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Photonic Phase Control of Magnetic Oxides

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Unconventional optical responses have been revealed for the perovskite manganese oxide, $Pr_{1-x}Ca_xMnO_3$, which is known to undergo the insulator-metal (I-M) transition relevant to the magnetic field induced melting of the charge-ordered (CO) state. Optical conductivity spectrum is drastically modified over 0-1 eV from a gap-like feature into a metallic band with application of magnetic field of 7 T. It was found that such an I-M transition can be caused by photo-excitation as well. The electrical conductivity and magnetization increase abruptly with irradiation of visible/IR laser, indicating the photo-melting of the CO state and the photo-generation of ferromagnetic metallic domains.

Keywords: photo induced insulator-metal transition, charge ordering, ferromagnetic metal, optical conductivity

INTRODUCTION

Since a discovery of colossal magnetoresistance (MR) phenomena[1], perovskite-type manganese oxides have been of current interest. Among a large number of manganites, $Pr_{1-x}Ca_xMnO_3$ system shows various interesting spin-charge coupled phenomena, such as real space charge-ordering/disordering transitions controlled by an external magnetic field[2]. In the charge-ordered (CO) state, nominal Mn^{3+} and Mn^{4+} species are alternately arranged[3] and the strong carrier localization takes place. Such a CO state is most stabilized at x=0.5 and the deviation of the doping level x from the commensurate value (x=0.5) weakens the robustness of the charge-ordering. Recently, Tomioka *et. al.* revealed that the CO state can

melt' into a double-exchange ferromagnetic metallic (FM) state[4] under external magnetic field, and that such a phase transition is of first order with a large hysteresis[2]. More lately, it has been observed that such a phase transition can be triggered by other external stimuli than a magnetic field: Keimer and his coworkers found the insulator-metal (I-M) transition by illumination with X-ray in the x=0.3 crystal[5], and Asamitsu *et al.* observed that the conductivity in the same compound shows an abrupt increase with increase of electric field[6]. Another example is the I- M transition triggered by 'photocarrier injection' with visible-IR laser by Miyano *et al.* [7], which is interesting also in the light of the technical application.

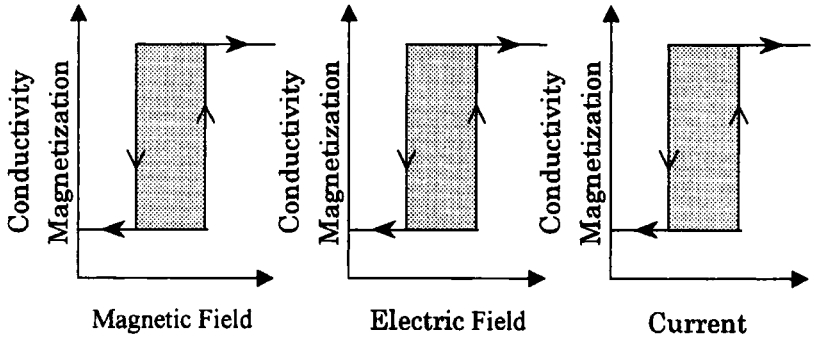

FIGURE 1 Exotic phase control achieved in $Pr_{1-x}Ca_xMnO_3$ system.

These results are summarized by schematic diagrams as shown in Fig. 1. Such phase transitions from the CO insulating state to the FM one are of first order with a large hysteresis. The energy levels of the two states are almost degenerate in the hysteresis region, which suggests that external stimuli (and their combination) can switch the electrical (I-M) as well as magnetic (antiferromagnetic-ferromagnetic) state. Thus, the $Pr_{1-x}Ca_xMnO_3$ system offers a versatile stage of "phase control".

In this paper, we investigate a variation of the optical spectrum with an external magnetic field and the electric and magnetic response upon photo-excitation in $Pr_{1-x}Ca_xMnO_3$ (x=0.3-0.4) crystals.

