

Hall effect in $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_{3+\delta}$ films with variable oxygen content

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Hall effects of the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_{3+\delta}$ film, which is believed an electron-doped manganite, have been experimentally studied, and a positive normal Hall coefficient is observed below the Curie temperature when the oxygen content of the film varies in a wide range. These observations may be attributed to the presence of excessive oxygen and composition distribution in the film, which may occur accompanying tetravalent ion doping. Removing excessive oxygen drives the system into the electron-doping state, however, the resistivity increases monotonically with oxygen loss, and the metal-to-semiconductor transition typical for a hole-doped manganite disappears. These results suggest the determinative role of hole doping for the resistive and magnetic behaviors in $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_{3+\delta}$.

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I. INTRODUCTION

In the double exchange (DE) scenario, the electron hopping between Mn ions of the manganites, with the help of intermediate oxygen, can produce a magnetic coupling among the ions.^{1,2} This implies a strong magnetic-resistive interplay in manganites, which is actually the underlying reason for the appearance of colossal magnetoresistance (CMR) effects that have received a world wide attention in recent years.³ It is obvious that the essential ingredient for the occurrence of the DE is the presence of Mn ions with different valences. LaMnO_3 is an antiferromagnetic (AFM) semiconductor at low temperatures because of the absence of Mn^{4+} ions.⁴ Without double exchange, the superexchange between Mn^{3+} ions becomes important. Meanwhile, due to the full occupation of the majority spin e_g band and the complete empty of the minority spin band, activation-type conduction is dominative in this oxide. Mn^{3+} ions can be oxidized into Mn^{4+} ions by replacing part La^{3+} ions with monovalent or divalent ions, equivalently to doping holes into the majority spin band. This provides an environment for the DE process, and actually the typical CMR and associated effects are observed in properly hole-doped LaMnO_3 .

There is a possibility to obtain electron-doped manganites through introducing tetravalent ions into La sites. The first work in this regard was done by Mandal and Das.⁵ They substituted Ce^{4+} for La^{3+} in LaMnO_3 , and observed similar behaviors to hole-doped manganites. However, subsequent work by Ganguly *et al.*⁶ revealed that the Ce-doped bulk LaMnO_3 is a multiphase mixture comprising of lanthanum-deficient manganate phases and Ce oxides. In an attempt to ascertain the electron-doped nature of tetravalent ion-doped manganites, $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ (LCEMO) thin films, and LCEMO-based magnetic tunnel junctions were subsequently fabricated. Photoemission/x-ray absorption spectroscopy and Hall effects, for the former, and magnetoresistance effect, for the latter, were studied.⁷ It seems that all the data obtained are consistent with each other and could be accommodated

into a frame based on electron doping. Other tetravalent ion-doped manganites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ with $A = \text{Sn, Zr, Sb, and Te}$ were also studied, and essentially the same behaviors as LCEMO were observed.⁸ To explain the strong magnetic-resistive correlation in tetravalent ion-doped manganites, the presence of DE between Mn^{2+} and Mn^{3+} has been proposed.

Electron-doped manganites are important members of the CMR family, and a new physics is expected for this kind of manganites noting the fact that the competitive DE, SE (super-exchange), and Coulomb interactions, thus the spin-charge-orbital correlation, which has been the source for the rich behaviors of hole-doped manganites, could be affected by the $\text{Mn}^{4+} \rightarrow \text{Mn}^{2+}$ conversion. However, whether tetravalent ion substitution can produce true electron doping is still a question because of the flexibility of the oxygen content in manganese perovskites. Zhao *et al.*⁹ demonstrated the difficulty to dope Ce into the LaMnO_3 system, and recent work suggested a holelike thermopower in the LCEMO film.¹⁰⁻¹² We noted that the oxygen content of the $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ films in previous work was not measured, and the resistive and magnetic behaviors as functions of oxygen content were not traced either. Although the Hall effect study indicated electronlike charge carriers, the measured electron density is rather high (~ 4.5 electrons/Mn site) compared with the expected value ~ 0.3 electrons/Mn site.⁷ This implies that electron mobility could be lower than hole mobility in manganites, which is completely different from the conventional semiconductor. Therefore, a systematic study on the carrier type in tetravalent ion-doped manganites is obviously necessary despite of the work mentioned above. In this paper, we report on the Hall effect and its variation with oxygen content for the LCEMO films. It is found that the normal Hall coefficient is positive below the Curie temperature even the oxygen content varies significantly. This result indicates the holelike character of charge carriers though the doped Ce ions are tetravalent. When the samples are driven towards a true electron-doping state by removing oxygen, the familiar metal-to-semiconductor transition (MST) disappears, and

