Theoretical simulation and experimental study on resistivity properties of mixed-phase $La_{2/3}Ca_{1/3}MnO_3$ thin films

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The theoretical simulation and experimental study are reported on the metal-to-insulator transition, thermal hysteresis behavior, magnetic-field-induced reduction, and anisotropic characteristics of resistivity for $La_{2/3}Ca_{1/3}MnO_3$ thin films deposited on $SrTiO_3$ (001)-oriented substrates tilted by 10° towards the [010] direction. The simulated results obtained by using a random network model based on phase separation scenario are in quantitative agreement with our experimental data and indicate that tilting (applying magnetic field) can increase (decrease) the scatterings and the activation energy, resulting in enhancement (reduction) of resistivity. All those results suggest that the intrinsic inhomogeneity and the lattice structure play the significant roles in the electrical conductivity and anisotropic transport properties. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2119413]

$La_{1-x}Ca_xMnO_3$ has been the focus of intensive studies due to its rich phase diagram and the colossal magnetoresistance (CMR) effect.[1] The material undergoes a phase transition from the low-temperature ferromagnetic (FM) phase to the high-temperature paramagnetic (PM) phase with a metal-to-insulator transition (MIT) of resistivity at $\sim 0.2 < x < 0.5$.[2] Depending on the doping level and the Jahn-Teller distortion, the doped $LaMnO_3$ compounds present anisotropic characteristics,[3] such as the anisotropic resistivity in $La_{2/3}Ca_{1/3}MnO_3$ measured along the *c*-axis and *a*-axis directions.[4] In addition, the unusual thermal hysteresis of resistivity has been observed in $La_{2/3}Ca_{1/3}MnO_3$ grown on MgO (001) substrate.[5] However, few studies have been carried out on the resistivity and its thermal hysteresis for the tilted $La_{2/3}Ca_{1/3}MnO_3$ film grown on vicinal cut $SrTiO_3$ substrate. Furthermore, the mechanism of those transport properties is still unclear. The double-exchange model[6] and Jahn-Teller phonon effect[7] are not sufficient in explaining the phase transition and the large mangnetoresistance.[8] A promising description is the phase separation scenario, suggesting that the manganite has a mixed-phase state with intrinsic inhomogeneity.[9] Many experimental results have showed that the coexisting clusters indeed exist in those manganites.[10,11] Mayr *et al.*[12] used a random resistor network based on the mixed-phase theory and obtained the good qualitative results of a MIT behavior. And we have obtained quantitative agreement with our experimental data about the MIT and the influence of magnetic field on resistivity based on the phase-separated framework for $La_{0.96}Te_{0.04}MnO_3$.[13]

In this letter, we report our work on the transport properties of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) thin films grown on 10° vicinal cut $SrTiO_3$ (STO) substrates. The experimental results show that the resistivity ρ exhibits a MIT and thermal hysteresis behaviors, and it can be reduced by applying magnetic field H. Furthermore, the resistivity displays anisotropic property with lower value measured along [100] direction and higher value measured along tilting direction. The simulated results being quantitatively consistent with our experimental data indicates that applying H can result in the resistivity reduction by suppressing the electron-electron scattering, magnon scattering, and activation energy but the tilting can induce the resistivity enhancement owing to the longer transport path. The studies reveal the phase separation theory combined with the crystal structure is crucial for understanding the transport properties of manganite.

LCMO thin films were deposited by facing-target sputtering (FTS) technique[14] on the STO substrates cut along the (001) surface with an intentional 10° vicinal cut towards the [010] direction. The substrate temperature was kept at 680 °C with the oxygen pressure being 60 mTorr during deposition. Then the films were annealed at 680 °C for 2 h under the atmosphere of oxygen. The thickness of the films is ~200 nm. The films were structurally characterized by a four-cubic diffractometer using Cu $K\alpha$ x rays. The curves of T-dependent resistivity were measured by the standard four-point probe method. In order to avoid the influence of the prior measured temperature during the warming and cooling process, each measured point of temperature was kept for 2 min before measurement. The current I was along [100] direction or along the tilting direction. The magnetic field H of 1 T was applied parallel to the electrical current and in the film plane.

