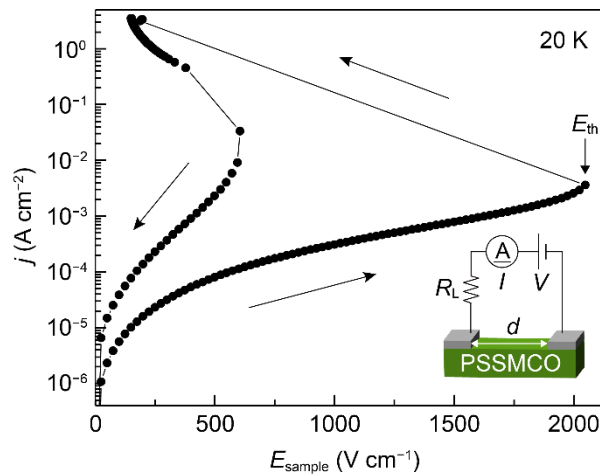

Fig. 2. Variation of j with E_{sample} at 20 K. The measurement circuit is shown inset.

Figure 3 shows the temperature dependence of the j-E_{sample} behavior. E_{th} and the conductivity on/off ratio both rapidly decreased with increasing T. The conductivity switching behavior almost disappeared at > ~100 K, at which point smooth nonlinear j-E_{sample} behavior was observed. This was in turn attributed to self-heating, as shown in Figs. 3(e) and

3(f). The switching behavior persisted even above the antiferromagnetic transition T of ~50 K. This coincided with the ρ anomaly at ~100 K, seen in the derivative plot of T-dependent ρ (Fig. 1, inset). This demonstrated the evolution of AFMI-CO domains in the FMI matrix in Region II, prior to the macroscopic antiferromagnetic transition.
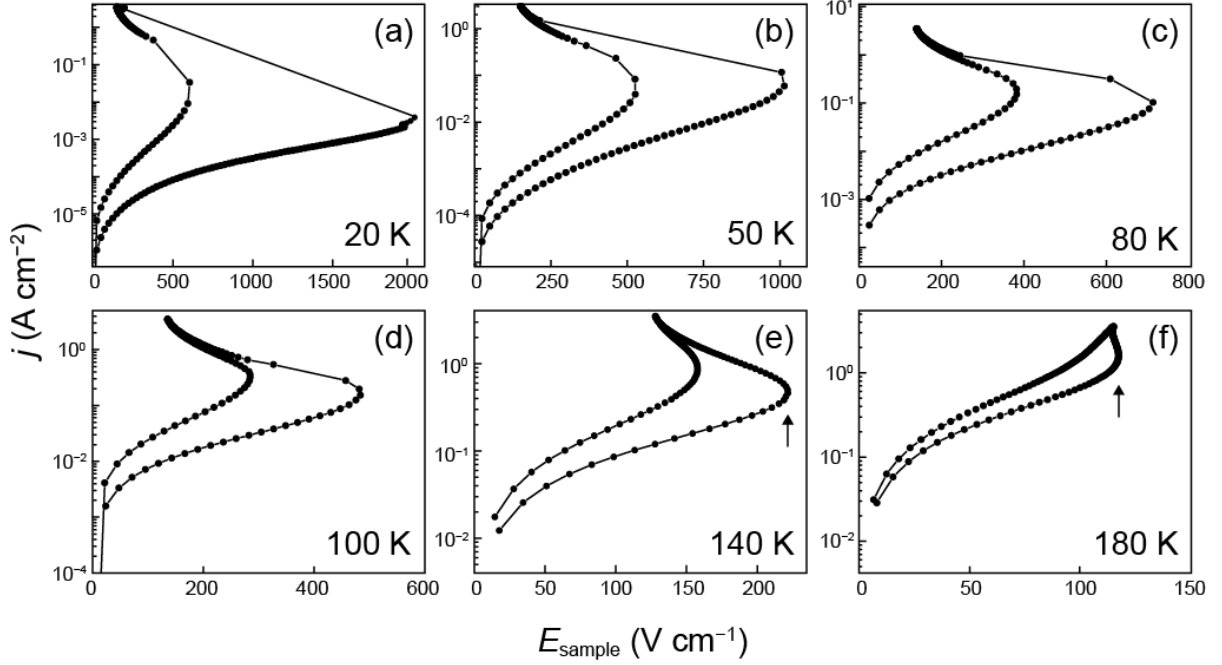

Fig. 3. j vs E_{sample} at various T, including the antiferromagnetic (~50 K) and ferromagnetic (~150 K) transition T.

