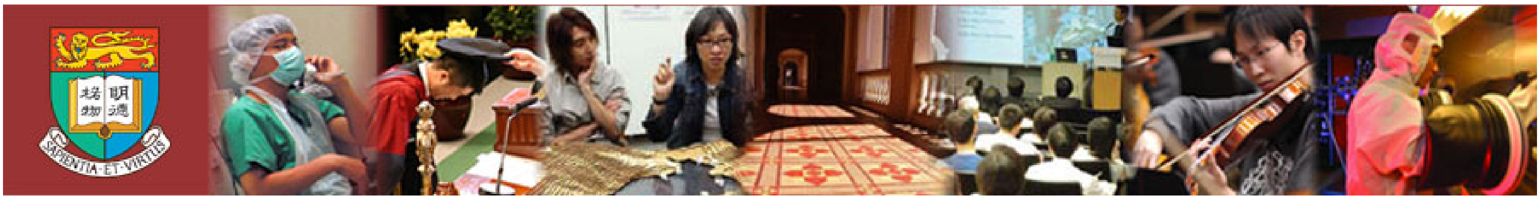

Title	**Current-induced metastable resistive state in epitaxial thin films of La1-xCaxMnO3 (x=0.2, 0.3)**
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Current-induced metastable resistive state in epitaxial thin films of $La_{1-x}Ca_xMnO_3$ $(x=0.2, 0.3)$

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The influence of a transport dc current on electric resistivity has been investigated in epitaxial thin films of $La_{1-x}Ca_xMnO_3$ $(x=0.2, 0.3)$. A most prominent finding is the appearance of a remarkable resistive peak at temperatures well below the Curie temperature T_c. Such a resistive peak is developed when the dc current over a critical value was applied in a temperature cycling from 300 to 10 K. The resistance peak turns out to be extremely sensitive to a weak current. Even a very small current could greatly depress the height of the peak. Such a current-induced state with high resistivity is metastable compared to the pristine state. The stability of the induced state has been also studied. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1870128]

The phenomena of colossal magnetoresistance (CMR) in mixed-valent manganites have attracted considerable attention in recent years due to the related physics and potential applications. Phase separation together with concomitant percolation conductivity is an intrinsic feature of the mixed-valent systems and it may even lie at the very core of the CMR.[1–3] Recently, along with numerous publications on CMR, several reports on the effects of colossal electroresistance (CER) in mixed-valent manganites have appeared.[4,5] The majority of studies of CER effects were performed mainly using charge-ordered samples involving current injection into highly conducting filamentary paths.[4] An applied current bias could lead to a transition from the electrically insulating charge-ordered state to a ferromagnetic metallic state. The effects of an electric-field in heterogeneous-doped manganites have also been studied.[5] An electric field influences CMR in $La_{0.7}Ca_{0.3}MnO_3$/normal-metal heterostructures through the field-stimulated injection of polarized spins. Current induced metastable resistive states have been also reported in single crystals of manganites.[6,7]

Recently we reported a giant ER near the T_c in epitaxial thin films of $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.85}Ba_{0.15}MnO_3$.[8] Further studies on the influence of electric currents on the transport of the mixed-valent manganites revealed that a current with a high density can significantly affect the balance of multiphase coexistence and cause a series of changes of transport properties.[9] In this letter, we report metastable resistive states introduced by a large current in $La_{1-x}Ca_xMnO_3$ (LCMO) epitaxial thin films. A remarkably high resistive peak is induced at a low temperature. Such a resistance peak is found extremely sensitive to the applied current. A weak current flow (<50 μA) can strongly depress this resistance peak. Similar observations were repeated on at least three films for each composition, demonstrating that should be a well repeatable effect.

The present $La_{1-x}Ca_xMnO_3$ $(x=0.2, 0.3)$ thin films, with thickness ~80, 110 nm, respectively, were grown on $SrTiO_3$ substrates. The details of film preparation and characterization can be found in our previous report.[8] In order to apply a current with high density, the films were patterned into a micro-bridge of 0.05 mm in width and 0.2 mm in length.

