Bidirectional and persistent photoinduced phase change in manganite thin films

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Abstract. Photoinduced phase change in manganite thin films are described, which are bidirectional between metallic and insulating states and persistent within the laboratory time scale. The phenomena are due to the strong cross-coupling between electronic, magnetic, and elastic interactions. Among them, the elastic part is particularly important to make the process slow and the effect persistent or at least metastable. Observations supporting this view are presented.

1. Introduction
In strongly correlated systems, photoinduced effect is unique in that the energy scale of photons is much larger than other external stimuli typical in solid state science. As a consequence, one can expect emergence of a novel transient phase not found in thermal equilibrium. Another consequence is that a persistent photoinduced phase change is possible even though the initial and final states are separated by an extremely high potential barrier. As a well recognized member of the strongly correlated systems, photoinduced phenomena have been vigorously pursued in manganites among other materials. Although many photoinduced phenomena have been discovered, it seems that the essential aspect has been missed; the photoinduced structural change and the importance of associated elastic energy.

In order to illustrate the point, I chose manganites with the composition Pr_{0.55}(Ca_{1-y}Sr_y)_{0.45}MnO_3 (PCSMO) (y = 0.2, 0.25 and 0.4). They are in the vicinity of a bicritical point, below which two phases separated by a first-order phase transition line are in competition. The transformation between the two can be initiated by various means including photoexcitation [1].

2. Overall phase diagram
The samples were fabricated using the pulsed-laser deposition technique. The characterization of the samples has been described elsewhere [2]. They were deposited on a perovskite (LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7} (011) substrates. The choice of substrates of non-tetragonal symmetry is dictated by the mode of lattice deformation allowed under the substrate constraint that the films are epitaxially and coherently clamped to the substrate [3]. This arrangement is essential to realize films exhibiting a first-order phase transition accompanied by (sometimes large) structural change [4].

The temperature dependence of resistivity under various magnetic fields are shown in figures 1 for y = 0.2, 0.25 and 0.4. The behavior is well explained in terms of the phase diagram schematically shown in figure 2 [5]. The PCSMO’s prepared here are located in the vicinity of a bicritical point. The ordinate of figure 2 is temperature and the abscissa is a parameter that characterizes the itinerancy of electrons, i.e., the one-electron bandwidth, w. At higher temperatures, a paramagnetic insulating (PI)
state is stable. The PI phase is transformed via second-order phase transition (depicted by dashed lines in figure 2) into charge- and orbital-ordered insulating (COOI) state or ferromagnetic metallic (FM) state depending on $w$. The two low temperature phases are symmetrically incompatible and thus are separated by a first-order phase transition (solid line in figure 2).

As the temperature is lowered, the sample $y = 0.2$ undergoes a PI to COOI transition under zero magnetic field as indicated by a vertical arrow in figure 2. In manganites, the increase in the magnetic field is equivalent to the increase in $w$ due to the double exchange interaction. Therefore, the abrupt change in the resistivity from insulating to metallic character around 200 K (figure 1 top panel) signals the lateral shift of the sample in the phase diagram crossing the bicritical point. This process is illustrated by a horizontal arrow in figure 2. Interestingly, the first-order phase boundary is slanted so that the sample $y = 0.25$ crosses it at a very shallow angle as the temperature is lowered in zero magnetic field (figure 1 middle panel). The resulting coexistence (and hysteresis) region (schematically depicted by dotted lines in figure 2) is extremely wide. This feature allows us to observe various nonlinear and persistent phenomena.

It is to be noted in figure 1 that the magnetically induced FM state in $y = 0.2$ sample and magnetically enhanced FM state in $y = 0.25$ sample both show quantitatively similar temperature dependence as that of $y = 0.4$ sample. This proves the assertion above that the effect of the magnetic field is physically equivalent to enlarging the parameter $w$.

3. Photoinduced phase change
A simple way of monitoring the phase change between metallic (M) and insulating (I) states is to measure resistance under photoexcitation. Since the $y = 0.25$ sample shows wide hysteresis in resistivity in warming and cooling scans as shown in figure 1 middle panel, this is an ideal system to study. Indeed, within the hysteresis loop, persistent photoinduced phase changes were found as indicated by dotted arrows in figure 3 [2],[6]. The photoinduced jump from one branch of the hysteresis loop to the other has a critical temperature $T_c$ (ca. 80 K). Below $T_c$, only I to M transition occurs while above $T_c$, only M to I transition occurs. Referring to figure 2, $T_c$ is the temperature at

![Figure 2. Electronic phase diagram of PCSMO samples. Dotted lines indicate the stability limit of the first-order phase transition line (nearly vertical solid line).](image)

![Figure 1. Temperature dependence of resistance under magnetic field.](image)
which the vertical arrow corresponding to \( y = 0.25 \) crosses the solid line. Two temperatures indicated by \( T^\uparrow \) and \( T^\downarrow \) in figure 3 are the stability boundary temperatures depicted by dotted lines in figure 2.

