Photoinduced spin-state transition of $Co^{3+}$ in the layered perovskite manganite thin film



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# Photoinduced spin-state transition of $Co^{3+}$ in the layered perovskite manganite thin film

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**Abstract**

The photoinduced effect, at different temperatures, on layered perovskite manganite $La_{1.2}Sr_{1.8}Mn_{1.8}Co_{0.2}O_7$ thin film deposited on a $SrTiO_3(100)$ substrate has been studied using a He–Ne laser (632.8 nm) with the power of output 25 mW at low temperatures. The electrical transport and magnetic properties of the film are investigated systematically in the temperature region from 20 to 300 K. The resistance shows a significant decrease at low temperatures ($T < 90$ K) under laser irradiation, which can be interpreted in terms of the spin-state transition of $Co^{3+}$ ions. The magnetic field combined with the laser is also used to detect the photoinduced effect of the spin-glass state. The time dependence of the metastable system under several applied fields was also discussed. The system has the ability to keep a persistent memory of the magnetic history imprinted in its zero-field resistance.

## 1. Introduction

Recently, both electronic states and transport properties of perovskite manganites with the general formula $A_{1-x}B_xMnO_3$ (where A and B are trivalent and divalent, respectively) have been extensively studied to elucidate the unusual transport behaviours. One of the attractive phenomena is the metal–insulator transition (MIT) which can be induced by varying the temperature [1], pressure [2], oxygen isotope [3], electric field [4] and magnetic field [1, 5]. As is well known, photoirradiation (also called photodoping) is an important method for investigating the electronic states and transport properties of the perovskite manganites. The MIT induced by x-ray [6] and pulsed laser irradiation [7] for $Pr_{0.7}Ca_{0.3}MnO_3$ at low temperatures has been reported on. It is also observed that an x-ray induced structural transition occurs in $La_{0.875}Sr_{0.125}MnO_3$ crystal [8]. Conductive and resistive transients in $La_{0.7}Ca_{0.3}MnO_3$ film

  

induced by a 1.5 eV pulsed laser have been reported by Zhao *et al* [9]. Compared with the case for the manganites $A_{1-x}B_xMnO_3$, little attention is paid to the layered perovskite manganites $A_{n-nx}B_{1+nx}Mn_nO_{3n+1}$, which also exhibit the CMR effect [10]. At $n = 2$ the $MnO_2$ sheets are separated by rock-salt layers and the $MnO_6$ octahedra form a two-dimensional (2D) network, in which the dimension is decreased. The $n = 2$ compound ($La_{1.2}Sr_{1.8}Mn_2O_7$, $x = 0.4$) shows a MIT accompanying a large magnetoresistance (MR) [11]. To the best of our knowledge, no photodoping study on layered perovskite manganites has been reported so far. On the other hand, the understanding of the spin-state transition of $Co^{3+}$ ions is one of the most important subjects in the investigation of the cobalt-series material, and a lot of work has been focused on it [12–14]. In this paper, we report on the effect of photodoping on the transport properties and the spin-state transition of $Co^{3+}$ in layered perovskite manganite $La_{1.2}Sr_{1.8}Mn_{1.8}Co_{0.2}O_7$ thin film. The results obtained will undoubtedly be beneficial not only to the understanding of the physical mechanism of transport properties but also in the future applications of these CMR materials such as in optical switching and magnetic recording devices.

## 2. Experiment

The thin film of $La_{1.2}Sr_{1.8}Mn_{1.8}Co_{0.2}O_7$ (LSMCO) used in this experiment was grown on a heated $SrTiO_3(100)$ substrate by the off-axis dc magnetron sputtering technique with the substrate temperature of 650 °C. In order to compensate for the oxygen deficiency and improve the properties, the thin film was annealed in 1 atm oxygen at 750 °C for 2 h. The structure and phase purity of the film were checked by means of x-ray diffraction using Cu K$\alpha$ radiation at room temperature. The temperature dependence and time dependence of the resistance of the film under zero and an applied field were measured by a standard four-probe method in the temperature range from 20 to 300 K obtained by means of cryogenic refrigeration equipment. The temperature dependence of the magnetization was measured by a commercial superconducting quantum interference device (SQUID) magnetometer. The sample was mounted in a vacuum room that was sealed by a double quartz glass window. A He–Ne laser with wavelength $\lambda = 632.8$ nm was used to illuminate the sample perpendicularly through the window. The laser power was about 25 mW.