there are no signs for the reappearance of this transition for further oxygen release until the sample becomes unstable because of over deoxygenization. This result suggests that the MST is exclusively related to hole-doping for our LCEMO films.

II. EXPERIMENT

Two LCEMO films of the thickness of ~ 120 nm were grown on the (001)SrTiO₃ substrates using pulsed laser ablation technique following the procedure described elsewhere.¹³ The temperature of the substrate was kept at 700 °C and the oxygen pressure at ~ 100 Pa during the deposition. A post annealing at 700 °C for 15 min in air was performed after deposition to improve the crystal quality of the film (called as-prepared sample hereafter). A careful x-ray diffraction study shows that the film is single phase and epitaxially grown. Analyses of the energy dispersive x-ray spectrometry (EDX) reveal a composition in agreement with that of the target within an error of 5% (La:Ce:Mn=0.7:0.3:1).

One of the two films was patterned by the conventional lithographic methods into a four-terminal Hall geometry, while another was reserved for x-ray photoelectron spectroscopy (XPS) analysis. To remove oxygen, the two samples were simultaneously heated, in a vacuum of $\sim 10^{-4}$ Pa, to a predetermined temperature between 150–600 °C at a rate of ~ 100 °C/h, then, without temperature maintenance, cooled to room temperature. Lower temperatures were preset first to control the release of oxygen, then higher temperatures for a further oxygen deprivation. Before each annealing, the longitudinal resistivity and transverse resistivity (Hall resistivity) were measured as functions of applied field and temperature. This process was repeated until the film became unstable due to over oxygen losing.

III. RESULTS AND DISCUSSION

As shown by the previous work, the oxygen content in the film can be characterized by its Curie temperature.¹⁴ Figure 1 shows the longitudinal resistivity of the film as a function of temperature. The film is metallic near the room temperature, and undergoes a MST with the decrease of temperature, producing a resistivity peak at T_p . Magnetic measurement indicates that the resistive transition occurs accompanying a paramagnetic-ferromagnetic transition ($T_p \approx T_c$) (inset in Fig. 1). These are behaviors similar to those previously observed in LCEMO.⁷ Vacuum annealing causes a progressive low-temperature shift of the MST, accompanying a slight transition broadening and considerable resistivity increase. The MST temperature reduces from ~ 285 – ~ 200 K, which covers the reported $T_p=250$ K. Such a variation of the MST will correspond to a variation of the oxygen content of $\delta \sim 0.05$ in the case of divalent ion-doped manganese.¹⁵ The lattice parameter of LCEMO cannot be detected because of the coincidence of the diffraction peaks of LCEMO and the SrTiO₃ substrate. We further prepared a film on LaAlO₃, and repeated the post annealing done for the film on SrTiO₃. It showed that the out-of-plane lattice parameter of LCEMO