MAGNETIC FIELD INSULATOR-METAL TRANSITION AND OPTICAL SPECTRA

First, let us discuss a variation of the electronic structure with magnetic field in terms of optical spectra. For reference, we show in Fig. 2(a) temperature dependence of resistivity (ρ) under 0 and 7 T of magnetic field. The ρ -T curve at 0 T shows a steep increase around T_{co}, indicating occurrence of the charge-ordering phase transition. In the CO state below

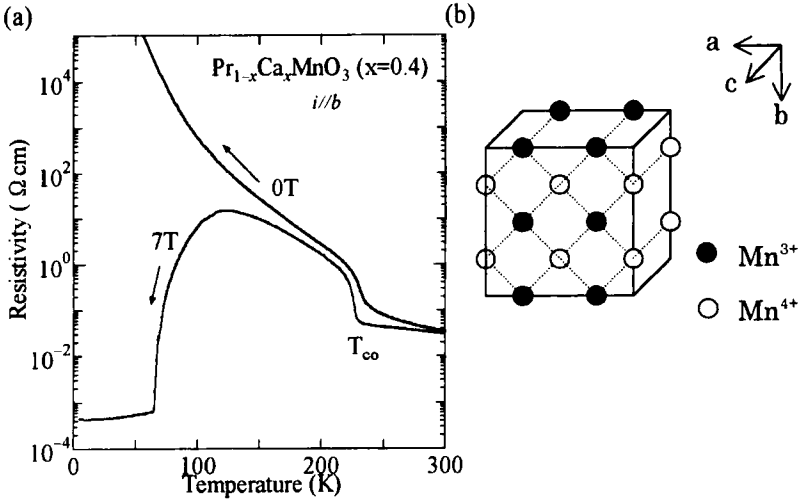

FIGURE 2 (a): Temperature dependence of resistivity in $Pr_{0.6}Ca_{0.4}MnO_3$ under 0 T and 7 T. (b): The ordering pattern of Mn^{3+} and Mn^{4+} in the charge ordered state deduced by Jirak *et al.* [3].

T_{co}, Mn^{3+} and Mn^{4+} are alternately arranged in the ab-plane and the same cations are ordered rod-like along the c-axis[3] as depicted in Fig. 2(b). Below T_{co}, antiferromagnetic spin ordering is realized around 170 K (T_N), and canted antiferromagnetic ordering subsequently occurs at ~40 K (T_{CA}). As mentioned above, the CO state is transformed into the FM one with an external magnetic field. The behavior of the ρ -T curve at 7 T (Fig.

2(a)) is nearly parallel with the 0 T curve from T_{co} to 120 K, except that the ρ-value is a little smaller. However, the 7 T curve starts to decrease around 100 K and turns into a highly metallic value ($\rho \sim 10^{-4}\,\Omega$ cm) below 60 K, indicating that the double-exchange FM state is realized. Such an I-M transition with a few tesla of magnetic field is characteristic of the *discommensurated* (x<0.5) CO state in the manganites[2].