The temperature dependent magnetization under a magnetic field of 100 Oe reveals that the Curie temperature T_c of present $La_{1-x}Ca_xMnO_3$ $(x=0.2, 0.3)$ thin films is at 272 and 273 K, respectively. We found that the T_c slightly fluctuates from sample to sample and also weakly depends on thickness. The present two compositions with different thickness happen showing a similar T_c. For $La_{0.7}Ca_{0.3}MnO_3$, the T_c is comparable to that of its bulk, but for the $La_{0.8}Ca_{0.2}MnO_3$, the T_c is much higher than that of the bulk material (~190 K).[10] Such a phenomenon is consistent with a previous report,[11] in which one found that the unit cell volume of $La_{0.8}Ca_{0.2}MnO_3$ film is much smaller than that of its bulk. It was suggested that the reduction in the unit cell volume due to strain effect would enhance the transfer integral of electron hopping between Mn^{3+} and Mn^{4+} and thus T_c.[11] Shown in Figs. 1(a) and 1(b) are the temperature dependent resistance of $La_{1-x}Ca_xMnO_3$ $(x=0.2, 0.3)$ films measured using different currents from 0.01 to 5.1 mA for $x=0.2$ film, and from 0.01 to 10.1 mA for $x=0.3$ case. All measurements were carried out in cooling process with the same rate ~3 K/min. A striking observation is the significant decrease of the peak resistance (R_p) as the current increases. Our previous report on $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.85}Ba_{0.15}MnO_3$ thin films also revealed a similar behavior.[8] The widening of the resistance peak with the increase of current recorded in the cooling process is associated with self-heating effect.[9]

Apart from the main transitions at T_c a small jump of resistance occurrs with increasing current flow for both $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ films (see Fig. 1). We cannot give a clear explanation for such a feature at this moment. An interesting phenomenon we found, for both $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ films, is the existence of a critical value of the applied current. As can be seen from Figs. 1(a) and 1(b), when the initially applied current is lower than 3.6 mA for the $La_{0.8}Ca_{0.2}MnO_3$ film or 8.2 mA for the film of $La_{0.7}Ca_{0.3}MnO_3$, the residual resistance and the *R-T* curves re-measured under 0.01 mA remain unchanged. However, as long as the applied current exceeds 3.6 mA for $x=0.2$ film or 8.2 mA for $x=0.3$ film the residual resistance abruptly increases, and simultaneously the *R-T* curves re-measured using a small current (~0.01 mA) show a quite different behavior comparing with the initial case.

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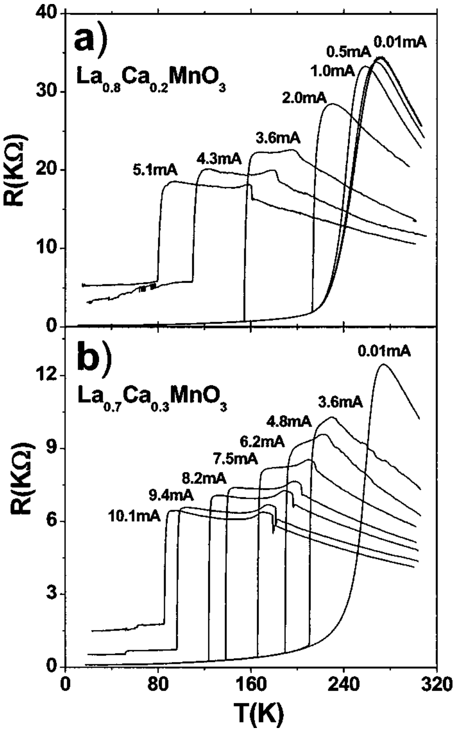

FIG. 1. The R-T dependences for as-prepared $La_{1-x}Ca_xMO_3$ thin films with different currents measured in cooling process. (a) $x=0.2$ film. (b) $x=0.3$ film.

Figures 2(a) and 2(b) present the re-measured R-T curves in both cooling and warming process using a small dc current of $I=0.01$ mA, which was applied along the same direction as that of the exciting current, after different R-T measurements for $x=0.2$ and $x=0.3$ films. The currents were applied in a sequence of 0.05, 1, 2, 3.6, 4.3, 5.1 mA for $x=0.2$ film and 3.6, 4.8, 6.2, 7.5, 8.2, 9.4, 10.1 mA for $x=0.3$ film. All the R-T curves are found almost reversible in the temperature cycles. The state developing for both $x=0.2$ and $x=0.3$ films with the increase of applied current is clearly manifested. When the applied current exceeds a critical value (about 3.6 mA for $x=0.2$ film and 8.2 mA for $x=0.3$ film), an additional peak at low temperature T_L is developed with the resistance peak at T_c remaining. With increasing current from 4.3 to 5.1 mA for the $La_{0.8}Ca_{0.2}MnO_3$ or from 9.4 to 10.1 mA for the case $La_{0.7}Ca_{0.3}MnO_3$, the additional peak at T_L increases significantly and the residual resistance abruptly increases while the peak at T_c still keeps unchanged. It is worthy to point out that for both films all re-measured R-T curves using 0.01 mA after different large current treatments are fully repeatable. We made the measurements using the same current of 0.01 mA for many times. All results coincide very well.

