PHYSICAL REVIEW B

CONDENSED MATTER AND MATERIALS PHYSICS

THIRD SERIES, VOLUME 57, NUMBER 24 15 JUNE 1998-II

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Stability of a photoinduced insulator-metal transition in $Pr_{1-x}Ca_xMnO_3$

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(Received 11 March 1998)

A photoinduced insulator-metal transition has been found in crystals of $Pr_{1-x}Ca_xMnO_3$ with various doping levels ($x=0.31$, 0.35, 0.40, 0.45, and 0.50). The current-voltage relationship and the temperature dependence of the stability of the metallic region indicate that the metallic states of all x are of the same origin, and exclude the Joule heating as the mechanism of sustaining the metallic phase. The driving force for the transition is clearly the collapse of the charge-ordered state by the photocarriers. [S0163-1829(98)51724-9]

The phase transitions in perovskite manganites induced by external field have drawn much attention in recent years.[1] The effect is brought about because in perovskite manganites $R_{1-x}A_xMnO_3$ (R=trivalent rare earth element and A=divalent alkaline earth element), charge, spin, orbital, and lattice are strongly correlated.[2–6] Among the manganese oxides, $Pr_{1-x}Ca_xMnO_3$ is unique in that the transfer integral between Mn atoms is rather small because of the low tolerance factor,[1] which results in the localization of the e_g electrons at all hole doping levels of x. The charge-ordered insulating (COI) state is relatively unstable against the ferromagnetic metallic (FM) state because of the gain in the kinetic energy mediated by the double-exchange mechanism[2,3] in the latter phase, and thus the COI-FM transition has been found with the applied magnetic field,[1] stress field,[7] electric field,[8] or with the irradiation of x rays.[9] The stability of the COI state, of course, depends on x. At $x=\frac{1}{2}$, the charge ordering is commensurate with the lattice periodicity and should be most stable; indeed, a high field of 30 T is needed to cause the magnetic-field-induced COI-FM transition at $x=\frac{1}{2}$ as opposed to the relatively low field of 4 T at $x=0.3$.[10]

We have recently reported that the irradiation of visible-IR light can also induce the COI-metal (COI-M) transition in $Pr_{0.7}Ca_{0.3}MnO_3$.[11,12] The metallic phase is similar to that observed in the electric-field-induced transition but behaves somewhat differently from those observed under other external stimuli. Most notably, the metallic phase induced by light or voltage is not stable at the removal of the applied potential, even for $x=0.3$ at low temperature. Therefore, a question naturally arises if the state arrived at via the photoinduced transition is a genuine stable state (albeit not a true ''phase'' in the equilibrium thermodynamic sense) rather than a state maintained by other trivial mechanisms, e.g., the Joule heating. In order to answer this question, we studied the stability of the photoinduced conducting state of $Pr_{1-x}Ca_xMnO_3$ ($x=0.31$, 0.35, 0.40, 0.45, and 0.50).

The samples are single crystals of $Pr_{1-x}Ca_xMnO_3$ ($x=0.31$, 0.35, 0.40, 0.45, and 0.50) grown by the floating-zone method. The details of a sample preparation method and chemical analysis were reported in a previous paper.[13] The samples are in the form of disks whose surfaces were mechanically polished to a mirror surface. Au electrodes separated by a 50-μm gap (about 4-mm long) were vacuum