The main concept of the random network model is that the system, i.e., a $N \times N$ matrix, is composed of two phases with different conductive properties.[12,13] One is FM metallic regions with resistance $R_M(T)$, the other is PM insulating regions with resistance $R_I(T)$. The total effective resistance $R_{\rm eff}$ is determined by the parallel connection of $R_M(T)$ and $R_I(T)$. A quantity f, defined as f=(the number of FM lattices)/(the number of total lattices), represents the fraction of FM metallic sites ($0 \leq f \leq 1$), decreases with the increasing T and should change rapidly near T_c, similar to the T-dependent magnetization. To calculate $R_M(T)$ and

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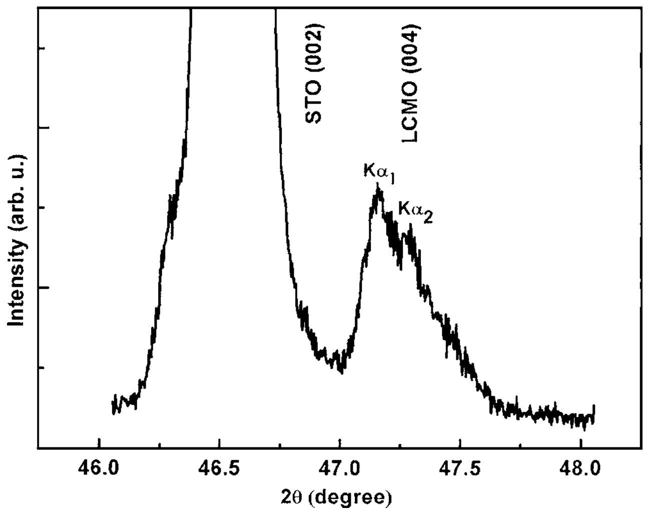

FIG. 1. X-ray diffraction pattern of LCMO film prepared on a 10° vicinal cut STO substrate.

$R_I(T)$, we assume $\rho_m(T)=\rho_{m0}+\rho_{m1}T^2+\rho_{m2}T^{4.5}$ and $\rho_i(T)=\rho_{i0}\exp[E_0/(k_BT)]$ are the T-dependent resistivities for each FM site and PM site, respectively. ρ_{m0} is the residual ρ at $T\sim 0$ K, the T^2 term indicates the electron scattering[15] with the coefficient ρ_{m1}, and the $T^{4.5}$ term denotes the magnon scattering[16] with the coefficient ρ_{m2}. ρ_{i0} is the high-T residual ρ, E_0 is the activation energy, and k_B represents the Boltzmann constant.[17,18] Using the Breadth-First Traversal algorithm,[19] the path lengths of the metallic and insulating domains are found to derive $R_M(T)$ and $R_I(T)$, respectively. Finally, the effective ρ can be obtained according to the size of the sample.

The x-ray diffraction result is shown in Fig. 1. For this sample grown on the STO substrate with 10° tilting, we adjusted ϕ or χ axes of the diffractometer to around 10° and searched for the peak at the expected 2θ of substrate. Then, the normal $\theta/2\theta$ scan was obtained after the alignment. The distinguishable $K\alpha_1$ and $K\alpha_2$ peaks in the $\theta/2\theta$ pattern of diffraction indicate the sample is of high crystal quality.

The experimental T-dependent resistivity curves of LCMO measured along [100] direction are presented in Fig. 2. We find the resistivity displays a MIT from low-T metallic property to high-T insulating characteristic. Furthermore, it should be noticed that the resistivity exhibits the thermal hysteresis behavior with and without H. The MIT temperature is 280 K on warming but 265 K on cooling without H, as shown in Fig. 2(a). We believe that thermal hysteresis of resistivity is due to the intrinsic inhomogeneity, and did not come from the experimental error, because the temperature difference of the resistivity peaks is as large as 15 K between warming and cooling, while the measurement step is only as small as 5 K in this temperature range. Furthermore, at each temperature step, 2 min stopping was held to allow enough thermal relaxation. Based on the model and simulating method mentioned above, the simulated results of T-dependent resistivity, which agree well with the experimental data, are obtained on the 100×100 matrix, as also given in Fig. 2(a). According to the observation of a local magnetic hysteresis and magnetic inhomogeneity in $La_{0.33}Pr_{0.34}Ca_{0.33}MnO_3$,[20] we can deduce that the FM fraction f on cooling is slightly smaller than that on warming at a fixed T, especially in the intermediate temperature range. In LCMO, we take the similar assumption and only adjust f by keeping other parameters unchanged. Then the thermal hysteresis of resistivity is obtained, which is coincide with the observation in $Pr_{0.65}Ca_{0.21}Sr_{0.14}MnO_3$.[21]