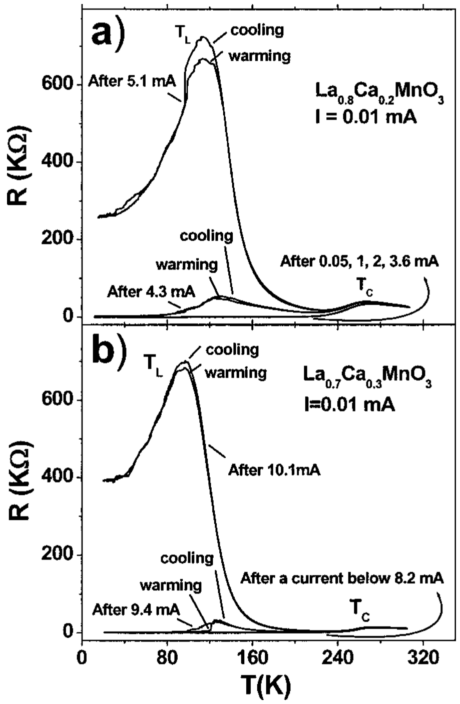

FIG. 2. The re-measured R-T curves for $La_{1-x}Ca_xMO_3$ thin films in cooling and warming process using a same small current of $I=0.01$ mA after different R-T curve measurements. (a) $x=0.2$ film, current application in a sequence of 0.05, 1, 2, 3.6, 4.3, and 5.1 mA. (b) $x=0.3$ film, current application in a sequence of 0.01, 4.8, 6.2, 7.5, 8.2, 9.4, 10.1 mA.

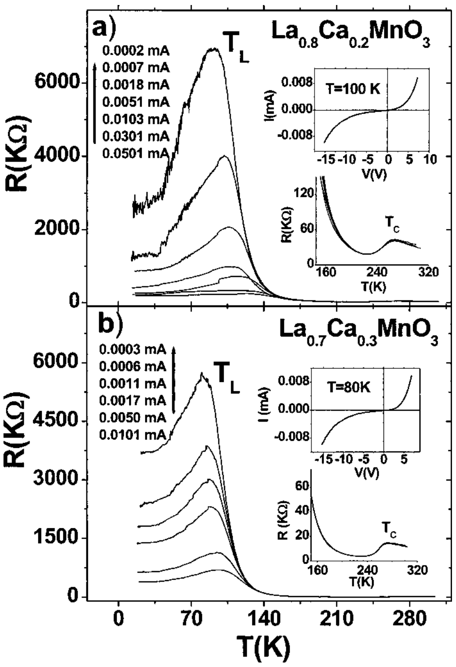

FIG. 3. The R-T dependences of $La_{1-x}Ca_xMO_3$ thin films with different small currents for the state induced (a) by 5.1 mA in $x=0.2$ film, (b) by 10.1 mA in $x=0.3$ film. Upper inset of (a) and upper inset of (b) show the I-V curve at T_L for the corresponding films. Lower inset of (a) and lower inset of (b) plot the details of the peak at T_c under different small currents for the corresponding films.

The most intriguing feature for both $x=0.2$ and $x=0.3$ films is that such an induced resistance peak at T_L is found extremely sensitive to an applied current while the resistance peak at T_c keeps insensitive to small currents. Figures 3(a) and 3(b) display the R-T curves measured on cooling using small dc currents for the states induced by 5.1 mA in the $La_{0.8}Ca_{0.2}MnO_3$ film and 10.1 mA for $La_{0.7}Ca_{0.3}MnO_3$, respectively. The dc currents were applied along the same direction as that of the exciting current for the both cases. One can find that even a rather weak current can strongly influence the magnitude of the resistance peak at T_L but does not affect the peak at T_c. The details of the peak at T_c under different weak currents were plotted in the lower inset of Figs. 3(a) and 3(b). For the $x=0.2$ film, the relative reduction of the resistance peak ($R_{\text{small-current}}$-$R_{\text{big-current}}/R_{\text{big-current}}$) at T_L reaches ~3100% upon current changing from 0.0002 mA

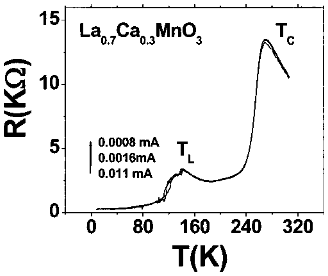

FIG. 4. The *R*-*T* dependences for a $La_{0.7}Ca_{0.3}MO_3$ thin film with different currents of 0.0008, 0.0015, and 0.011 mA after bipolar sweeping a small current of 0.01 mA for 20 cycles.