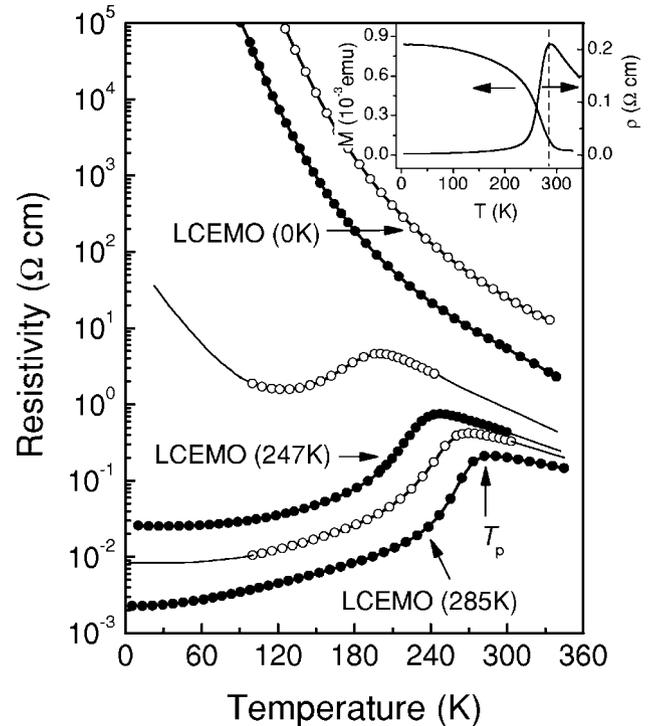


FIG. 1. Temperature-dependent longitudinal resistivity against vacuum annealing. The inset shows the magnetic moment ($H=0.05$ T) and resistivity as functions of temperature for the as-prepared LCEMO film. The two curves corresponding to $T_p=0$ are obtained by vacuum annealing the film at 400 and 500 °C, respectively. Dashed line marks the simultaneous occurrence of resistive and magnetic transitions. Solid lines are guides for the eye.

grows from ~ 0.3884 to ~ 0.392 nm with vacuum annealing, and the relative change is as large as $\sim 0.92\%$. It should be noted that the resistive curve corresponding to $T_p=247$ K exhibits exactly the same resistivity-temperature dependence as that previously reported. The MST becomes ambiguous with further oxygen loss and, finally, unidentifiable. No signs for the reappearance of the MST with oxygen loss are observed when we progressively increase the temperature of vacuum-annealing until the sample become unstable: The film absorbs oxygen even at room temperature when exposed to air as revealed by x-ray diffraction data.¹⁵ In contrast, the overall resistivity shows a monotonic increase with the decrease of oxygen content.

It has been proposed that the DE between Mn²⁺ and Mn³⁺ determines the magnetic and transport properties of LCEMO. The Mn²⁺:Mn³⁺ ratio is 0.3:0.7 in stoichiometric LCEMO if all the Ce ions are tetravalent. The Mn²⁺ content in as-prepared sample could be small due to post annealing that introduces excessive oxygen into the film as confirmed by the shrinkage of the out-of-plane lattice constant of LCEMO.¹⁵ It is interesting that oxygen deflection yields a continuous low temperature shift of MST. This conflicts with the electron-doping scenario, which suggests a T_p growth with the increase of the Mn²⁺/Mn³⁺ ratio due to oxygen loss. It is fascinating that the vacuum annealing effects nearly exactly mimic those of the hole-doped manganites,¹⁶ for which oxygen release leads to a decrease of the content of Mn⁴⁺

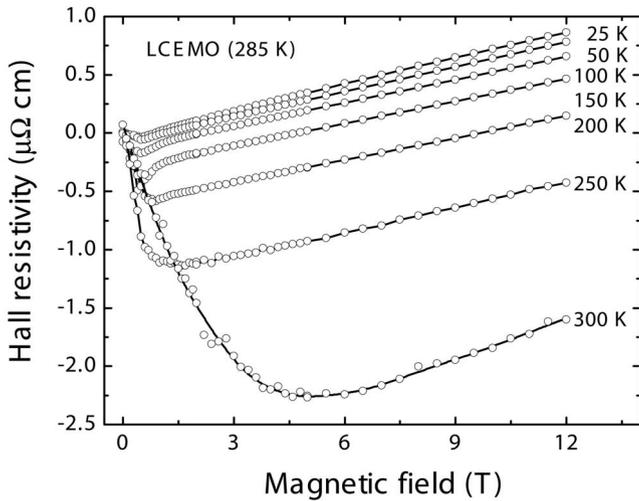


FIG. 2. Field dependence of the Hall resistivity of the as-prepared LCEMO film ($T_p=285$ K) measured at various temperatures.

ion, thus a reduction of T_p . Therefore, these results suggest the holelike character of the charge carriers in LCEMO.