## 3. Results

The XRD study indicated that the crystal structure of the bulk sample is of single phase with the $Sr_3Ti_2O_7$-type tetragonal perovskite structure, having the lattice parameters $a_0 = 0.386$ nm $c_0 = 1.99$ nm. The x-ray diffraction pattern of the film indicates that the film has no extra second phases and grows along the ($h$00) direction. The rocking curve of the (200) diffraction peak with the value of full width at half-maximum (FWHM) of 0.46° reveals an excellent structural order. The lattice parameter $a_0$ for the film is 0.384 nm which is close to the value for the bulk sample that we used for the sputtering target.

The temperature dependence of the resistance $R(T)$ under zero and an applied field of 0.34 T is shown in figure 1. The inset of figure 1 shows the temperature dependence of the magnetization. Except for the MIT at a temperature of about 143 K (defined from $dR/dT = 0$ for the $R(T)$ curve), the most remarkable feature in the $R(T)$ curve is an upward 'tail' at low temperature, below 88 K. That is to say, the sample shows another MIT transition at 88 K. We think that one of the reasons for this low temperature MIT is closely related to the spin-state transition of $Co^{3+}$ ions from the high spin state (HS state, $t_{2g}^4e_g^2$) or intermediate spin state (IS state, $t_{2g}^5e_g^1$) to the low spin state (LS state, $t_{2g}^6e_g^0$) which results in a decrease in number of the $e_g$ electrons and an increase of the resistance. As is well known, the Co

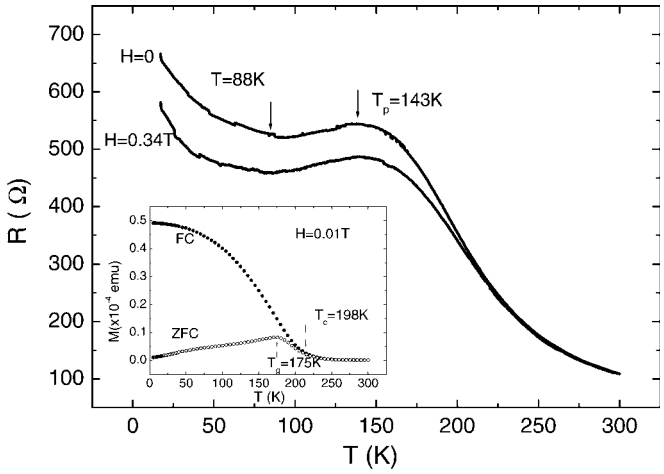


**Figure 1.** The temperature dependence of the resistance for $La_{1.2}Sr_{1.8}Mn_{1.8}Co_{0.2}O_7$ film under zero (curve 1) and an applied field of 0.34 T (curve 2); the inset shows the temperature dependence of the magnetization for the film in zero-field cooling (ZFC) and field cooling (FC) modes at $H = 0.01$ T.

ions lie in the LS state at low temperature. Another possible reason for this low temperature MIT is the localization of $e_g$ electrons occurring because of the substitution of $Co^{3+}$ ions for $Mn^{3+}$ ions. The substitution of $Co^{3+}$ ions for $Mn^{3+}$ ions may cause competition between $Co^{3+}$–O–$Mn^{4+}$ exchange and $Mn^{3+}$–O–$Mn^{4+}$ double exchange, which results in the formation of a cluster glass (CG) when the cluster moments are randomly frozen [15]. The CG state is observed from the little bump at 175 K in the zero-field cooling (ZFC) $M(T)$ curve. But the upturn of the $R(T)$ curve does not appear immediately accompanying the formation of the CG state. We attribute this disagreement to the following: in the temperature region from 143 to 88 K, the $Mn^{3+}$–O–$Mn^{4+}$ double exchange dominates although a competition between $Co^{3+}$–O–$Mn^{4+}$ superexchange and $Mn^{3+}$–O–$Mn^{4+}$ double exchange exists, which keeps the system metallic. But for temperature below 88 K, the spin-state transition of $Co^{3+}$ combined with the localization of $e_g$ electrons results in an increase of resistance causing a MIT at low temperature. In addition, the disagreement between the MIT temperature ($T_p = 143$ K) and the Curie temperature $T_c = 198$ K (defined from the extremum of the $dM/dT$ curve) reflects the anisotropy of magnetic and electrical transport features of the layered perovskite manganite, which is consistent with previous reports [16].

