Photoinduced Insulator-to-Metal Transition in a Perovskite Manganite

K. Miyano,[1] T. Tanaka,[1] Y. Tomioka,[2] and Y. Tokura[1,2]
[1]*Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan*
[2]*Joint Research Center for Atomic Technology (JRCAT), Tsukuba 305, Japan*
(Received 3 March 1997)

We have observed an insulator-to-metal (I-M) transition triggered by the photocarrier injection into the charge-ordered (CO) state of a perovskite manganite crystal, $Pr_{0.7}Ca_{0.3}MnO_3$. The photocurrent is a highly nonlinear function of applied electric field and of light intensity; both show a threshold behavior for the I-M transition. The dependence of the anomalous photocurrent on the excitation photon energy and the temperature excludes the laser heating as the cause of the effect, suggesting the photocarrier-mediated collapse of the CO state. [S0031-9007(97)03338-3]

PACS numbers: 71.30.+h, 71.28.+d, 72.40.+w

Perovskite manganites with the formula $R_{1-x}A_xMnO_3$ (R = trivalent rare earth element and A = divalent alkaline earth element) offer a vast playground in which one can test the concept of the "phase control." Here, charge, spin, orbital, and lattice act as independent degrees of freedom, yet they are strongly coupled so that the balance between the resulting phases is very subtle and susceptible to the external stimuli. This is most notably exemplified by their extremely large magnetoresistance [the so-called colossal magnetoresistance (CMR)], which is viewed as a magnetic-field induced insulator-to-metal (I-M) transition [1]. In this case the control parameters are the electronic bandwidth and the doping level. The bandwidth control is afforded through the dependence of the transfer energy on the lattice distortion [2]: the smaller the ionic radii of cations at the A site of the perovskite lattice, the smaller is the transfer integral. The amount of the divalent ions, x, controls the level of doping, which, on the one hand, can promote the delocalization of the charge via the double-exchange mechanism [3] and, on the other hand, can favor localization through the formation of a charge-ordered state [4], manifested by the charge-density modulation at the Mn site. The modulation is stabilized at a certain charge distribution commensurate with the lattice periodicity. The charge-ordered state is thus very stable at $x = 0.5$ when small cations such as R = Pr and A = Ca are chosen [5]. When one reduces x, the charge-ordered state becomes less stable and, around $x = 0.3$, the system is on the verge of the transition from the charge-ordered insulator (COI) to the ferromagnetic metal (FM) so that the (energetically minuscule) magnetic field can cause the COI to FM transition and hence the CMR. This report deals with a similar I-M transition mediated by the creation of carriers via photoabsorption of visible-IR light [6].

The sample is a single crystal $Pr_{0.7}Ca_{0.3}MnO_3$ grown by the floating-zone method as described previously [1]. A thin slice was cut from a boule and the surface was mechanically polished to a mirror surface. It was annealed at 1000 °C for 24 h under O_2 flow to remove the surface stress. Au electrodes separated by a 50 μm gap (~2 mm long) were vacuum evaporated onto the surface. The sample was mounted in a continuous-flow type cryostat for maximum heat conduction. The wiring consisted of thin 50 Ω Teflon coaxial cables.

Without an external field, this material undergoes a series of phase transitions [1]. At room temperature it is a paramagnetic insulator. Below 200 K, it is the COI. It turns into an antiferromagnet around 130 K (T_N), and finally into a canted antiferromagnet around 115 K (T_{CA}). The resistance of the sample shown in Fig. 1 is (aside from a multiplicative factor due to the electrode geometry) in good agreement with the published data [1]. Although the electric field used in the experiment is relatively strong (up to 4 kV/cm; see below), the I-V relationship is linear in this range as shown in the inset of Fig. 1.