The Hall resistivity was measured by a commercial physical property measurement system (PPMS-14H). The direction of the Hall voltage was carefully checked by the standard sample (copper) to guarantee a correct conclusion. The experiment was performed in the temperature range from 25 to 300 K and the magnetic field (H) range from 0 to 12 T. The temperature fluctuation is controlled below 0.01 K during the measurements, and the alternative current mode was used to eliminate undesired effects. Two Hall voltages were measured by rotating the sample by 180° around applied current for a fixed field to remove the offset voltage due to the asymmetry of the Hall terminals or subsisting magnetoresistance.

Figure 2 shows the Hall resistivity (ρ_{xy}) against magnetic field for the as-prepared sample. It is clear that ρ_{xy} can be classified into two well defined parts: the sharp drop in the low field range and the linear increase with applied field in the high field range. The former is called anomalous Hall effect, due to the rotation of magnetic domains, while the latter is the ordinary one. This is a typical feature of ferromagnet, and a simple description¹⁷

$$\rho_{xy} = R_S \mu_0 M + R_H \mu_0 H \quad (1)$$

has been given if the demagnetization factor is set to 1, where R_S and R_H are the anomalous and ordinary Hall coefficients, respectively, μ_0 the vacuum permeability, and M the magnetization. The increase of temperature has no obvious influence on the normal Hall effect in the beginning and causes a visible inclining of the linear part of the $\rho_{xy}-\mu_0 H$ curve when $T \geq 250$ K in the mean time enhancing the anomalous Hall effect, especially near the Curie temperature. It is interesting to note that the $\rho_{xy}-\mu_0 H$ slope for the linear part of this curve is positive. This reveals the hole-like character of the charge carriers, that is to say, the substitution of Ce does not produce electron-doping in the present case.

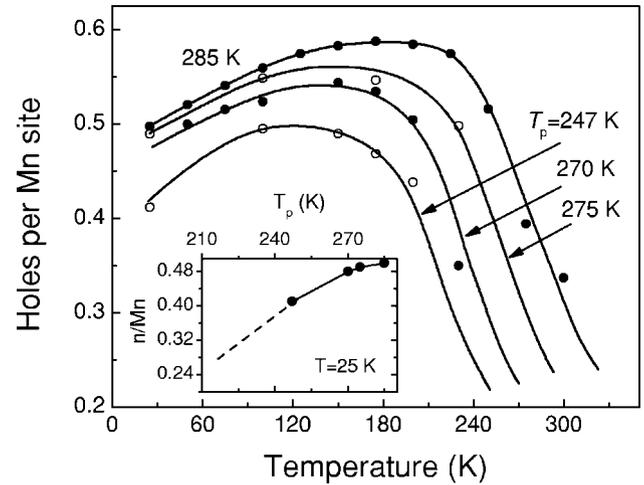


FIG. 3. Carrier density as a function of temperature. The inset plot shows the carrier numbers/Mn site as a function of the Curie temperature of LCEMO at a fixed temperature 25 K. Solid and dashed lines are guides for the eye.

This result is consistent with the previous vacuum annealing data.

The MST temperature of the as-prepared film is much larger than the reported value (285 K vs 250 K), which implies significant oxygen nonstoichiometry in this sample. We further studied the influence of vacuum annealing on Hall effect to trace the variation of carrier type and density. It is found that the general features of the $\rho_{xy}-\mu_0 H$ relation remain unaffected except for a change in the value of anomalous and ordinary Hall resistivity. We would like to emphasize that a holelike, instead of electronlike, Hall effect is still observed in the cases $T_p=247$ K, for which electron doping has been proposed by various authors.⁷ In fact, the Hall effect keeps holelike down to $T_p=230$ K, below which ($T_p < 230$ K) the large offset voltage and magnetoresistance disturb a reliable determination of ρ_{xy} .