(the lowest limit our current source can reach) to 0.05 mA. Similarly, for the $x=0.3$ case, the relative reduction of the resistance peak reaches ~750% upon current changing from 0.0003 to 0.01 mA. Interestingly, the isothermal current-voltage (*I*-*V*) curves measured near T_L show asymmetric non-ohmic behavior for the new states in both $x=0.2$ and $x=0.3$ films, as shown in the upper inset of Figs. 3(a) and 3(b).

To study the stability of the resistive states induced by currents, the samples were stored in air at room temperature for several weeks and then repeated the measurements. No changes of the transport properties could be found. On the other hand, perturbations, such as bipolar sweeping a small current alternatively along positive and negative directions, can make these resistive states collapse. Figure 4 displays *R*-*T* curves of $x=0.3$ film measured on cooling using different small dc currents after sweeping a small current of 0.01 mA in this manner for 20 cycles. It is found that the peak value at T_L becomes much smaller compared to that observed in the fresh state created by 10.1 mA and, importantly, it is no longer sensitive to a small current. Furthermore, we found that an application of a suitable large dc current can occasionally eliminate the induced resistive state. However, our repeated measurements indicate that bipolar sweeping a small current alternatively along positive and negative directions for numerous cycles could definitely erase the induced resistive state. Such observations also indirectly confirmed that the possible loss of oxygen due to self-heating cannot be the origin for the induced resistive state. Very recently, Markovich[7] *et al.* reported the electric-field/current-induced metastability in $La_{0.8}Ca_{0.2}MnO_3$ single crystal. It was found that an application of current pulses at low temperatures could lead to appearance of the states with high resistance. Similar to the behaviors observed in the present films, the freshly established state also exhibits strong instabilities. Sometimes it may even spontaneously return to a pristine state. It seems that the current-induced metastable state with high resistance is a universal phenomenon at least in LaCaMnO systems.

It is clear that the induced resistive peak at low temperatures, in the present films, cannot be attributed to the self-magnetic field due to the applied current. Assuming the film is an infinite uniform plane, the self-magnetic field produced by an applied current with a density similar to the present exciting currents is $\sim 10^{-4}$ T only. Phase separation should be a key element for understanding the experimental observations. It has been a well established fact that metallic and insulating phases coexist in a broad range of phase space even for $La_{1-x}Ca_xMnO_3$.[2,5] It has been observed that two ferromagnetic (FM) phases with distinct orbital order (OO) and different conductivity co-exist in a wide temperature range in $La_{1-x}Ca_xMnO_3$, especially for the low-doped samples.[10] In one phase an antiferrodistorsive-type OO is favored by FM superexchange interactions, behaving insulating characteristics, while in another phase the ferrodistorsive-type OO promote double exchange interactions, exhibiting metal behavior.[11] It was experimentally found that an electric field could directly affect the directional order of orbitals and thus alter the magnetic and conducting states.[12] When the applied current is high enough, the associated electric field distributed in the phase space may strongly impact the orbital order of the phases and enforce a thorough change in the topology of the phase coexistence. Eventually a new state with new coexistence of the phases may appear.

The induced resistive state behaves more sensitive to the external perturbations compared to the as-prepared state. A small current could strongly influence the formed coexistent multiphase, leading to a colossal ER. The non-ohmic and the negative differential resistance behaviors are also consistent with that observed in the typical charge or orbitally ordered state.[4] Sweeping a small current alternatively along positive and negative directions could erase the resistive state. This fact implies that an asymmetric barrier, likely the depletion region in *p*-*n* junctions, might remain in the phase space, which is interdependent to the new coexistance of the phases. When a considerable electric field was repeatedly applied in a reverse direction, the asymmetric barrier can be removed, like the breakdown behavior in *p*-*n* junctions. Simultaneously, the interdependent multiphase coexistence in the freshly created states would collapse, the *I*-*V* curves become linear and symmetric, and the enhanced resistance at T_L nearly disappears. To well understand the nature and modulation process of the large current on the coexistent multiphase, more detailed studies are still needed.

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