The persistent photoconductivity (PPC) effect (resistivity change induced by laser illumination cannot be recovered by switching off the laser) in the CG state of the $ABO_3$ system has been reported in our previous work [17]. To investigate the influence of laser illumination on the spin state of $Co^{3+}$ ions and the CG state in such a layered perovskite manganite (327 system) and also to compare with the photoinduced results observed for cubic perovskite manganite, the film is illuminated using the same He–Ne laser with wavelength $\lambda = 632.8$ nm throughout the whole experiment. The time dependence of the resistance at different constant temperatures ($T = 30$, 50, 60, 80, 90 and 100 K), with the laser turning on and off every 5 min, is shown in figure 2. The resistance decreased when the laser was turned on from 30 to 80 K (at $T = 30$ K, the resistance decreased by about 10 Ω as the film was illuminated for 5 min) and it did not return to the previous value but recovered partly upon stopping the illumination. The sudden decrease of $R$ under illumination can be attributed to

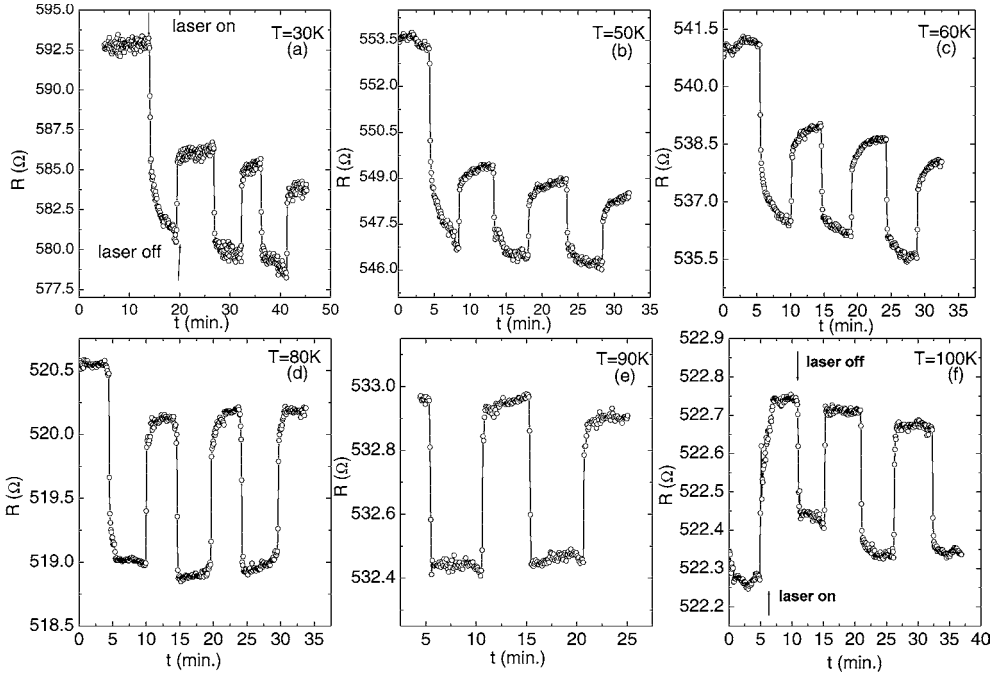


**Figure 2.** The time dependence of the resistance for $La_{1.2}Sr_{1.8}Mn_{1.8}Co_{0.2}O_7$ film at different constant temperatures ($T = 30, 50, 60, 80, 90$ and 100 K) with the laser turned on and off every 5 min.

two independent mechanisms. One originates from the heat effect of the sample ($dR/dT < 0$) and the other comes from the spin-state transition of $Co^{3+}$ ions from the LS to the HS (or IS) state under laser illumination. However, the heat effect disappears when the laser is turned off and the transformed spin state keeps a memory of the history, which makes $R$ not return to the value from before illumination until $T = 80$ K, as shown in figures 2(a)–(d). When $T = 90$ K, we have a different case from that for $T \leqslant 80$ K; e.g. the resistance decreases under illumination and returns exactly to the value from before illumination when the laser is switched off, as shown in figure 2(e). When $T > 90$ K, the resistance increases under laser radiation, as shown in figure 2(f), which only results from the heat effect due to the laser irradiation in the temperature region of $T > 90$ K where $dR/dT > 0$. In order to get a better description of this behaviour, $R(T)$ curves are measured with real time illumination, i.e., keeping up illumination during the process of measuring $R(T)$, and no real time illumination, i.e., illuminating for a period of time at low temperature in advance and stopping illumination during the process of measuring $R(T)$. Figure 3(a) shows the $R(T)$ curves with real time illumination, denoted as curve 2, and without illumination, denoted as curve 1. Figure 3(b) shows the $R(T)$ curves with illumination for one hour at 20 K then stopping illumination (i.e., no real time illumination, denoted as curve 2, and without illumination, denoted as curve 1). Both figures 3(a) and (b) indicate that resistance values after real time illumination and with no real time illumination are lower than those obtained without laser illumination in the temperature region below 88 K, which shows that the variation of the photoinduced resistance includes the intrinsic properties of the sample under the action of a laser except for the heat effect produced by laser illumination. In addition, figure 3 displays that $R(T)$ curves with and without illumination are well superposed above 88 K. This temperature is in accordance with that of the appearance