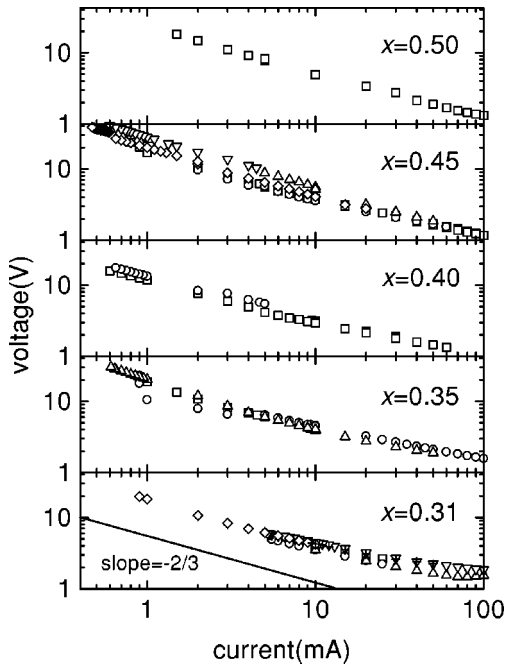

FIG. 1. Relationship between the current and the voltage applied to the sample (I-V curve) after the photoinduced COI-M transitions in $Pr_{1-x}Ca_xMnO_3$ for various x. Relationship $V \sim I^{-2/3}$ seems to hold at low I. The temperature was $T \simeq 10$ K but the I-V curves are insensitive to T.

evaporated onto the surface. The samples were mounted in a continuous-flow type cryostat for maximum heat exchange.

The wavelength of the excitation light was 0.53 μm (the second harmonic of a YAG laser). A constant current power source was used to apply a voltage across the electrodes with a variable load resistor in series. A current source rather than a voltage source was necessitated in order to measure the I-V characteristics under a stable condition in the presence of the negative differential resistance (see Fig. 1 below). The initial insulating state has such a high resistance that the output voltage of the current source was at a limiting value, which was usually set at 120 V. The load resistor protects the sample from the transient overcurrent and suppresses the oscillation of the power supply due to the negative differential resistance of the sample.

The COI-M transition can be induced by light at all composition x. Figure 1 shows the relationship between the current and the voltage applied to the sample (I-V curve) after the photoinduced COI-M transition. The I-V curves of the samples of different x show negative differential resistance and are very similar to each other.[12] At lower current, a relationship $V \sim I^{-2/3}$ seems to hold, but its implication is not clear, although it is certainly related to the filamentary nature of the current path.[12,14] When the total differential resistance (differential resistance of the sample plus the load resistance) becomes negative, the constant current power supply becomes unstable and starts to oscillate as shown in Fig. 2. The frequency of the oscillation is governed not by the material property but by the response time of the power supply. The dynamics of the oscillation is not clear but seems to be much faster than indicated by Fig. 2. At a certain level of instability, the current momentarily becomes zero and the metallic state reverts to the insulating state.

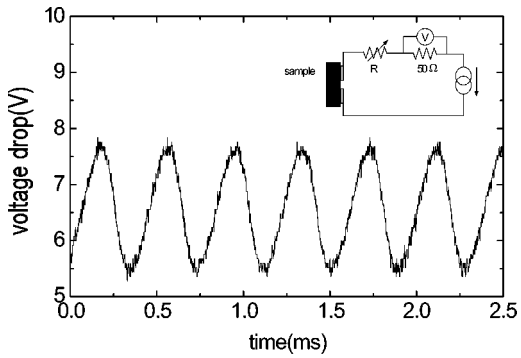

FIG. 2. Current oscillation due to the negative differential resistance for $x = 0.30$ and at $T = 22$ K. The voltage across a reference resistor (50 Ω) is shown. Inset: setup for measurement of the oscillation.

Because of the negative differential resistance, the photoinduced conducting phase was characterized by monitoring the voltage necessary to maintain a certain current as a function of temperature (V-T curve) as depicted in Fig. 3. The current was held at 1 mA, 2 mA, or 5 mA. The temperature was increased after the transition induced at low temperature (around 10 K). The voltage is essentially independent of the temperature up to 60–80 K, while it depends somewhat on the composition (the discontinuity will be discussed below). This strongly suggests that the local heating of the conducting path is not the mechanism for the high conductivity. As

