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X-Ray Effects in Charge-Ordered Manganites: A Magnetic Mechanism of
Persistent Photoconductivity

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RECEIVED**JAN 11 1999****OSTI****ABSTRACT**

Charge-ordered manganites of composition $\text{Pr}_{1-x}(\text{Ca}_{1-y}\text{Sr}_y)_x\text{MnO}_3$ exhibit persistent photoconductivity when illuminated by x-rays. We review transport and x-ray diffraction data as functions of x-ray exposure, magnetic field, and temperature which shed light on the origin of this unusual behavior. The experimental evidence suggests that the mechanism primarily involves a ferromagnetic polarization of local spins by hot electrons generated by the x-rays.

Keywords: Persistent Photoconductivity; hot electrons; colossal magnetoresistance; x-ray diffraction

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1. Introduction

Persistent photoconductivity (PPC) has been observed in a variety of semiconductors, and two general mechanisms have been identified. The most common of these involves a large relaxation of the lattice around certain types of impurity complexes (DX centers) when a photoelectron is released [1]. Because of the lattice distortion, recapture of the electron involves a substantial momentum transfer, and recapture by photon emission is thus not allowed. Phonon-assisted recapture is possible at high temperatures, where the relevant phonon states are thermally populated, but becomes extremely inefficient at low temperatures. The lifetimes of photogenerated carriers in semiconductors doped with DX centers can therefore easily reach days or weeks at low temperatures. An alternative mechanism invokes mesoscopic or macroscopic electric field inhomogeneities which separate electron-hole pairs, thus preventing recombination [2]. This effect has been demonstrated in artificially structured semiconductor devices with built-in inhomogeneities [3] but is generally thought to be of little importance in clean, homogeneous materials [1].

A photoinduced change in electrical conductivity by several orders of magnitude has recently been observed in the manganite perovskite $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ when the material is exposed to an x-ray beam [4]. As previously observed in semiconductors, this effect occurs only at low temperatures (below $\sim 40\text{K}$) and is reversed on thermal cycling. However, there are also substantial differences between this newly discovered phenomenon and conventional PPC in semiconductors that are suggestive of new and interesting physics. Rather than merely changing the carrier density, x-rays induce a transition between two thermodynamically distinct (insulating and metallic) phases in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. Moreover, conventional PPC is induced by visible light with a photon energy large enough to bridge the gap between the impurity level and the conduction band. In the manganites, PPC is *not* observed in response to visible light unless a high electric field is applied at the same time [5]. The light-induced conductivity change results in the formation of current carrying filaments which persist only as long as the electric field is maintained [6]. It is therefore better described as electric breakdown triggered locally by light exposure. (Electric breakdown also occurs in the absence of light exposure at comparable electric fields [7].) These findings suggest that $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ becomes electrically conducting only in the presence of high energy ("hot")

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electrons generated either by incoming radiation with high photon energies or by a high external electric field.

In this article we present x-ray diffraction and magnetotransport data that shed new light on the mechanism of x-ray PPC in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and related manganites. We will argue that a genuinely new, *magnetic* mechanism is required to describe the photoeffects in these materials. Our approach relies to a large degree on a comparison of the transport characteristics as a function of x-ray illumination and magnetic field. In the absence of either of these external perturbations, the material is semiconducting (with an average valence of +3.3 distributed uniformly over the Mn sites) at high temperatures, and charge-ordered insulating (with a static superlattice of Mn^{3+} and Mn^{4+} ions) below $\sim 200\text{K}$. The charge-ordering transition is presumably driven partly by polaronic self-trapping of charge carriers due to the Jahn-Teller distortion of the Mn^{3+} ions, and partly by correlation effects. Application of a magnetic field exceeding $H_c \sim 4\text{T}$ at low temperatures results in a first-order transition from the charge-ordered insulating to a metallic state that connects smoothly to the semiconducting state at high temperatures [8].

