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Unusual x-ray transport phenomena in $La_{1-x}Sr_xMnO_3$

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An interesting memory effect occurs when $La_{1-x}Sr_xMnO_3$ ($x \sim 1/8$) is repeatedly exposed to x rays. While the ''dark'' conductivity remains unaffected by the irradiation history, the conductivity is markedly enhanced upon exposure to x rays at low temperatures. Immediately after renewed exposure, it recovers the value attained at the end of the previous exposure. We provide a qualitative explanation of this unusual effect in terms of three distinct states with different orbital correlations.

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Manganese oxides exhibit a rich variety of ground states whose interplay gives rise to various transport anomalies including especially ''colossal'' magnetoresistance. In addition to temperature and magnetic field, charge transport in some manganese oxides is also extremely sensitive to a number of perturbations, including doping, external pressure, substrate-induced strain, and perhaps most surprisingly, x rays. Specifically, x-ray illumination was shown to induce a transition from a charge-ordered antiferromagnetic insulator to a ferromagnetic metal in the $Pr_{1-x}Ca_xMnO_3$ family and related compounds.[1,2] Since the mechanism of this transition is still poorly understood, we have conducted further investigations along the same line in a different family of manganites, $La_{1-x}Sr_xMnO_3$, near $x=1/8$. We report the discovery of a memory effect that sheds light on the microscopic mechanisms underlying the behavior of these materials under x-ray illumination.

The phase diagram of $La_{1-x}Sr_xMnO_3$ at low doping is complex, and the nature of the various phases of this system is the focus of much current activity. For $x \sim 1/8$, three phases are observed:[3–5] At high temperatures, the system is paramagnetic and insulating. On cooling, at around 220 K, a transition into a ferromagnetic metallic state occurs, followed by another transition to a ferromagnetic insulating state at around $T=150$ K. In the low temperature state, new structural reflections characteristic of charge and orbital ordering (CO) appear in neutron[6] and x-ray[7] diffraction patterns. In both $La_{1-x}Sr_xMnO_3$ and $Pr_{1-x}Ca_xMnO_3$, the intensities of these reflections gradually diminish upon x-ray illumination at low temperatures.[1,2,8] The reflections in the two materials differ, however, in their dependence on photon energy close to the Mn K edge.[7,9] Moreover, a magnetic field destabilizes the charge ordered state in $Pr_{1-x}Ca_xMnO_3$[10] while it stabilizes the one in $La_{0.875}Sr_{0.125}MnO_3$.[5,7] It were these differences which originally motivated the present x-ray photoconductivity study of $La_{0.875}Sr_{0.125}MnO_3$. Our experiments have revealed that the CO state of this material is converted to a distinct state that is also *insulating*, in contrast to the case of $Pr_{1-x}Ca_xMnO_3$. A more conducting state with a temperature dependent conductivity of metallic character is realized only under nonequilibrium conditions, while the material is being irradiated. The interplay between these three states gives rise to the observed memory effect. We provide a qualitative explanation of this unusual behavior.

The data presented here were obtained on a 4000 Å thick film of nominal composition $La_{0.88}Sr_{0.1}MnO_3$ [effective hole concentration $x=0.12$ (Ref. 11)] grown epitaxially on a $SrTiO_3$ substrate with a pulsed laser deposition technique described earlier.[11] Four 2000 Å thick Au contacts were evaporated on a 200 Å thick Cr buffer layer as shown in the inset to Fig. 1. The contact resistances were below 1 Ω. The sample was placed in a cryomagnet with x-ray transparent windows, and the experiment was conducted at beamline X22B at the National Synchrotron Light Source at the Brookhaven National Laboratory. The x rays were directed normal to the film, while the magnetic field was applied in the plane of the film. The transport properties were measured using the four-point probe technique, with the beam spot placed between the voltage (center) contacts. Note that when the current is kept constant, the four-point probe will only show changes taking place between the voltage contacts. The x-ray fluence was 5×10^{10} sec^{-1} at a photon energy of 8 keV, on a beam spot of $\simeq 0.2$ mm diameter. At this energy