To further investigate the phase crossover behavior, E_{th} and the conductivity on/off ratio are shown as a function of T in Fig. 4. Here, E_{th} for the non-threshold switching regime was defined as the strongest E_{sample} that could be applied [see arrows in Figs. 3(e) and 3(f)]. The switching on/off ratio was defined by $\Delta R/R_{th}$, where $\Delta R = R_{th}-R_3$ (where R_{th} is the resistance at the threshold field, and R_3 is the resistance at the third measured point from the threshold). The switching behavior transformed from abrupt to gradual with increasing T. This was the reason for using the third point from the threshold to confirm the completeness of switching, especially for an abrupt transition [The resistances at the fourth and fifth points exhibited similar $\Delta R/R_{th}$ with T behavior. Resistance at the second point exhibited intermediate switching states, as shown in Figs. 3(c) and 3(d)]. A gradual transition in

switching behavior and decreasing E_{th} occurred with T increasing from Region III ($T < 50$ K, AFMI-CO phase) to Region I ($T > 150$ K, PMI phase). The discontinuous switching behavior in the AFMI-CO phase and the low-T side of Region II ($50 < T < 100$ K) became continuous at 140 K. This continuous increase in conductivity was interpreted as self-heating, which is typical of insulating/semiconducting materials with negative temperature coefficients of resistivity. These observations showed the onset of a major FMI phase lacking CO, in the high-T side of Region II ($100 < T < 150$ K).

Conductivity switching can only be observed when switchable AFMI-CO domains block conduction between electrodes. Thus, the absence of switching at $> \sim 100$ K was attributed to the opening of a less insulating network by FMI domains. At ~ 100 K, the fraction of the AFMI-CO phase probably became comparable to that of the FMI phase. The growth of AFMI-CO domains was also supported by the increase in E_{th} to at least twice that at 140 K, as shown in Figs. 3(d) and 3(e).

In Region III ($T < 50$ K), the abruptness in switching and E_{th} increasing with decreasing T indicated the progressive evolution of the AFMI-CO phase. The switching behavior at 20 K was more robust and abrupt than that at 100 K. This suggested that the system at 20 K was dominated by the AFMI-CO phase, with only a minor FMI phase contribution. The abrupt increase in j at 20 K after E_{th} was because of the partial melting of the CO phase, and its transformation to a more conductive state in the presence of E_{sample}.
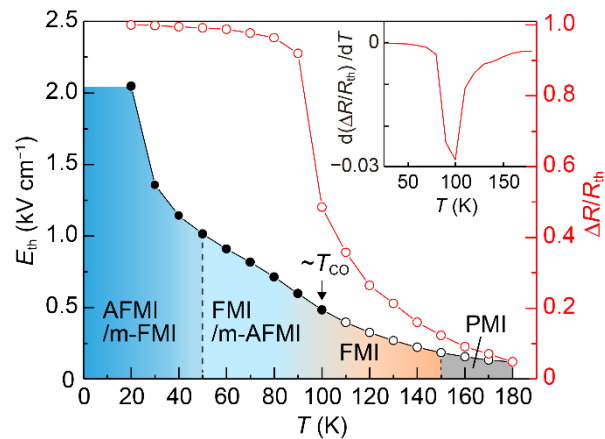
Fig. 4. Variation of E_{th} (left axis) and the resistance on/off ratio (right axis) with T. Gradual and abrupt transitions in switching are depicted by open and filled circles, respectively. Inset shows the derivative plot of on/off ratio with T, where the minimum corresponded to the CO temperature. m-AFMI and m-FMI indicate minority phases.

From the electrical switching behavior and resistivity and magnetization measurements, the following conclusions can be made: (a) AFMI-CO and FMI domains coexisted across the wide temperature range of Region II ($50 < T < 100$ K). The local growth of the microscopic AFMI-CO phase may have simultaneously occurred with the macroscopic ferromagnetic transition at ~150 K; (b) Region III ($T < 50$ K) was dominated by AFMI-CO domains, with a weak FMI domain signature. The resistivity and magnetic measurements were closely related with electrical switching. Electrical switching can aid our understanding of, and prove the existence of, frustration-induced effects (e.g., charge ordering, electronic phase separation) in manganites and other strongly correlated systems.

To get deeper insights into the correlation between the electrical switching behavior and the change in the magnetic ordering, it is worth investigating the change in magnetization under application of an electric field simultaneously with the measurement of conductivity. The development of such measurement systems would broaden the range of materials to be studied by the electrical switching technique.

In summary, we carried out electrical switching of the Type I-II crossover manganite compound, PSSMCO, and explained the evolution of complex electronic phases. In the AFMI-CO phase, conductivity switching was observed upon the application of an electric field. E_{th} increased with the evolution of AFMI-CO domains. The conductivity on/off ratio varied with T, and its derivative peak corresponding with the weak CO signature in the T-dependent ρ plot was observed. A crossover regime existed in the FMI phase, where local AFMI-CO clusters probably formed because of frustration by Cr-substitution. Conductivity

switching has previously been studied largely in terms of its potential in switching and sensing devices. The current study demonstrates that conductivity switching is a versatile tool for studying the physics of electronically and/or magnetically frustrated systems.

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