2. Experimental Details

The measurements were performed in a vertical-field superconducting magnet mounted on a two-circle goniometer at beamline X22B (photon energy 8 keV, flux $5 \times 10^{10}/\text{sec}$) at the National Synchrotron Light Source at the Brookhaven National Laboratory, USA. Inside the magnet, the orientation of the sample can be adjusted by a miniature rotation stage, and its temperature can be varied from 1.5 to 300K. An ion chamber was used to monitor the incident x-ray beam. The x-ray fluence (that is, the cumulative number of photons incident per mm^2 of sample surface) was estimated from the monitor counts. The diffracted beam was detected by a scintillation detector. The samples were single crystals of $\text{Pr}_{1-x}(\text{Ca}_{1-y}\text{Sr}_y)_x\text{MnO}_3$ synthesized by a floating zone method described previously [8]. The crystal surface was polished with diamond paste to better than $1 \mu\text{m}$. Two 4000 Å thick Au electrical contacts about 2 mm apart were evaporated on a 200 Å thick Cr buffer layer and annealed at 500°C for 10 hours. The x-ray beam illuminated the region between the contact pads. This experimental setup allows simultaneous measurements of the electrical conductivity and of the intensities

of superstructure reflections characteristic of the cooperative Jahn-Teller distortion in the charge-ordered insulating state [9].

3. Results

The superlattice reflections due to charge ordering occur at commensurate reciprocal lattice vectors $(H, K/2, L)$, K odd, indexed on an orthorhombic lattice with room temperature lattice constants $a = 5.426\text{\AA}$, $b = 5.478\text{\AA}$, and $c/\sqrt{2} = 5.430\text{\AA}$. The central observations [4] on $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ are shown in Fig. 1a. The x-ray penetration depth is about $2\text{ }\mu\text{m}$, and the enhancement of the electrical conductivity by several orders of magnitude shows that a thin metallic film is created on an insulating background when the material is exposed to x-rays (inset in Fig. 1). Inside this metallic film, the cooperative Jahn-Teller distortion relaxes.

At first sight, these observations are consistent with the large lattice relaxation model of PPC, with the role of the local lattice distortions around DX centers now played by the cooperative Jahn-Teller distortion. However, in addition to the visible light experiments of Miyano and coworkers [5, 6] mentioned in Section 1, some of our own subsequent x-ray experiments call for a different model. In particular, all of the compounds $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, and $\text{Pr}_{0.65}\text{Ca}_{0.245}\text{Sr}_{0.105}\text{MnO}_3$ respond to x-ray exposure with a conductivity enhancement of the same order of magnitude as $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, but do not always also exhibit a diminution of the superlattice reflections.

An example is given in Fig. 1b for $\text{Pr}_{0.65}\text{Ca}_{0.245}\text{Sr}_{0.105}\text{MnO}_3$. This compound shares with $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x=0.3-0.5$) a large hysteresis regime in the (H,T) phase diagram identified in the magnetotransport measurements of Tomioka *et al.* [8] (insets in Fig. 1). As illustrated in Fig. 1b, significant x-ray PPC is observed throughout the entire hysteresis region [10], but an x-ray induced depression of the Jahn-Teller distortion is found only in a narrower region below the dashed line. Following arguments given in Ref. [11], we associate the dashed line with the thermodynamic phase boundary between charge-ordered and metallic states. These measurements are inconsistent with models in which the PPC is entirely a consequence of the large lattice relaxation. Rather, the x-ray induced relaxation of the Jahn-Teller distortion appears to be a secondary effect associated with the thermodynamic

instability of the charge-ordered state.

In order to elucidate the actual mechanism of x-ray PPC, we have carried out a systematic study of the current-voltage (I-V) characteristics of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ as function of both x-ray exposure and magnetic field. The effect of a magnetic field on these materials is much better understood than the effect of x-rays. Briefly, the nearly cubic crystal field splits the Mn 3d-orbitals into a lower-lying triplet (t_{2g}) occupied by three electrons that form a local spin-3/2, and an e_g doublet partially occupied by delocalized conduction electrons. In the generally accepted "double exchange" model [12], the field aligns the local t_{2g} spins ferromagnetically and facilitates hopping of the conduction electrons between adjacent Mn sites. This is believed to be the primary origin of the "colossal magnetoresistance" in the manganites. A synopsis of the evolution of the I-V curves with x-ray illumination in zero field, and with magnetic field after a brief x-ray exposure at $T=5\text{K}$, is given in Fig. 2. By repeating the magnetic field dependent measurements without x-ray exposure, we verified that for all curves of Fig. 2b the conductivity is dominated by the conducting film created by the initial brief x-ray illumination, with negligible contribution of the bulk of the crystal. Both sets of curves in Fig. 2 can thus be directly compared and, remarkably, turn out to be closely similar. The parallel evolution of the transport characteristics across the insulator-metal transition suggests that in both cases the dominant effect of the external agent (magnetic field, or hot electrons generated by x-ray illumination) is a forced polarization of the local spins. A *magnetic* mechanism thus appears to be responsible for PPC in the manganites.