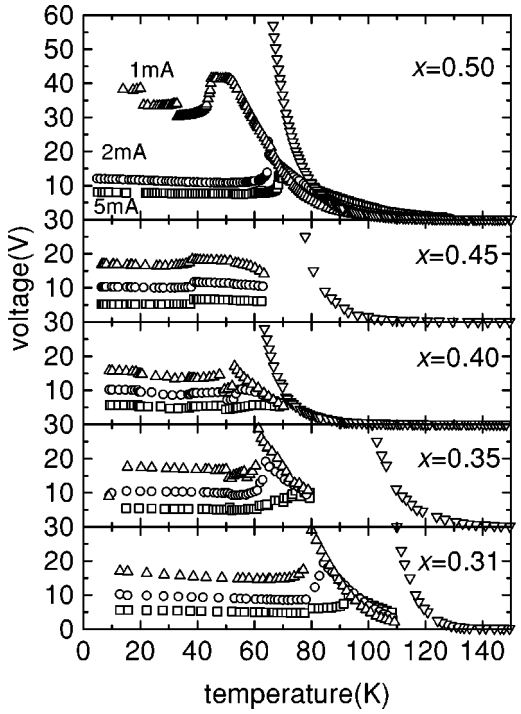

FIG. 3. Temperature dependence of the voltage necessary to maintain a constant current (V-T curve) after the COI-M transition measured on heating. Square, circle, up triangle, and down triangle indicate the voltages for 5, 2, and 1 mA, and the hypothetical voltage curve for 1 mA, respectively. The difference between the hypothetical curve and the measured voltage at 1 mA above the peak is the heating effect. Below the peak, the voltage is almost constant: metallic phase.

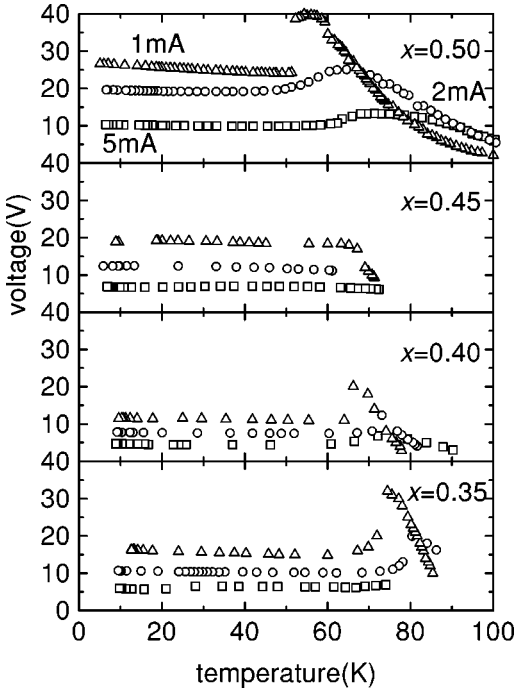

FIG. 4. The V-T curve of the cooling process for $x=0.35$, $x=0.40$, $x=0.45$, and $x=0.50$.

the temperature was further increased, voltage peaks were observed. Above the peak, the sample behaves as a normal resistive material; the differential resistance is positive and the state is reversible after a momentary removal of the applied current, in contrast to the state below the peak. The local heating certainly affects the resistivity above the peak. In Fig. 3, the hypothetical voltage curve for a 1 mA current is also drawn, which we calculated by multiplying 1 mA by the resistance obtained by a standard four-probe method. The difference between this hypothetical curve and the measured voltage at 1 mA above the peak is the heating effect and it is quite significant for $x=0.35$. Note that the peak shifts to higher temperature as the current is increased. There seems to be a common ''phase boundary'' in the I-T plane.

Figure 4 shows the V-T curve in the cooling process. No laser pulse was used in these measurements. There are clear voltage peaks, below which the samples are metallic. This is the voltage-induced insulator-metal (I-M) transition reported earlier.[8] The similarities between Figs. 3 and 4 are striking. We therefore conclude that the low-temperature conductive phases in Figs. 3 and 4 are identical. From Fig. 4 and from the observation that the voltage-induced transition becomes progressively difficult below 60 K, one can imagine that the ''potential barrier'' that separates the COI and FM phases starts to grow around 60–80 K, below which the stability has double minima and above which COI is the only minimum (see Fig. 5 below). One can then suspect that the photoinduced phase transition is in fact nothing but the voltage-induced transition aided by the temperature swing above 60–80 K due to local heating by the laser light. We have already discussed[11] that this is unlikely by showing the temperature independence and photon energy dependence of the transition behavior.