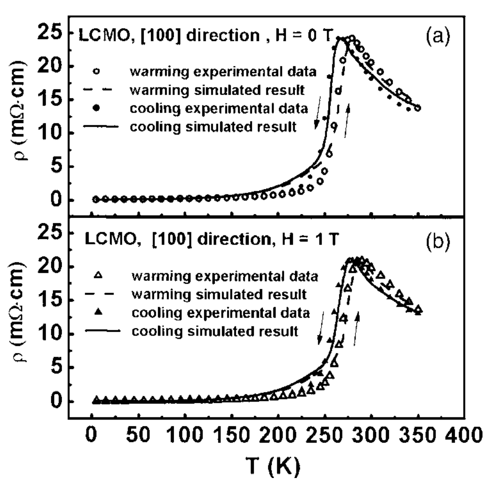

FIG. 2. Experimental and simulated ρ-T curves of LCMO film along the [100] direction without (a) and with (b) H in a warming and cooling cycle. The arrows indicate the evolution of temperature.

TABLE I. Parameters used in simulation for LCMO film along [100] direction with and without H, respectively.

H (T)	ρ_{m0} (mΩ cm)	ρ_{m1} (mΩ cm K^{-2})	ρ_{m2} (mΩ cm K^{-4})	ρ_{i0} (mΩ cm)	E_0/k_B (K)
0	0.15	9.80×10^{-6}	3.92×10^{-11}	6.45	230
1	0.13	8.75×10^{-6}	3.50×10^{-11}	6.45	205

After applying H, there is a remarkable reduction in resistivity, as presented in Fig. 2(b) The maximum values of magnetoresistance (MR), defined as $\mathrm{MR}=[\rho(H)-\rho(0)]/\rho(H)$, where $\rho(H)$ and $\rho(0)$ are the resistivities with and without H, respectively, are ~ -0.96 at 265 K on warming and ~ -1.0 at 250 K on cooling, exhibiting CMR effect. Although the MIT still exists under H, it seems that H shifts the MIT temperature to a higher value, being 290 K on warming and 275 K on cooling. Fäth *et al.*[11] pointed out that this H-induced shift of MIT temperature is due to the reason that the random spin disorder around T_c can be removed partially under H, causing a fraction of insulating regions to be converted into metallic regions. So, we consider that H will result in the increasing of f, suggesting f is the function of not only T but also H. By changing f slightly and adjusting the coefficients of FM and PM resistivity formula, we obtain good simulated results consistent with the experimental data with H, as also shown in Fig. 2(b). The corresponding coefficient parameters used are listed in Table I without and with H. It can be found that ρ_{m0}, ρ_{m1}, and ρ_{m2} are smaller than those without H for the reason that H suppresses the

TABLE II. Parameters used in simulation for LCMO film without H along the [100] direction and tilting direction, respectively.

Direction	ρ_{m0} (mΩ cm)	ρ_{m1} (mΩ cm K^{-2})	ρ_{m2} (mΩ cm K^{-4})	ρ_{i0} (mΩ cm)	E_0/k_B (K)
[100]	0.15	9.80×10^{-6}	3.92×10^{-11}	6.45	230
tilting	0.19	1.33×10^{-5}	5.33×10^{-11}	7.50	280