The I-M transition was monitored by observing the photoinduced conduction. An OPO (optical parametric oscillator) excited by a pulsed YAG laser was used for optical excitation. The photon energy was in the range

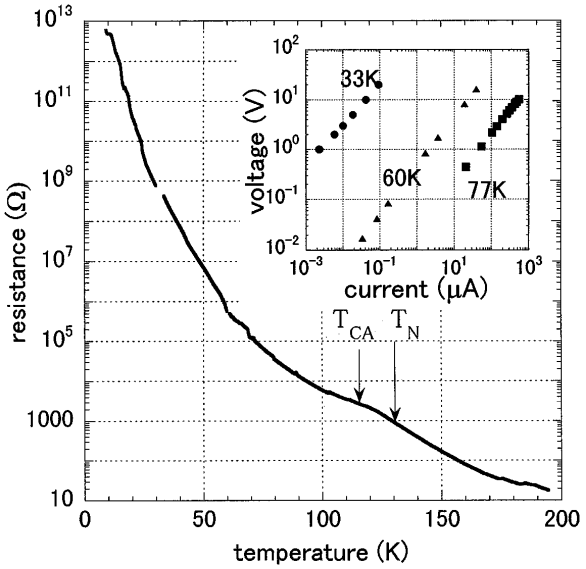

FIG. 1. The resistance of the sample and the I-V relationship (inset) at some representative temperatures. Within this voltage range (50 μm electrode separation) the resistance is Ohmic.

0.6 to 3.5 eV and the pulse duration was 5 ns. The temporal profile of the laser pulse and the photocurrent was monitored with a digitizing oscilloscope. In order to avoid spurious ringing in the fast pulse detection, we were obliged to use the input impedance of the oscilloscope (50 Ω) as the reference resistor despite the obvious disadvantage of the lower sensitivity.

The photocurrent was linear in terms of the applied voltage and laser power for 3.5 eV photoexcitation at low power level. The current properly followed the laser pulse shape and the sign reversed when the polarity of the applied voltage was inverted. No sign of contact potential nor thermoelectric effect was seen.

However, as the photon energy was reduced, the linear response became more and more difficult to observe. It appears that there is a threshold power for the photocurrent (see Fig. 5 below). When the photocurrent was large enough for observation, it already showed a pronounced tail as shown in Fig. 2(a), which is a photocurrent for a single laser shot of 1.2 eV photon energy taken at 30 K. The shape of the leading edge coincides with that of the laser pulse but the tail lasts well after the 5 ns pulse is gone. As the optical energy per pulse was increased, the leading edge grew rapidly and the tail became further and further pronounced [Fig. 2(b)]. The response is clearly nonlinear. The sample eventually undergoes the I-M transition [Fig. 2(c1)] whose longer trace is shown in Fig. 2(c2). The applied voltage was manually shorted after each shot in order to avoid a possible cumulative effect. The laser energy of each shot is marked in Fig. 2 as the fraction of the minimum energy at which the transition did occur: the 100% level corresponds to 5 μJ over the area of 0.015 mm^2. The final voltage drop across the sample was 1 V, corresponding to a sample resistance of 5 Ω; before the transition it was ~1 GΩ (Fig. 1). Considering the laser spot size in the electrode gap (0.05 × 0.3 mm^2) and the penetration depth of the light (about 0.2 μm), [7] the resistivity of the sample should be less than 1 mΩ cm, which is far less than the resistivity at room temperature [1].

As seen in Fig. 2 and also Fig. 3 below, the instantaneous response of the photocurrent is followed by an oscillatory structure which is reproducible. It is not due to the ringing in the circuitry but due to the sudden voltage drop across the sample caused by the large photocurrent. As will be discussed below, the photocurrent is very sensitive to the applied voltage whose fluctuation feeds back into the current and results in an oscillation. The transition is reproducible. The process shown in Fig. 2(c) can be repeated scores of times without an obvious sign of fatigue or change in the threshold laser power level: as will be discussed later, the metallic state returns to the insulating state on removal of the voltage.