The driving mechanism of the photoinduced phase change is electronic rather than heating. This is shown in figure 4, in which the action spectra are shown. Here, the minimum power density required for the photoinduced phase change is plotted as a function of the photon energy. The spectrum for the I-M transition appears to be related to the charge transfer (CT) excitation in the COOI state. Because the CT excited state should be electronically much more extended, the transition from metastable I phase to stable M phase is quite natural. Note that the absorption spectrum has much less photon energy dependence compared to the cutoff around 0.5 eV shown in figure 4: thus the sample heating is not likely to be the cause of the transition.

On the other hand, the action spectrum for the M-I transition is not obvious. Being in the metallic state, the absorption extends to low energy, which has no obvious relationship with figure 4. Furthermore making the electrons in the M state more extended would not lead to the I state. One possible mechanism is the destruction of the magnetic order by photoexcitation: photons with enough energy to flip the spins are required. At this moment, it is only hypothesis but it should be pointed out that irradiation with laser pulses just below \( T_c \) does not lead to the M-I transition despite the inevitable heating of the sample should not depend so critically on whether above or below \( T_c \). In fact, it creates more metallic state than the initial state below \( T_c \). This was confirmed by transport and spectroscopic measurements.

Of course, the heating effect of light is significant. One can easily bring the M phase below \( T_c \) to I phase by a cw laser illumination. In this case, the resistance trace clearly shows that the sample follows the heating (lower) branch of the hysteresis curve. Under pulsed excitation on the other hand, the transient resistance goes even above the maximum of the heating branch of the hysteresis loop without reaching the stable I state. It is likely that the transient highly insulating state differs from the states that appear in thermal equilibrium. The responses to the cw and pulsed excitations are thus completely different.

Although the non-thermal nature of the photoinduced transition is obvious, the physical basis is not clear. It is established from ultrafast pump and probe experiments that the electrons and lattice thermalize in less than a ps \([7]\). Even long-range magnetic order reaches thermal equilibrium much faster than a ns. Therefore within the 5 ns light pulse used here, the system must be in thermal equilibrium. However this conclusion is inconsistent with the observation described above. One way out of the puzzle is to assume an extremely slow process with fairly large energy scale. Coherent lattice motion is a possibility. Because the associated elastic energy is long range, the response can be slow and cost high energy, and hence the two phase competing state can be very stable. A few observations are listed here to backup this view.
1. A sub ps (~ 150 fs, 1.55 eV) light pulse can cause the transition just as the ns pulse. Therefore, the light simply acts as a trigger. Provided that the light pulse does not leave the sample in the excessively heated state long after the excitation, the instantaneous power density seems to be the relevant parameter.

2. The response of the sample after the light pulse is gone can be rather slow. The dashed arrows in figure 3 indicate the resistance history after photoexcitation that was traced with the oscilloscope. Because of the relatively high resistance of the sample, the time scale that can be followed with an oscilloscope is only tens of microseconds. Involvement of macroscopic deformation is suspected after the impulsive excitation. In fact, a time resolved x-ray structural study in another manganite film revealed a new structure with long-range order but without any corresponding phase in thermal equilibrium lasting at least ns [8]. A macroscopic structural competition is a possible cause.

3. Two distinct structures were found in the ground state of the $y = 0.25$ sample in zero magnetic field [9]. The M and I phases coexist at low temperatures and the coexistence is very robust.

4. Conclusions
Features not discussed extensively in the literature, i.e., the slow and persistent (but not thermal) photoresponse of manganites, are described. Elastic energy is pointed out as an important element that can have response much slower than the electronic or magnetic degrees of freedom. Because of the intimate coupling between all physical parameters, a description that the elastic energy determines the electronic state or vice versa may not be fruitful [10], of course. However, the frozen-in structures that are incompatible and competing each other seem essential to realize robust metastable state separated from the homogeneous true stable state with a large potential barrier that can only be overcome with photon energy quanta.

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References
[1] For a general review of photinduced phase transition in manganites, see for example, Tokura Y 2006 J. Phys. Soc. Jpn. 75 011101
[2] Takubo N, Ogimoto Y, Nakamura M, Tamaru H, Izumi M and Miyano K 2005 Phys. Rev. Lett. 95 017404
[3] Nakamura M, Ogimoto Y, Tamaru H, Izumi M and Miyano K 2005 Appl. Phys. Lett. 86 182504
[4] Wakabayashi Y, Bizen D, Kubo Y, Nakao H, Murakami Y, Nakamura M, Ogimoto Y, Miyano K and Sawa H 2008 J. Phys. Soc. Jpn. 77 014712
[5] Tomioka Y and Tokura Y 2002 Phys. Rev. B 60 104416
[6] Takubo N, Onishi I, Takubo K, Mizokawa T and Miyano K 2008 Phys. Rev. Lett. 101 177403
[7] See for example, Beaurepaire E, Merle J-C, Daunois A and Bigot J-Y 1996 Phys. Rev. Lett. 76 4250
[8] Koshihara S – unpublished data
[9] Wakabayashi Y – private communications
[10] Uozu Y, Wakabayashi Y, Ogimoto Y, Takubo N, Tamaru H, Nagaosa N and Miyano K 2006 Phys. Rev. Lett. 97 037202