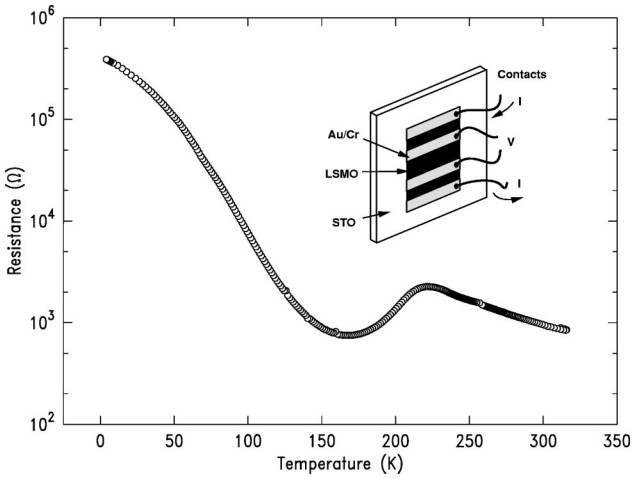

FIG. 1. Resistance of the $La_{0.88}Sr_{0.1}MnO_3$ film as a function of temperature, measured with a constant current of 1 μA with no x-ray illumination. The inset shows the contact configuration. The area between voltage contacts is $\sim 0.5\times 3.5$ mm.

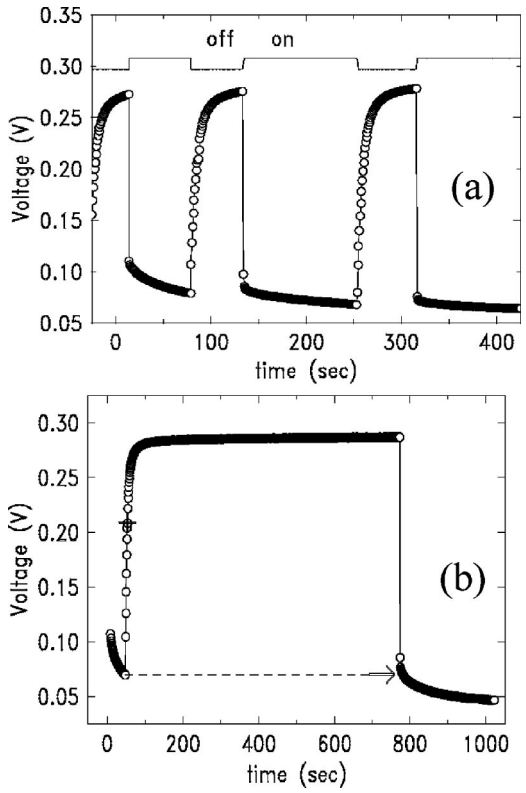

FIG. 2. (a) Voltage at a constant current of 10 μA at $T=5$ K monitored as a function of x-ray irradiation. The line above is the state of the x-ray shutter as indicated. (b) Detailed demonstration of the ''memory effect,'' showing that the memory is maintained for $\sim$100 times the apparent recovery time constant ($\sim$7 sec, taken as 63% of the rise). The x rays are off during the time period indicated by the dotted line ($\sim$730 sec). Note the very fast ($<$1 sec) recovery of the original relaxation curve after the x rays are switched on.

the x-ray penetration depth for this material is several μm, so that the film is uniformly illuminated. This represents a distinct advantage of thin film versus bulk samples which, when irradiated, necessarily become inhomogeneous near the surface. However, very similar data were in fact obtained on a bulk single crystal of composition $La_{0.875}Sr_{0.125}MnO_3$ grown by the floating zone technique.[12]

The ''dark'' resistance of the thin film sample (that is, the resistance measured without x-ray irradiation) is shown in Fig. 1. The sequence of insulating, metallic, and reentrant insulating regimes as a function of temperature parallels that of bulk samples,[4,5] with some differences in detail presumably attributable to substrate-induced strain[11,13] or slight differences in composition. Figure 2 shows that the electrical resistance at $T=5$ K decays with cumulative dose in a manner similar to other manganites,[1,2] following a stretched-exponential time dependence observed before in response to x-ray irradiation and other stimuli.[1,2,14] However, unlike $Pr_{1-x}Ca_xMnO_3$ and related compounds whose x-ray photoconductivity is persistent, in the $La_{0.88}Sr_{0.1}MnO_3$ film the resistance recovers to the dark level when the x rays are switched off. When the material is again exposed to x rays, the resistance falls very quickly to the *same* level attained immediately before the x rays were switched off and resumes