The transition is also sensitive to the applied voltage. Figure 3 shows the dependence of the photocurrent on the applied voltage, in which the laser energy was kept at 87%

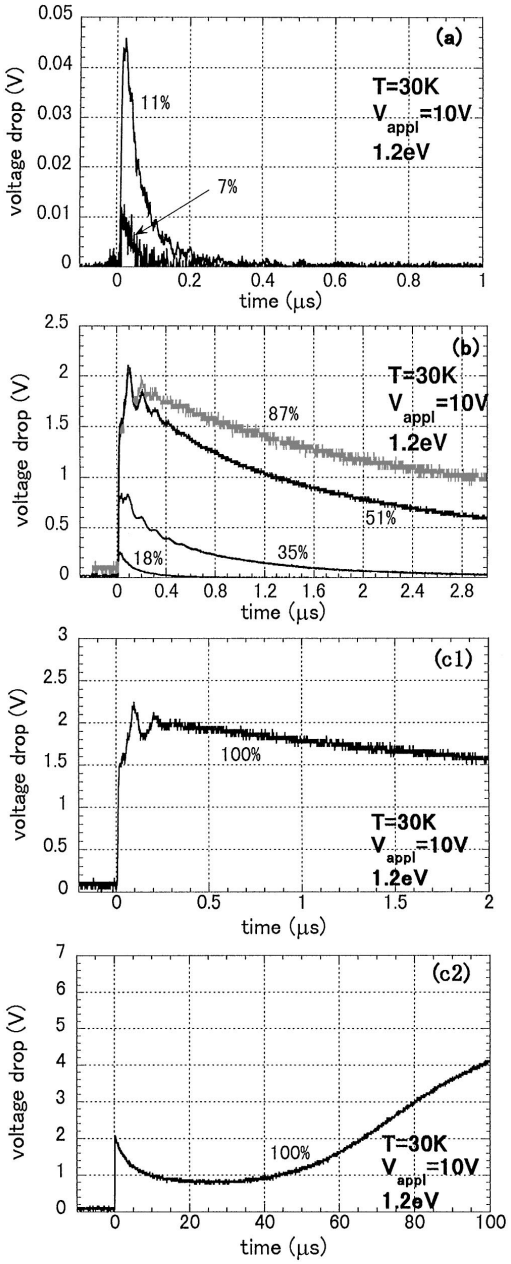

FIG. 2. Evolution into the I-M transition after a single shot of 1.2 eV laser pulse. Ordinate: the photocurrent measured across a 50 Ω reference resistor. Percentage next to the curves indicates the amount of energy per pulse relative to the minimum energy for the transition to occur [100% in (c)]. (c2) is the long time trace of (c1).

in the scale of Fig 2. The instantaneous current as well as the tail are highly nonlinear functions of the voltage. The transition shows clear threshold characteristics: the transition occurs at 11 V but not at 10.5 V, despite the extremely long tail as seen in Fig. 3(b). (For the shape of the current over a longer time scale, see Fig. 4.) Under a given experimental condition, the threshold value is well defined.

One might suspect that the transition is driven by the runaway temperature rise caused by the current. Since