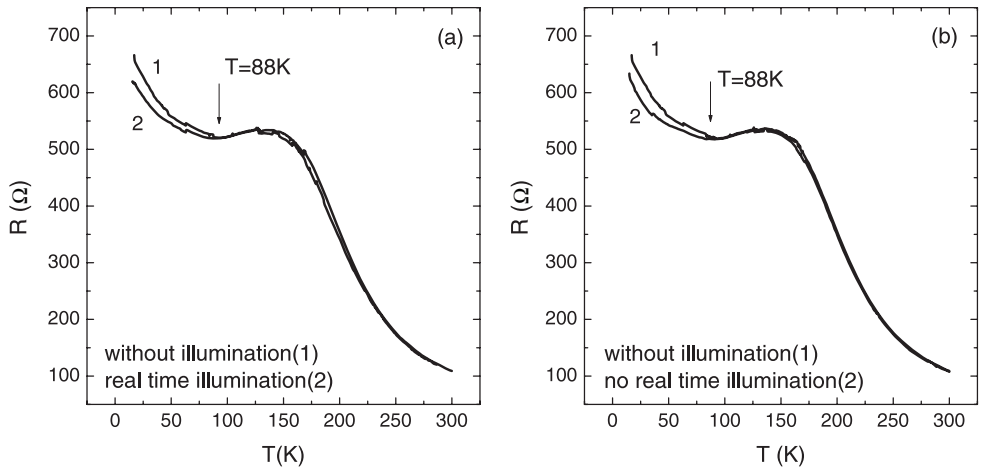


**Figure 3.** (a) The temperature dependence of the resistance for $La_{1.2}Sr_{1.8}Mn_{1.8}Co_{0.2}O_7$ film with real time illumination (curve 2) and without illumination (curve 1); (b) the temperature dependence of the resistance with no real time illumination (curve 2) and without illumination (curve 1).

of the spin-state transition, as shown in figure 2. Therefore, it is concluded that the laser illumination produces both a heat effect and a spin-state transition effect at low temperatures, below 88 K, and only produces a heat effect when $T$ is above 88 K.

As is well known, the glassy system usually shows metastable state properties which are comparable to those of the phase separation (PS) manganites [18] and the competition between the coexisting phases gives rise to interesting time dependent effects such as the dynamical effect and the persistent memory effect [19]. To study the behaviour of the glassy state under the action of applied fields, the resistance as a function of time is measured upon the application of several $H$ values from $H = 0.1$ to 0.34 T at $T = 50$ K, as shown in figure 4(a). This shows that $R$ jumps as the field is applied and removed due to the MR effect mentioned in relation to figure 2. It is worth noting that $R$ (after removal of $H$) does not return to the value before the application of $H$ for $H$ less than 0.3 T. The hysteretic behaviour of $R$ in the low magnetic field after application and removal of $H$ indicates that the system is able to keep a memory of the magnetic history imprinted in its zero-field resistance [19]. This persistent resistance value observed after $H$ is removed indicates that, in the metastable state, the ferromagnetic (FM) phase may be growing against the non-FM phase under the low field. But upon increasing the magnetic field to $H = 0.3$ T, little hysteretic behaviour is observed and $R$ returns to its previous value after the field is removed. This implies that the metastable system could approach its equilibrium state under the assistance of an external $H$ less than 0.3 T. Figure 4(b) shows the photoinduced effect under an applied field and the inset of figure 4(b) shows the relaxation of $R$ at $T = 50$ K measured after the field is removed. The magnetic field has little influence on the photoinduced effect, indicating that these two factors are independent. As the system under 0.34 T is in the equilibrium state, decrease of $R$ under laser illumination is impossible due to the photoinduced growth of a CG or the reformation of a CG. From the comparison of figure 4 with figure 2(b), we can see that the decreases in value of $R$ under laser illumination at zero field and $H = 0.34$ T are the same. This indicates that, no matter whether the system is in equilibrium or not, the photoinduced effect is the same. Therefore, this confirms our conclusion that there only exists a photoinduced spin-state transition of $Co^{3+}$ from the LS to the HS or IS state due to the photoexcitation. Furthermore, no resistance relaxation is observed at $T = 50$ K after $H$ is removed, which also confirms that the system can keep the equilibrium state for a long time.