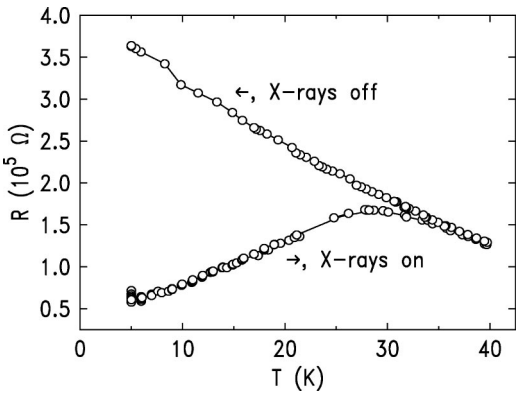

FIG. 3. Temperature dependence of the voltage at a constant current of 1 μA. For the lower branch, the conductivity was allowed to relax completely under x-ray illumination at low temperatures. Data were then taken on warming, with the x rays on. Around 35 K, the curve joins the unirradiated cooling curve (upper branch). The arrows indicate the direction of the temperature sweep.

its decay with the same (much slower) time constant. Remarkably, the system thus retains a ''memory'' of its history of past illuminations that is hidden when the x-ray beam is off.

Figure 2(b) shows that the memory effect is maintained for $\sim$100 recovery time constants. This demonstrates that beam heating cannot be responsible for maintainting the low resistivity. Further, Fig. 3 shows that the resistivity under x-ray illumination has a metallic temperature dependence up to $T\sim35$ K where the difference between illuminated and dark levels disappears. Above this temperature, the resistivities measured under both conditions show identical temperature dependences. This rules out ohmic heating as the origin of the observed behavior. Behavior consistent with heating was in fact observed when the experiment was repeated under illumination with visible light (photon energy $\sim$1.5 eV) from a Ti-sapphire laser. The only effect of laser irradiation on the temperature dependent resistivity (Fig. 1) was a constant temperature shift over the entire range up to room temperature. No memory effect was found using a laser beam power up to 6000 times that of the x-ray beam ($\sim$60 μW).

While x-ray diffraction measurements are difficult on thin film manganites because the relevant superlattice reflections are superposed by Bragg reflections from the substrate, both the x-ray induced decay of the superlattice (found earlier in Ref. 8 where transport measurements were not reported) and the memory effect were reproduced in a bulk single crystal of $La_{0.875}Sr_{0.125}MnO_3$.[12] This shows explicitly that structural features such as strain domains peculiar to thin film samples[13] are not essential for the phenomena reported here. As previously reported,[8] the x-ray induced structural modification occurs only below $T\sim40$ K, consistent with the temperature dependence of the photoconductivity shown in Fig. 3. While not persistent as in $Pr_{1-x}Ca_xMnO_3$, the experimental evidence thus indicates that the photoinduced conductivity change in $La_{1-x}Sr_xMnO_3$ is also associated with x-ray induced structural modifications. In contrast to well known photoconductivity effects in semiconductors, the modifica-

tion of the diffraction pattern in both manganites demonstrates a coherent response of a macroscopic number of atoms to the x-ray illumination.

Based on these considerations, we conclude that the insulating CO state is converted into a distinct, different phase that is also insulating in the absence of x-ray illumination, but lacks a cooperative lattice distortion. In order to identify this phase, we turn to the current theoretical literature. The insulating behavior of $La_{1-x}Sr_xMnO_3$ at low doping was attributed to an ''orbital polaron'' bound state in which the relatively small number of Mn^{4+} holes polarize the e_g orbitals on neighboring Mn^{3+} sites.[15] Indeed, according to a recent proposal[16] the CO ordered state at $x\sim 1/8$ can be regarded as a lattice of orbital polarons. The interpolaron interactions stabilizing this state are, however, weak, and several nearly degenerate states with different ordering patterns can be found.[16–18] Directly or indirectly, x-ray irradiation releases some fraction of the valence electrons out of the polaronic bound states,[1,2] thus disrupting the CO phase. A disordered state with purely incoherent orbital-lattice correlations (also proposed theoretically[15]) may then be realized as these electrons are kinetically prevented from restoring long range order at low temperature when the x rays are switched off, becoming instead trapped by defects (for instance, by the random potential fluctuations due to the Sr acceptors). Some regions of the sample are thus left in the CO state while others are converted to a disordered state which we ascribe to a ''polaron glass.'' The history-independent dark conductivity of the sample indicates that the conductivity of this disordered state is comparable to that of the CO state. This is not unexpected since according to the model of Ref. 15 the orbital polaron is self-trapped. The origin of the insulating behavior at low doping is thus predominantly local, so that the arrangement of the polarons on long length scales should not have a major influence on the resistivity. Finally, it is interesting to note that new insulating phases were also invoked to explain other recent experiments, although their microscopic nature was not specified.[19,20]