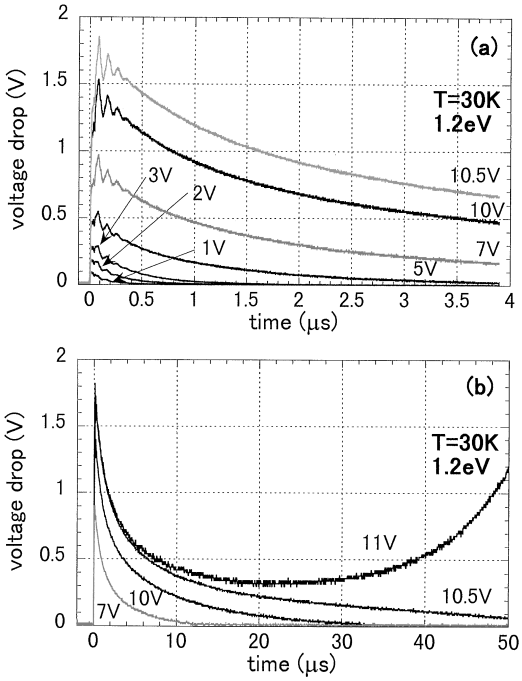

FIG. 3. Photocurrent dependence on the applied voltage. The experimental condition was identical to that in Fig. 2 except for the laser energy which was fixed at 87% in the scale of Fig. 2. Note the change of the time scale from (a) to (b).

the sample was immersed in the continuous flow of He gas, the temperature rise by a single laser shot of a few tens of μJ is not likely. In order to make sure, however, we studied the temperature dependence of the transition, as shown in Fig. 4. The temperature was regulated by varying the flow rate of the He gas around the sample and was monitored by a Si sensor located on the Cu block on which the sample on an insulating layer was mounted. It is clear that the behavior is essentially temperature independent within the reproducibility of the transition.

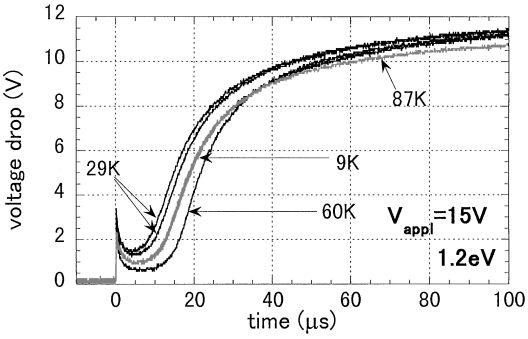

FIG. 4. The I-M transition at various temperatures with a fixed total energy (at 44% in the scale of Fig. 2 but with increased voltage of 15 V) of the laser pulse. Note that the initial resistance differs more than 8 orders of magnitude in this temperature range. At 87 K, the resistance is low enough so that the current is barely discernible before the application of the laser pulse.

Further evidence against the heating scenario is provided by the photon energy dependence of the photocurrent. The optical reflectivity of the sample is rather featureless and the penetration depth of the light is nearly constant ($\sim$0.2 μm) in the energy range used in this experiment [7]. Thus, for a laser pulse of a given total energy, the energy deposited into the sample should be insensitive to the laser wavelength. However, the photocurrent depends on the photon energy as is illustrated in Fig. 5. On the one hand, the photocurrent shows a threshold behavior which is smaller for the higher photon energy and is negligible at 3.5 eV, as mentioned earlier. On the other hand, the I-M transition occurs at a *lower pulse energy* for the *lower photon energy*. At 3.5 eV, the energy needed for the transition was at least 1 order of magnitude larger than that at 0.6 eV; also it was hard to avoid damage to the sample. The photon number rather than the total optical energy deposited into the system may be the more relevant parameter for the I-M transition to occur.

There is still much to be learned about the nature of the metallic state observed here. We notice, however, that the I-V characteristics of the photoinduced metallic state is identical to that of the metallic phase obtained under the large applied voltage at higher temperature ($\geq$100 K); the process can be viewed as a voltage-driven breakdown [8]. It is, therefore, natural to interpret the temporal behavior (e.g., Fig. 4) in terms of a similar breakdown, perhaps related to the charge-ordering-collapsed state as follows: Two separate processes clearly contribute to