The voltage ''jumps'' occasionally in $x=0.40$, $x=0.45$, and $x=0.50$ in the heating process, whereas no ''jump'' is

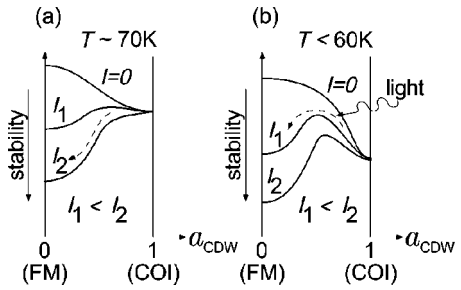

FIG. 5. Schematics of the relative stability between the ferromagnetic metallic state and charge-ordered insulating state. The horizontal axis represents the amplitude of the charge-density wave a_{CDW}. $a_{\mathrm{CDW}}=0$ and 1 correspond to FM and COI, respectively. At around 70 K, (a) potential barrier decreases as the current increases and a current-induced transition (dashed curve) occurs. At a much lower temperature, (b) the barrier can be overcome only with the assistance of the photon energy (dashed curve).

observed in cooling. The voltage jump is accompanied by the shift of the filamentary current path between the electrodes, which is visualized by the reflectance measurement.[14] After the current path is produced in the laser spot, the voltage ''jumps'' apparently when a more stable path is sampled in heating through the increased thermal fluctuation. In the cooling process, however, the path of minimum ''potential'' is always selected.

Because of the robustness of the COI state in the $x=0.50$ sample, the electric-field-induced transition upon cooling does not always occur, although the photoinduced transition is quite reproducible. In such a case, the conducting state maintained by the Joule heating does appear as shown in Fig. 6. As one can expect, there is no peak in the V-T curve and the voltage necessary to maintain a given current is much higher than the case in Fig. 4. It is clear that the smooth and steep negative variation of the voltage as a function of temperature and an order of magnitude larger voltage in Fig. 6 imply that the relatively low resistance (compare with the resistance data obtained by the standard four-probe method: inset) and the negative differential resistance at the low temperature are the result of local heating. Because the time constant for the temperature swing in the

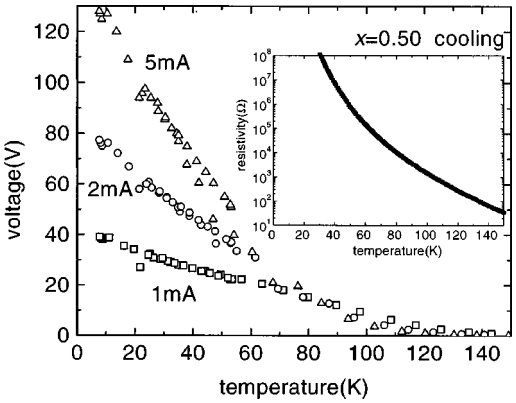

FIG. 6. Another example of the V-T curve of the cooling process in the $x=0.50$ sample. The temperature coefficient is negative in the whole temperature region (compare with Figs. 3 and 4). The conducting state is sustained by the Joule heating in this case. Inset: temperature dependence of resistance of the same sample.

sample is much longer than the speed of the feedback of the constant current source, no instability appeared even if no load resistance was inserted in the circuit. The exact condition for the occurrence or the absence of the electric-field-induced transition is not clear.

The metallic state discussed here is maintained by the current: the delocalizing effects of the injected current is the main mechanism of the destabilization of the COI state. Although a methodology to treat a system under a nonequilibrium but steady condition is well known[15] within linear regime, no theoretical framework exists that allows us to discuss the transition between equilibrium and nonequilibrium states, i.e., between the COI and current-sustained metallic state. Recognizing that the amount of the injected current is a meaningful parameter, we can nonetheless propose a functional form of relative stability as shown in Fig. 5. We chose the amplitude of the strongest Fourier component of the charge density wave (CDW) a_{CDW} to represent the order of the COI state. For example, $a_{\mathrm{CDW}}=\pm 1$ for the fully developed checkerboard pattern[9] of Mn^{3+} and Mn^{4+} in a $x=\frac{1}{2}$ crystal.