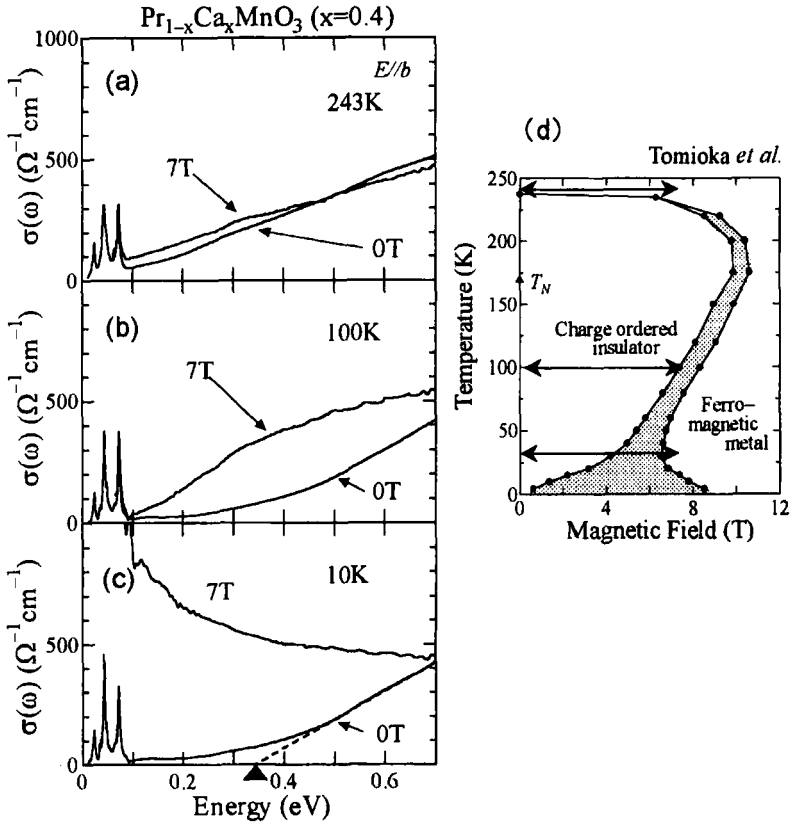

FIGURE 3 (a)-(c) Temperature and magnetic field dependence of optical conductivity spectra in $Pr_{0.6}Ca_{0.4}MnO_3$. (d) The electronic phase diagram in temperature-magnetic field plane.

Figures 3(a)-(c) show optical conductivity spectra ($\sigma(\omega)$) under 0 and 7 T of magnetic field in $Pr_{0.6}Ca_{0.4}MnO_3$ at selected temperatures[8]. For

comparison, we reproduce in Fig. 3(d) a phase diagram of the compound derived from the ρ -measurements by Tomioka *et al.* [2]. The hatched area represents a hysteresis. At 243 K ($> T_{co}$), the system remains as a paramagnetic insulator against a magnetic field (top arrow in Fig. 3(d)), and undergoes charge ordering phase transition at T_{co} ($\sim$240 K). The CO state persists under a magnetic field of 7 T at 100 K (middle arrow), while it is transformed into the FM one at 30 K (lower arrow).

Keeping these in mind, we discuss the temperature and magnetic field dependence of $\sigma(\omega)$. Above T_{co} (243 K, Fig. 3(a)), scarcely any difference is found between $\sigma(\omega)$ at 0 T and 7 T. (The spiky structures below 0.06 eV are optical phonon modes.) With decrease of temperature, however, the magnetic field dependence of optical spectra becomes remarkable. At 100 K (Fig. 3(b)), the $\sigma(\omega)$ at 0 T shows even a clearer gap-like feature than at 243 K. By contrast, the spectral weight around 0.3 eV is accumulated under 7 T, indicating that the optical-gap is reduced with the increase of a magnetic field. At the lowest temperature 10 K, the 0 T $\sigma(\omega)$ is scarcely changed from that at 100 K. We can evaluate the optical gap-value in the CO state (0.34 eV) as shown by a dashed line and closed triangle in Fig. 3(c). In striking contrast to the insulating feature at 0 T, the 7 T $\sigma(\omega)$ is drastically altered into a metallic band, indicating the appearance of the metallic state where the optical-gap is closed. These phenomena are quite unconventional considering that a magnetic field as low-energy perturbation (1 T $< 10^{-3}$ eV) can thus change the electronic structure up to a few eV, as it were *magnetochromism*.

PHOTO INDUCED INSULATOR-METAL TRANSITION

To be highlighted in the light of unconventional photoactivity is the I-M transition with photo-excitation in $Pr_{0.7}Ca_{0.3}MnO_3$. To overview the physical properties of the x=0.3 crystal, we show in Fig. 4 the temperature dependence of ρ under zero magnetic field. The insulating behavior of ρ resembles that of x=0.4 compound, but the phase diagram is very different as shown in the inset of the figure (cf. Fig. 3(d)). The hatched

area represents a hysteresis region, where the free-energy of the CO and FM state are comparable. The CO state at 30 K denoted with a closed circle has a high resistive value and is within the hatched region, in which the CO state should be viewed as metastable. Hereafter, we discuss the nature of photo-induced I-M transition at 30 K in the x=0.3 crystal.