The effective carrier number calculated from R_H using $R_H=1/en$ is shown in Fig. 3 as a function of temperature. It is ~ 0.5 holes/Mn site at $T=25$ K for the as-prepared sample. With the increase of temperature, the carrier number exhibits a slight growth and saturates at ~ 0.6 holes/Mn site above 150 K. This value is smaller than that observed in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (~ 2 holes/Mn site), but comparable to $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (~ 1 holes/Mn site).¹⁸ A steep drop of the carrier density appears as the temperature approaches T_p , which has been observed in other manganites before¹⁹ and attributed to the change of conduction mechanism around T_p .²⁰ Oxygen loss due to vacuum annealing leads to a decrease of n (Fig. 3 and its inset plot), consistent with the consideration that the introduction of oxygen vacancies will reduce the content of Mn^{4+} ions.

To get the knowledge about the valence of Ce and Mn ions in the film, XPS analysis was performed. The top panel of Fig. 4 shows the Mn-2p spectrum of LCEMO (0 K) and LCEMO (285 K), two typical states of the LCEMO film during the vacuum annealing. The XPS spectrum of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ was also presented for comparison. The coincidence of the Mn-2p spectrum of LCEMO (285 K) with

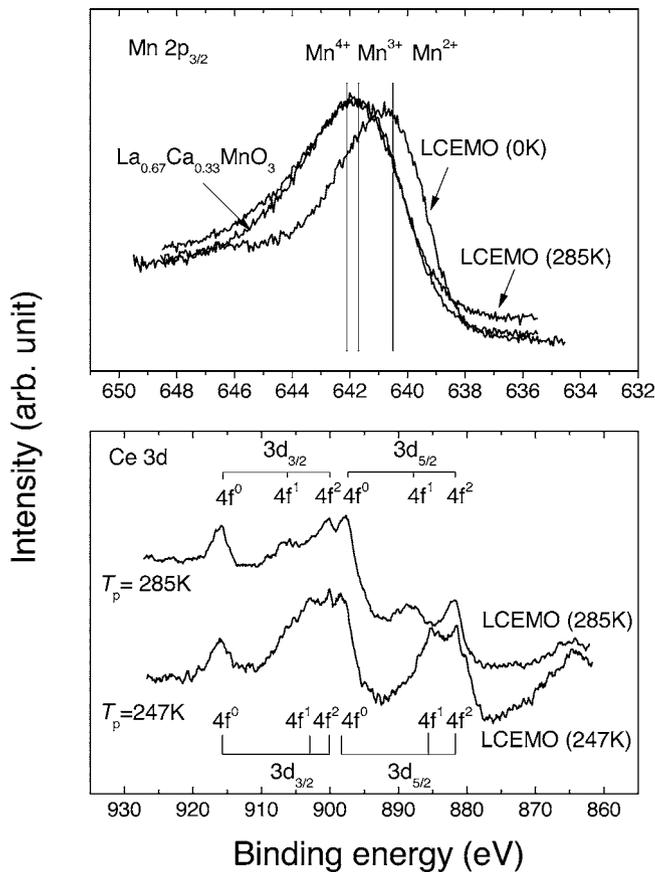


FIG. 4. Mn- $2p$ XPS spectra of LCEMO (0 K), LCEMO (285 K), and $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ($T_p=250$ K) (top panel) and Ce- $3d$ XPS spectra of LCEMO (247 K) and LCEMO (285 K) (bottom panel), collected at room temperature. Peak positions for Mn^{2+} , Mn^{3+} , and Mn^{4+} are marked by thin lines.