The most intriguing aspect of our data is the memory effect that comes to the fore only while the x rays are on. The anticorrelation between the intensity of the superlattice reflections and the conductivity under x-ray illumination suggests that the conductivity enhancement originates in the disordered regions not occupied by the CO state. Since previous work has shown that the CO state is stabilized by a magnetic field, this anti-correlation is further supported by the magnetic field dependent data of Fig. 4 which demonstrate that the saturation level of the resistivity (after prolonged irradiation) increases with field. While comparable to the conductivity of the CO state when the x rays are off, the memory effect indicates that the conductivity of the disordered state becomes significantly *larger* and acquires a metallic temperature dependence under x-ray illumination.

Even leaving aside the complications created by another x-ray induced phase, our understanding of the CO state in $La_{0.875}Sr_{0.125}MnO_3$ is still incomplete. Nonetheless, we can

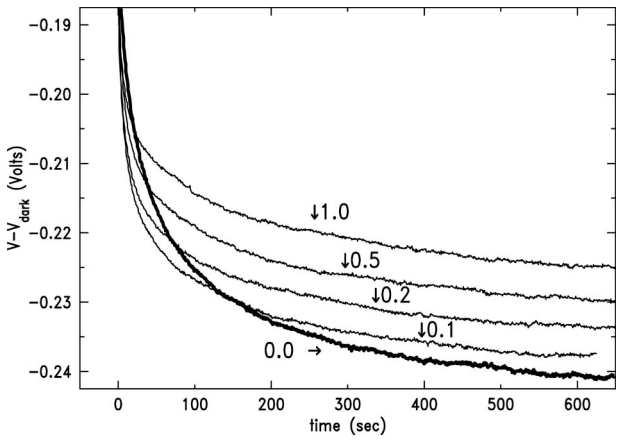

FIG. 4. Voltage as a function of x-ray illumination at $T=5$ K for different applied magnetic fields (indicated in T). The ''dark'' voltage has been subtracted from every decay.

give a plausible explanation of the memory effect within the same framework already used in the discussion above. Current theories[21] indicate that at least in isotropic ferromagnetic manganites such as $La_{0.875}Sr_{0.125}MnO_3$,[22] orbital fluctuations are a prerequisite for metallic conductivity. In the orbital polaron picture, both the lattice and the neighboring orbitals necessarily relax when x-ray photons release bound valence electrons from Mn ions. Due to the cooperative nature of the CO state, these locally generated orbital fluctuations are more strongly inhibited and therefore presumably less effective in promoting conductivity than in the state with quenched orbital disorder. The same picture also offers an explanation of the differences between $La_{0.875}Sr_{0.125}MnO_3$ and $Pr_{1-x}Ca_xMnO_3$: In the latter system the density of polarons is larger so that they are more prone to aggregate and to form a persistent metallic state under x-ray illumination. In addition, however, magnetic degrees of freedom must also play a role in $Pr_{1-x}Ca_xMnO_3$,[2] because its CO state is antiferromagnetic, as opposed to the ferromagnetic one observed in $La_{0.875}Sr_{0.125}MnO_3$.

In summary, we have reported the discovery of a memory effect in $La_{1-x}Sr_xMnO_3$ with $x\sim 1/8$ and have provided a qualitative model that explains this effect in terms of the interplay of three distinct and partially coexisting states: an orbitally ordered state observed before, a state with quenched orbital disorder, and a nonequilibrium state in which x-ray illumination helps maintain orbital fluctuations and sustain an enhanced conductivity. The memory, which is encoded in the volume fraction of these phases, is an unexpected consequence of the phase separation that appears to be ubiquitous in the manganites.[23] A full theoretical description of the nonequilibrium physics underlying this phenomenon is an interesting subject of further investigation.

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