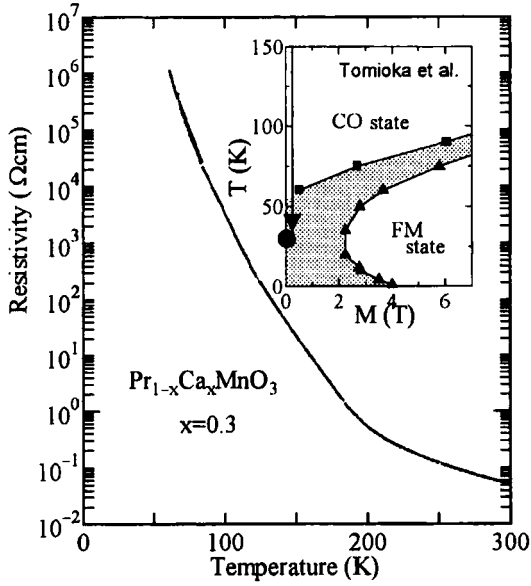

FIGURE 4 Temperature dependence of resistivity in $Pr_{0.7}Ca_{0.3}MnO_3$. Inset shows the electronic phase diagram of the compound in the temperature vs. magnetic field plane.

We show in Fig. 5 time dependence of voltage drop caused by irradiation of a laser pulse ($h\nu$ =1.2 eV, 5 ns in duration, and ~300 μ J/mm^2) at 30 K. The value of the voltage drop was measured across a 50 Ω load resister as depicted in the inset. The applied voltage 11 V is much smaller than the critical voltage at which the electric field-induced I-M transition takes place[6]. The voltage drop rapidly increases up to ~2 V just after the photo-excitation and such anomalous photocurrent once decays very slowly. However, the voltage drop across the sample gradually increases again after ~30 μ s, and is eventually stabilized

around 7.8 V as indicated by an arrow. The final sample resistance is ~5 Ω and much smaller than that before the photo-excitation (>1 GΩ).

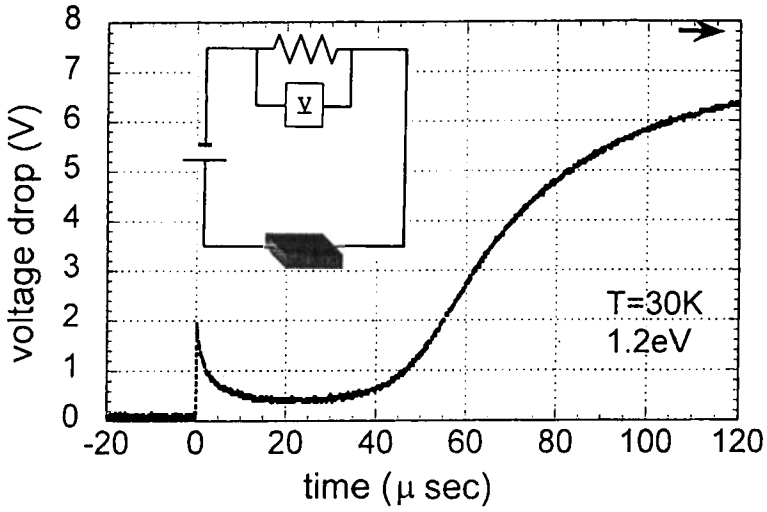

FIGURE 5 Time evolution of the resistance in $Pr_{0.7}Ca_{0.3}MnO_3$ after a single shot of 1.2 eV laser pulse. An arrow denotes the value of the final voltage drop.