After a brief x-ray illumination, or in a low magnetic field, the I-V curves of Fig. 2 are highly nonlinear. There are different possible origins of nonohmic conductivity in insulators [13]: For very large electric fields E , a distortion of the impurity wave functions can result in field emission of electrons from impurity levels (Poole-Frenkel effect). Related effects give rise to nonlinearities in the I-V characteristics of disordered semiconductors in the variable-range hopping regime, at somewhat lower E [14]. In both of these scenarios, E would have to be more than three orders of magnitude larger than in our measurements. Moreover, the conductivity should depend exponentially on temperature. If the observed nonlinearity were a simply consequence of current heating, it would also be strongly temperature dependent.

Figs. 3 and 4 show that none of these effects can be responsible for the nonlinear I-

V characteristics in the manganites. The current at fixed voltage is nearly temperature independent at low temperatures (Fig. 3), and the I-V curves at different fixed temperatures are identical within the experimental error (Fig. 4). A slight temperature dependence appears only at higher temperatures ($T \geq 20\text{K}$) as the phase boundary to the metallic state in the bulk of the sample is approached.

We have therefore considered an alternative model in which the I-V characteristics at low x-ray exposure and magnetic field are dominated by tunneling between isolated metallic clusters generated by x-ray irradiation. Charge-ordered insulating regions act as the barrier (inset in Fig. 5). Of course, x-ray exposure presumably results in a ramified network of tunnel junctions that would be difficult to model quantitatively, especially without detailed knowledge of the size distribution of the metallic droplets. However, if the conductance is dominated by a small number (N) of junctions, one may hope to capture the essential physics by a simple modification of Simmons's tunneling expression for a single metal-insulator-metal junction [15]:

$$I = \eta \left[\left(\phi - \frac{eV}{2} \right) e^{-A(\phi - \frac{eV}{2})^{1/2}} - \left(\phi + \frac{eV}{2} \right) e^{-A(\phi + \frac{eV}{2})^{1/2}} \right]$$

where J is the current density, t is the barrier thickness, ϕ is the barrier height, $\eta = ae/(2\pi\hbar t^2)$, a is the junction area, and $A = 4\pi t(2m)^{1/2}/\hbar$. For simplicity, we have assumed N identical junctions in series so that $V \rightarrow V/N$; parallel junctions renormalize the prefactor η . The line in Fig. 5 is the above expression with $\phi = 1.5\text{eV}$, $t = 15\text{\AA}$, $N = 2$, and the effective junction area a fitted to a particular measured I-V curve (data points in Fig. 5). The parameters are physically reasonable; the values of ϕ and t were in fact taken from a previously reported study of lithographically patterned trilayer manganite junctions [16]. Although the fitting parameters are of course underdetermined by these data alone, it is encouraging that our tunneling model results in a physically sensible interpretation of the I-V characteristics that is consistent with all of our data.

At high x-ray exposure and/or high magnetic field, the metallic clusters percolate through the sample and form a continuous current path with ohmic conductivity (Fig. 2). The tunneling and ohmic regimes are separated by an intermediate regime near the percolation threshold of the metallic clusters where the tunnel junctions dominating the conductivity

become extremely narrow, perhaps consisting only of a few atomic sites. In this regime, the I-V curves become unstable and exhibit erratic jumps even for extremely low injected currents (Fig. 6). These instabilities begin to occur at lower power densities as the temperature is increased (see, for instance, the region near 40K in Fig. 3), indicating that Joule heating is relevant in this regime.

We have performed two different types of measurements in this transition regime. Fig. 6a shows a typical sequence of I-V curves taken after x-ray exposure in zero magnetic field, with the x-ray beam *off*. Jumps between well defined I-V curves with higher and lower conductivities occur with equal likelihood in both directions. By contrast, the I-V curves of Fig. 6b were taken after the system was tuned just below the percolation threshold by the magnetic field, which was kept *on* during the measurements. In this case, jumps occur exclusively into states with higher conductivity.