Well above 60–80 K but below the paramagnetic insulator to COI transition temperature ($T_{\mathrm{COI}}\sim 240$ K), the COI state is quite stable. Around 60–80 K, the COI state is still absolutely stable at $a_{\mathrm{CDW}}=\pm 1$ when $I=0$ but second minima start to develop at $a_{\mathrm{CDW}}=0$ (FM) for larger I [Fig. 5(a)]. Because of the destructive effect of the current on the COI state, it is expected that FM is more favorable for larger I. This is in good qualitative agreement with Figs. 3 and 4; the larger the current is, the more stable the FM state. The ''potential barrier'' between FM and COI should be minimal since it can be easily overcome with the field of a few hundred kV/m. This is certainly much below the ordinary dielectric breakdown field.

When the temperature gets well below 60 K, the potential should show double minima[13] for $x=0.31$ and $x=0.35$ at $I=0$ and for all concentrations when the current is above $I_{\mathrm{min}}(<1$ mA) [Fig. 5(b)]. Although experimentally not observed, a well-defined I_{min} should exist, at which the fluctuating COI order wins over its destruction rate by the current. The potential barrier between COI and FM is now too high for a static electric field to overcome. The photon energy is thus essential to assist the transition.

We point out in passing that the observed phenomena (current filaments, negative differential resistance, current oscillations, etc.) are familiar in semiconductors in the bulk,[16] film,[17] and heterostructures.[18] Let us note that the mechanisms responsible for the phenomena are, for example, double injection, tunneling, and avalanche effect, which can be understood in terms of a band picture. The effect observed here, on the other hand, is distinct in that the collapse of the charge-ordering energy gap is at work.

In conclusion, we have shown that the COI-M transitions can be induced by light in perovskite manganites, $Pr_{1-x}Ca_xMnO_3$ ($x=0.31$, 0.35, 0.40, 0.45, and 0.50). The induced metallic states of all x, which appear to be metastable, are of the same origin, not sustained by heating caused by current. The potential barrier between the COI state and the metallic state exists, which can be overcome only with the assistance of photon energy in low-temperature region. The photocarrier generation is essential to melt the COI state and to cause the transition.

This work was supported in part by a 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. Suggestions by Dr. T. Mori and Dr. M. Fiebig and the technical assistance of H. Tamaru are appreciated.

[1] Y. Tokura, Y. Tomioka, H. Kuwahara, A. Asamitsu, Y. Moritomo, and M. Kasai, J. Appl. Phys. **79**, 5288 (1996), and references therein.

[2] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).

[3] P. G. de Gennes, Phys. Rev. **118**, 141 (1960).

[4] J. Kanamori, J. Appl. Phys. **31**, 14S (1960).

[5] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).

[6] S. Ishihara, M. Yamanaka, and N. Nagaosa, Phys. Rev. B **56**, 686 (1997).

[7] Y. Moritomo, H. Kuwahara, Y. Tomioka, and Y. Tokura, Phys. Rev. B **55**, 7549 (1997).

[8] A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, Nature (London) **388**, 59 (1997).

[9] V. Kiryukhin, D. Casa, J. P. Hill, B. Keimer, A. Vigliante, Y. Tomioka, and Y. Tokura, Nature (London) **386**, 813 (1997).

[10] M. Tokunaga, N. Miura, Y. Tomioka, and Y. Tokura, Phys. Rev. B **57**, 5259 (1998).

[11] K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **78**, 4257 (1997).

[12] T. Mori, K. Ogawa, K. Yoshida, K. Miyano, Y. Tomioka, and Y. Tokura, J. Phys. Soc. Jpn. **66**, 3570 (1997).

[13] Y. Tomioka, A. Asamitsu, Y. Moriotmo, and Y. Tokura, J. Phys. Soc. Jpn. **64**, 3626 (1995).

[14] M. Fiebig, K. Miyano, Y. Tomioka, and Y. Tokura, Science (to be published).

[15] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1969).

[16] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1969).

[17] D. Adler, H. K. Henisch, and N. Mott, Rev. Mod. Phys. **50**, 209 (1978).

[18] D.-F. Guo, Appl. Phys. Lett. **72**, 1010 (1998).