These results clearly indicate that the I-M transition is realized by the photocarrier injection into the CO state. It is worth noting here that such an I-M transition is very sensitive to the power and photon energy of the laser, suggesting that a simple scenario such as laser-induced heating is excluded. It is reasonable to consider that the final metallic state is ferromagnetic in nature as well as in the magnetic field-induced metallic state. Such a highly conductive state returns to the insulating one when the applied voltage is removed. It is likely that the electric current sustains the metallic domains produced by the photocarrier injection, forming current paths against the back pressure from the insulating (CO) medium. In fact, the threshold laser power for the photo-induced phase transition was observed to be reduced with increase of the applied electric field. Hereafter, we demonstrate the photo-induced I-M transition under external

magnetic field but a zero electric field.

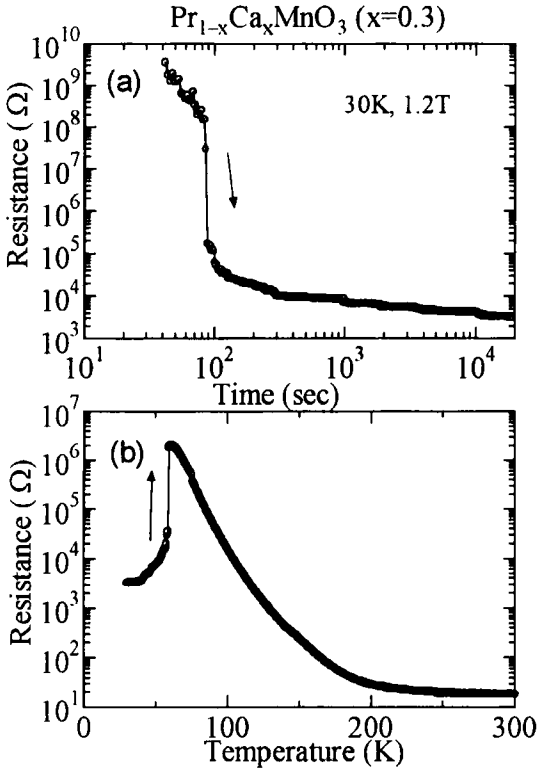

FIGURE 6 (a): Time evolution of the resistance in $Pr_{0.7}Ca_{0.3}MnO_3$ under 1.2 T after photo-excitation. (b): The temperature dependence of the resistance in the zero-field warming-run.

Figure 6(a) shows temporal variation of the resistance (R) after a pulsed photo-excitation under a magnetic field of 1.2 T. For the photo-excitation, we have utilized a single pulse (λ =532 nm, 5 ns in duration) from a Nd-YAG laser. No voltage was applied when the sample was shot with a laser pulse. There is scarcely magnetoresistance effect under 1.2 T at any temperature in this compound, and the R-value at 30 K is very large (> 1 G Ω) before the photo-excitation. With a single laser shot, however, the R drastically decreases by more than nine orders of magnitude, indicating

that the photo-induced I-M transition takes place. Such a large decrease of R continues until $\sim$100 s and it seems that the time scale of the decrease becomes more gradual after that. The latter slow variation of R is perhaps not directly relating to the photo-excitation, but is characteristic of the metastable state under the magnetic field, where the M shows gradual change as well (*vide infra*). The R-value finally decreases down to $\sim 10^3$ Ω after about five hours. Such a highly conductive state is preserved even after the magnetic field is removed. This is in contrast to the case of the photo-induced I-M transition under an electric field.

We show in Fig.6(b) temperature dependence of R (in the warming run) after photo-excitation under zero magnetic field. (The measurement was done during a much shorter period than the time scale of the gradual decrease of R.) The R-value shows an abrupt jump just below $\sim$70 K, which is consistent with the critical temperature for the magneto-transport measurements (see the inset of Fig. 4). This result clearly indicates that such a photo-induced conductive phase coincides with the FM state realized by a magnetic field. The large difference of the time scale of the photo induced I-M transition between under electric field ($\sim \mu$ s, see Fig. 5) and under magnetic one ($\sim$s, see Fig. 6) perhaps results from the different roles of these external fields during the photo-induced I-M transition: the electric field plays an important role in making current paths between FM domains as well as weakening the CO state, whereas the magnetic field only weakens the robustness of the charge-ordering. It is worth noting here that the time scale of the I-M transition with irradiation of X-ray ($\sim$s)[5] is consistent with the latter case.