These observations can again be explained in the framework of a magnetic model in which the alignment of local Mn spins in the narrow junction barriers predominantly determines the conductivity. Near percolation, even minute transport currents can supply enough heat to rearrange the spin configuration in the barrier. If no aligning field is present (Fig. 6a), such heating events switch between random spin configurations in which the conductivity is equally likely to be reduced or enhanced. If, on the other hand, a magnetic field is applied during the measurements, the final configurations should be generally characterized by enhanced ferromagnetic correlations and enhanced conductivity, as observed in the data of Fig. 6b.

4. Conclusion

In summary, we have identified a *magnetic* mechanism of PPC in the manganites which is operative only for "hot" photoelectrons generated by radiation in the x-ray regime of the electromagnetic spectrum. This mechanism is quite different from those responsible for PPC in conventional semiconductors. In particular, lattice distortions which are believed to be at the origin of most PPC phenomena observed in doped semiconductors [1] appear to play at most a secondary role in the manganites.

On a qualitative level, the mechanism may involve a nonequilibrium population of hot

carriers in extended states near the top of the Mn e_g band which interact with the local Mn t_{2g} spins via double exchange [12]. The x-ray photon energy (8 keV) is of course much larger than the difference between e_g and t_{2g} states, but there is a variety of possible pathways through which such a population could be created. For example, collisions can slow down the initial photoelectrons as well as generate lower energy secondary electrons. Lower energy electrons would also be created through the decay of core holes. Of course, this picture is entirely phenomenological and should be substantiated by microscopic calculations.

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Figure Captions

1. Electrical resistance and intensity of the (2, 1.5, 0) superlattice reflection characteristic of charge ordering as a function of x-ray exposure for (a) $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ $T=5\text{K}$ and (b) $\text{Pr}_{0.65}\text{Ca}_{0.245}\text{Sr}_{0.105}\text{MnO}_3$, at temperature $T=100\text{K}$. The insets in the lower panels show the magnetic phase diagrams [8]. Significant hysteresis is observed in the shaded regions, and the dashed line represents the estimated thermodynamic phase boundaries following Ref. [11]. The inset in the upper right panel illustrates the experimental geometry, as discussed in the text.
2. Current-voltage (I-V) characteristics of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ for various x-ray exposures (a) and magnetic fields after a brief x-ray exposure (b), at $T=5\text{K}$. The curves in (a) are labeled by the incident x-ray fluence (in units of 10^{13} photons per mm^2 incident on the sample). Those in (b) are labeled by the magnetic field applied after a brief x-ray exposure (4.4×10^{12} photons/ mm^2).
3. Temperature dependence of the current at fixed voltages of 5V (upper panel) and 3V (lower panel) after brief x-ray exposures of 1.3×10^{12} and 4.1×10^{12} photons/ mm^2 , respectively.
4. I-V curves after an x-ray exposure of 2.3×10^{12} photons/ mm^2 , taken at different temperatures.
5. I-V curve measured at $H=2\text{T}$ after an exposure of 4.4×10^{12} photons/ mm^2 . The line is the Simmons tunneling expression [15] for $N = 2$ series junctions with barrier height 1.5 eV and thickness 15 Å (see text). The inset shows a qualitative sketch of the microscopic situation underlying the tunneling model, with metallic islands (shaded) separated by charge-ordered insulating barriers.
6. Typical current-voltage characteristics close to the percolation threshold of (a) x-ray generated and (b) magnetic field generated metallic clusters. The curves in (a) were taken in the sequence $1 \rightarrow 4$ at the same x-ray exposure (1.3×10^{14} photons/ mm^2), with the x-ray beam off. Right (left) arrows in the legend mean that the current was

ramped up (down). The curves in (b) were taken in the sequence $1 \rightarrow 5$ at a field of 3.75T, with the field on.

$\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$

$T=5\text{K}$

$\text{Pr}_{0.65}\text{Ca}_{0.245}\text{Sr}_{0.105}\text{MnO}_3$

$T=100\text{K}$

Fig. 2

Fig. 3

Fig. 6