that of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ indicates a similar average Mn ion valence in the two films. This result reveals that the Mn^{3+} and Mn^{4+} ions dominate in LCEMO. As expected, the Ce ions are essentially tetravalent in the as-prepared sample as confirmed by the appearance of the triplet peaks marked by $4f^0$, $4f^1$, and $4f^2$, respectively, which has been a typical feature of Ce^{4+} . For the film with a $T_p \geq 230$ K, no significant change in the Mn- $2p$ spectra was observed. In this case the peak shift from Mn^{3+} to Mn^{4+} could be fairly small. In contrast, deoxygenization reduces the valence of Ce ions. It is clear that the $4f^1$ peak shifts from ~ 906 to ~ 903 eV after vacuum annealing, which has been ascribed to the appearance of Ce^{3+} .²¹ According to the XPS spectra in Fig. 4, the Ce ions are at a mixed valence state of Ce^{3+} and Ce^{4+} for $T_p=247$ K. Therefore, an idealized tetravalent ion doping can be realized only when significant excessive oxygen exists in the film. When the vacuum-annealing temperature is above 350 °C, peak shift towards Mn^{2+} becomes obvious, and Mn ions are mainly at the Mn^{2+} and Mn^{3+} mixed-valence state after deoxygenizing the film at temperatures above 400 °C [curve LCEMO (0 K)]. This results indicate that the LCEMO film has been driven from the hole-doped state into the electron-doped state simply by removing excessive oxygen. The content of the Mn^{2+} ions in LCEMO (0 K) could be

significant according to the position and shape of the Mn- $2p$ peak. In contrast, the resistivity shows a monotonic increase with the reduction of the average valence of Mn ions, without any sign for resistive transition (Fig. 1). These results, combined with the Hall effect study, strongly suggest that the MST is exclusively related to hole doping for our LCEMO film.

The reasons for the appearance of holelike doping effects, in addition to the partial $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ conversion, could be the presence of cation vacancies. There are two possibilities for introducing the cation vacancies. One is the excessive oxygen in the sample, which may always occur accompanying quadrivalent ion doping due to the requirement for chemical equilibrium. As a consequence, the Mn ions mainly stay at the state of Mn^{3+} and Mn^{4+} . Mn^{2+} ions could also exist, however, their content may not be high. It is easy to show that to get a $\text{Mn}^{4+}:\text{Mn}^{3+}$ ratio of 0.2:0.8, excessive oxygen of the content of $\sim 8\%$ is enough, within the tolerance of manganite perovskites. In fact, it has been revealed that for the manganites, Mn ions prefer to stay at the Mn^{3+} and Mn^{4+} mixed valence state, and in the case of $\text{Mn}^{4+}:\text{Mn}^{3+}=0.3:0.7$, it is difficult to remove oxygen from or insert oxygen into the manganite lattice.²² This explains why significant excessive oxygen always exists in the LaMnO_3 films prepared under the condition for an ordinary hole-doped manganite film. With this in mind, excessive oxygen in LCEMO is possible. The other possibility for the cation vacancies is the composition distribution in the sample. Recently, Yanagida and collaborators reported that nanometer-sized Ce-rich domains prefer to be formed in the LCEMO film,¹⁰ resulting in cation vacancies in the film. This chemical inhomogeneity is beyond the capture of x-ray diffraction because of the small domain size and low domains density. To get the knowledge about the microstructure of our sample, a transmission electron microscope (TEM/Philips CM200) study was performed for the as-prepared LCEMO film. Figure 5 is a typical TEM image near the LCEMO-STO interface. In addition to confirming the epitaxial growth of the LCEMO film [area A in Fig. 5(a)], the high-resolution TEM image indicates the presence of minor strip-structured domains (area B) of the size of several nanometers. These domains exhibit a different crystal structure from the simple perovskite phase as demonstrated by the electron diffraction patterns in Figs. 5(b) and 5(c), and randomly disperse in the background of the main phase. A further analysis on lattice constant and relative orientation with respect to the perovskite phase indicates that these domains may exhibit a crystal structure similar to that of CeO_2 . The lattice constant of CeO_2 is 0.541 nm, and the lattice spacing of (110) is close to that of (001) of LCEMO film and STO substrate, which means that the CeO_2 can grow on the LCEMO film epitaxially with a rotation of 45° . Strip-structured domains with a definite orientation with respect to the background were also observed by Yanagida *et al.*,¹⁰ and proved to be Ce oxides. This result indicates that the LCEMO film is a multiphase mixture comprising of Ce-deficient manganate phases and Ce oxides, and the holelike behavior originates from the former. Unlike bulk sample, the domains of the Ce oxides in the film are nanometer sized and their density is not high. As a consequence, they cannot be