There is a supporting evidence that the FM state is realized with photo-excitation. We show in Fig. 7 the time dependence of the M under 1.2 T in $Pr_{0.7}Ca_{0.3}MnO_3$. (We made use of a SQUID magnetometer for the measurement.) The relatively large value of the M ($\sim 0.88\ \mu_B$/Mn site) is due to the canted antiferromagnetic ordering as mentioned before. Three arrows indicates the timing of the pulse photo-excitation (λ =532 nm), and all the measurements were done successively for the identical sample with intermittent zero-field warming (up to 300 K) between events of the

laesr illumination. For comparison, we also show the time dependence of M with closed circles without photo-irradiation. As the time increases, the

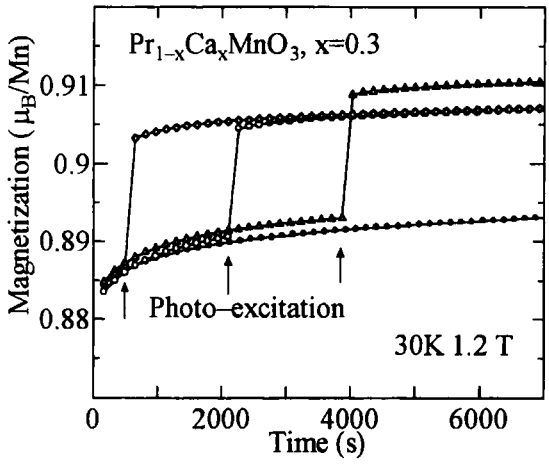

FIGURE 7 Evolution of magnetization by photo-excitation under 1.2 T and 30 K in $Pr_{0.7}Ca_{0.3}MnO_3$. Arrows show the timing of a pulse photo-excitation.

M also shows gradual increase, indicating that the CO state under 1.2 T is metastable in nature, decaying very slowly. The M-value jumps upon the photo-excitation by $\sim$1 %, indicating that the laser illumination clearly induces ferromagnetic domains (4.0 μ_B/Mn site). The quantity of the created FM domains are roughly reasonable considering the laser spot ($\sim$ 1 mm ϕ), penetration depth estimated from an optical spectrum ($\sim$0.2 μ m), and the total sample volume ($\sim 3 \times 10^{-4}$ cm^3). Such an increase of the M cannot be attributed to simple laser-heating because the M arising from the canted antiferromagnetic ordering would decrease upon heating.

SUMMARY

We have studied the electronic-structural change from a charge ordered (CO) to a ferromagnetic metallic (FM) state in $Pr_{1-x}Ca_xMnO_3$ with

application of a magnetic field in terms of optical spectroscopy. Optical conductivity spectrum is changed from gap-like in the CO state into metallic at 7 T accompanied with a large spectral weight transfer over ~ 1 eV. These results, as it were *magnetochromism*, are quite unconventional considering the small energy of the magnetic field. We have also presented some evidences that the CO state can be transformed into the FM one with photo-excitation. Resistance drastically decreases with a single shot of visible/IR laser. The time scale of such an insulator-metal transition depends on the type of the external field (electric or magnetic), which tends to destabilize the CO state and hence promote the photo-induced transition. Magnetization shows a conspicuous increase with the photo-excitation by a pulsed laser beam, clearly indicating that the photo-generated metallic state is ferromagnetic. These observations show that $Pr_{1-x}Ca_xMnO_3$ is promising as a new intriguing photoactive system as well as colossal magnetoresistive material.

Acknowledgments

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