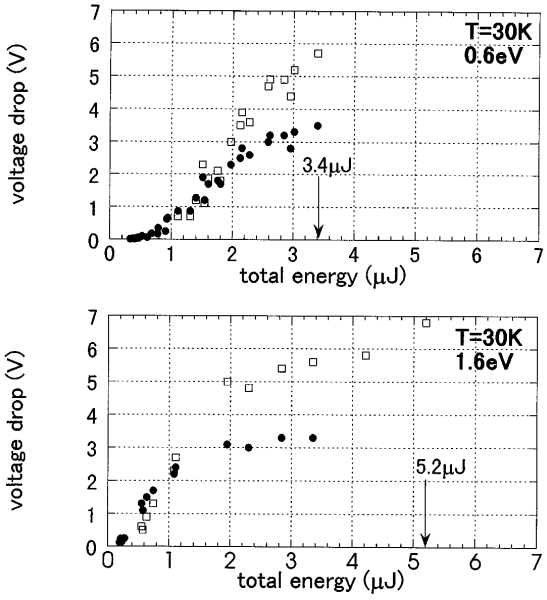

FIG. 5. The photocurrent dependence on the photon energy (0.6 and 1.6 eV) and the total laser pulse energy deposited on the sample in the electrode gap region. The applied voltage was 10 V. Filled and open symbols are for the height of the leading edge and the peak, respectively, of the current pulse; cf. Figs. 2 and 3. The minimum pulse energy for the I-M transition is indicated by an arrow.

the transition. One is the fast photocarrier generation whose leading edge follows the light pulse; the other is the slow rise of the current triggered by the photocarriers. The slow process is apparently driven by the applied potential, since the rate of the rise depends on the applied voltage. However, the fast part is not a simple photocarrier generation either, because it is by itself highly nonlinear, as shown in Fig. 4. The fast part scales as the area of the electrode gap irradiated by the laser for a given energy density, but the slow part is rather insensitive to this feature. It is, therefore, reasonable to assume that photocarrier injection creates metallic patches whose dynamics under the external electric field leads to the formation of a complete current path. The final current path thus formed is probably filamentary, since the I-V characteristics are independent of experimental conditions. Although the exact size of the metallic region is not clear from our experiment, it should be quite small since the minimum optical spot width to cause the transition is less than 10 μm. In accordance with this observation, the transition is not permanent, in the sense that the sample reverts to an insulator after removal of the applied potential. It is likely that the metallic region surrounded by the insulator is under mechanical and possibly magnetic stress sufficient to convert the metallic state back to the insulating state.

In conclusion, we have presented clear evidence for an I-M transition triggered by photocarrier generation in a perovskite manganite, $Pr_{0.7}Ca_{0.3}MnO_3$, in which the metallic state is the result of the collapse of the charge-ordered state. Because in this material the insulating state is antiferromagnetic and the metallic state is ferromagnetic [4], the observed transition unequivocally implies that we have produced an optically induced ferromagnetic metal. The details of the time evolution of the photoinduced current under various conditions could provide a clue to the understanding not only of the I-M transition but also of the dynamics of the first-order phase transition.

The work was supported in part by Grant-in-Aid for COE Research of the Ministry of Education, Science, Sports and Culture. Part of the work, supported by NEDO, was performed in JRCAT under the joint research agreement between NAIR and ATP. The technical assistance of Dr. T. Mori and suggestions by Professor M. Gonokami are appreciated.

[1] Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, J. Phys. Soc. Jpn. **64**, 3626 (1995), and references therein.
[2] H. H. Hwang, S.-W. Cheong, P. G. Radaelli, M. Marezio, and B. Batlogg, Phys. Rev. Lett. **75**, 914 (1995).
[3] P. G. de Gennes, Phys. Rev. **118**, 141 (1960).
[4] H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura, Phys. Rev. B **52**, R13145 (1995).
[5] Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, and Y. Tokura, Phys. Rev. B **53**, R1689 (1996).
[6] It was recently found that a prolonged exposure to x ray also causes an I-M transition in these materials, although the mechanism is not understood. V. Kiryukhin *et al.*, Nature (London) **386**, 813 (1997).
[7] Y. Okimoto, Y. Tomioka, and Y. Tokura (unpublished).
[8] A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura (to be published).