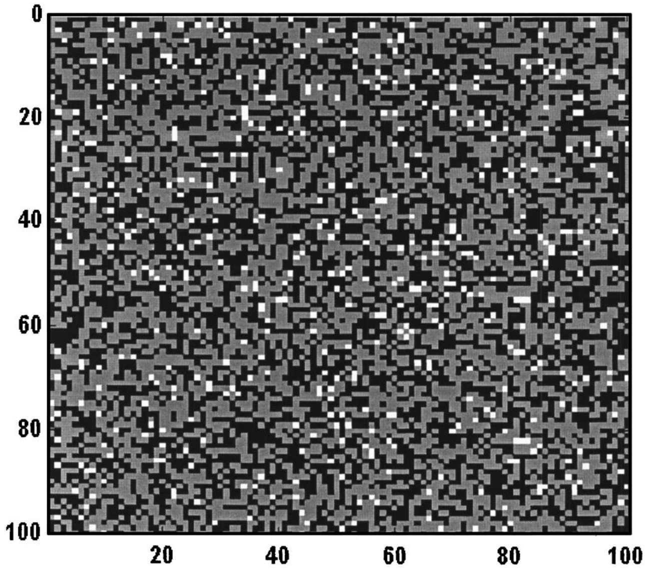

FIG. 3. Simulation result for H-induced enhancement of the metallic FM fraction f at $T \sim 265$ K. Black and gray denote the FM and PM regions with and without H, respectively. And white represents the PM regions without H that turns into the FM regions with H.

spin scattering of conductive carriers by driving the local orientation of magnetization aligned.[22] Moreover, the value of E_0/k_B is lowered, indicating H can result in the decrease of E_0. The unchanged ρ_{i0} suggests that H may not reduce ρ of the PM components at very high T. Figure 3 schematically demonstrates the H-induced effect on the increasing of f at $T \sim 265$ K on a 100×100 matrix.

Our experimental data measured along tilting direction without H are shown in Fig. 4, showing the resistivity in the tilting direction also displays the MIT. Compared with the results along [100] direction, the resistivity of LCMO is indeed anisotropic even if the tilted angle is only 10°, with higher value along tilting direction. The maximum value of anisotropy ratio, defined as the ratio of resistivity along tilting direction to [100] direction, is ~1.58 for the cooling process without H at ~240 K. In addition, the MIT temperatures remain unchanged along [100] and tilting directions. The simulated result consistent with our experimental data along tilting direction is also given in Fig. 4. The corresponding coefficient parameters used are listed in Table II for along the [100] direction and tilting direction without H. We find that ρ_{m0}, ρ_{m1}, and ρ_{m2} along tilting direction are higher

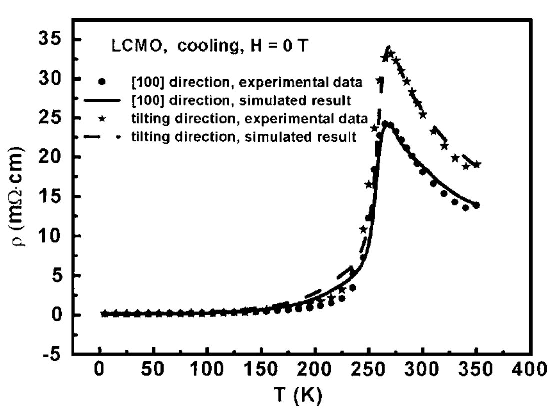

FIG. 4. Experimental and simulated ρ-T curves of LCMO film on cooling without H along the [100] direction and tilting direction, respectively.

than those along [100] direction for the reason that the tilting increases the spin scattering and decreases the effective hopping probability due to the longer transport path. Furthermore, the increased E_0/k_B indicates tilting can enhance E_0, resulting in the increasing of resistivity. Finally, the unchanged ρ_{i0} is also reasonable because tilting may not reduce the resistivity of the PM components at very high T.

In summary, we have grown LCMO thin films on (001)-oriented STO substrates tilted by 10° towards the [010] direction. The experimental results show that resistivity displays the MIT behavior, thermal hysteresis phenomenon, and anisotropy with lower value along [100] direction and higher value along tilting direction. Furthermore, the applied magnetic filed can reduce the resistivity to induce large MR. The excellent agreement between the simulation and the experimental data further verifies that phase separation indeed lies in the material of LCMO and indicates our model is appropriate for describing transport behavior of the manganite with the intrinsic inhomogeneity in the form of coexisting competing phases. And it can be concluded that the crystal structure plays an important role in anisotropy of resistivity.

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