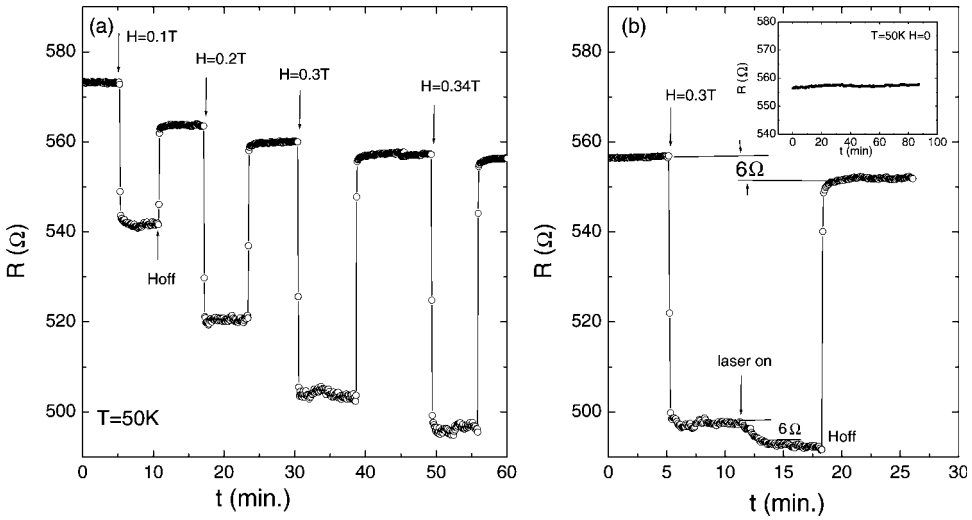


**Figure 4.** (a) Resistance at $T = 50$ K as a function of time for $La_{1.2}Sr_{1.8}Mn_{1.8}Co_{0.2}O_7$ film upon application of $H = 0.1, 0.2, 0.3$ and 0.34 T. (b) The time dependence of the resistance in $H = 0.34$ T combined with laser illumination. The inset in (b) shows the relaxation of the resistance at $T = 50$ K after the magnetic field was removed.

## 4. Discussion

The energy required for exciting the spin-state transition of $Co^{3+}$ from the LS state to the HS or IS state can be calculated according to the electron configuration and the energies of the different orbitals of each state of $Co^{3+}$ [20]. If the spin flip is not considered here, the required energy is 0.65 eV for the LS–IS transition and 2.3 eV for the LS–HS transition. However, the energy of a laser photon equals $h\nu = 1.96$ eV which lies just in between the above two energy values. Hence, it is possible for a laser photon to excite one or two electrons from the $t_{2g}$ orbital to the $e_g$ orbital which makes a $Co^{3+}$ LS state transform into a $Co^{3+}$ IS or HS state. Such a transition increases the number of mobile $e_g$ electrons, which results in the decrease of the resistance under laser illumination. Furthermore, the decrease in the value of $R$ under illumination is independent of the strength of the laser (not shown here).

A transition of the spin state has been observed as a temperature effect and a doping effect [21–25]. However, the transition of the spin state induced by laser illumination was observed first for our 327 systems. This phenomenon is undoubtedly significant, not only for the study of the mechanism of CMR but also for further applications such as in optical switching. The ability to keep a persistent memory of the magnetic history imprinted in the zero-field resistance can be applied in magnetic recording devices.

## 5. Conclusion

In summary, we have successfully deposited layered perovskite manganite $La_{1.2}Sr_{1.8}Mn_{1.8}Co_{0.2}O_7$ on a $SrTiO_3(100)$ substrate. The electrical transport, magnetic properties, MR and photoinduced effect are investigated systematically. The $R(T)$ curve shows an upturn 'tail' at low temperature, which originates from the spin-state transition and the localization of $e_g$ electrons due to the formation of CG. The MR effect appears below $T_c$ (198 K) and increases

with decreasing temperature. Furthermore, at low temperature, the metastable system can approach its equilibrium state with the assistance of an external $H$ less than 0.3 T and the system can keep a memory of the magnetic history. The comparison of the photoinduced effects in zero and an applied field, of $H = 0.34$ T, reveals that there is no growth of CG under laser illumination and only the spin-state transition of $Co^{3+}$ ions from the LS to the HS (or IS) state under laser illumination is observed in the low temperature region below 88 K. This transition stems from the excitation of a spin from the $t_{2g}$ orbital to the $e_g$ orbital, which increases the number of mobile $e_g$ electrons and thus decreases the resistance under laser illumination.

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