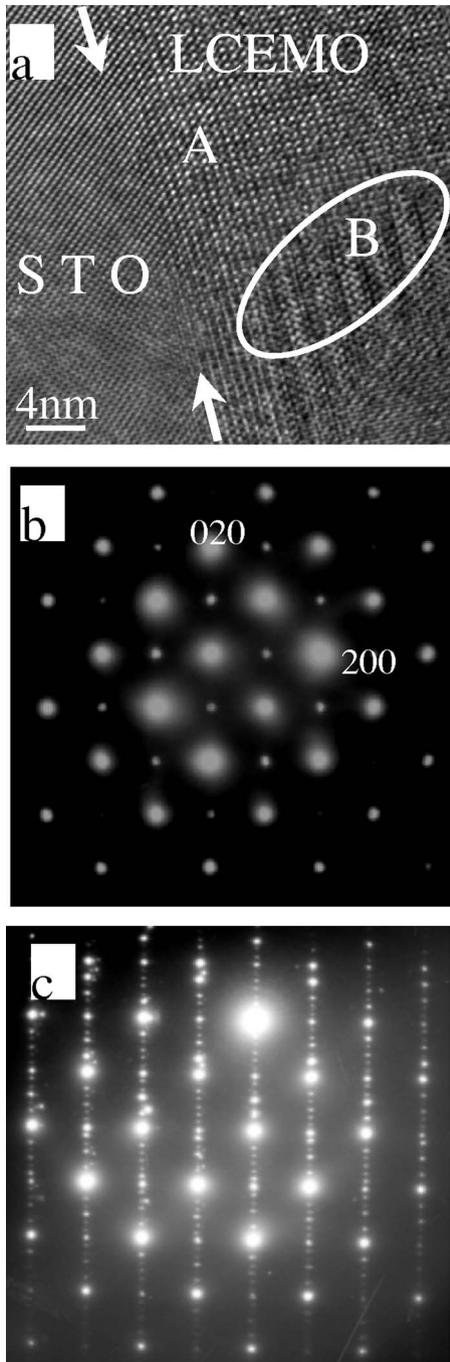


FIG. 5. (a) High-resolution TEM image of as-prepared LCEMO film. (b) Electron diffraction pattern of the area A. (c) Electron diffraction pattern of the stripe-structure domains (area B).

detected by x-ray diffraction. The presence of significant cation vacancies is consistent with the fact that the residual resistivity of our LCEMO film is significantly high compared with $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ($\sim 2.3 \times 10^{-3} \Omega \text{ cm}$ vs $\sim 4 \times 10^{-4} \Omega \text{ cm}$).

The conclusion here is different from that obtained by Mitra *et al.*⁷ The reason is not very clear at present. One possibility is that the preparation condition for the LCEMO film is crucially important. We noticed that the substrate temperature, oxygen pressure, and laser energy reported by Mi-

tra vary in a wide range. The experiment conditions we used situated essentially in the same range. However, other factors such as the purity of the target, the quality of the substrate, and the growth mode of the film may be important for the formation of a chemically uniform LCEMO film. Unfortunately, these were not reported in the literatures, which makes it difficult for a careful comparison of our experimental condition with others. The target-substrate distance was also suggested to be crucial for the formation of a LCEMO film without CeO_2 impurity.⁷ In the present studies, the target-substrate distance has been tuned between 3 and 5 cm in our experiment (only the results of 4 cm are presented here). However, all the resultant films show holelike behavior as confirmed by the Hall effect studies. This indicates that under these conditions a chemically uniform LCEMO film cannot be obtained. Our results are consistent with those obtained by Ganguly *et al.*,⁶ Zhao *et al.*,⁹ and Yanagida *et al.*^{10,11} It is obvious that further work is required to reveal the origin for these differences.

Another possibility is that the magnetic and resistive behaviors are actually dominated by the DE between Mn^{3+} and Mn^{4+} , instead of Mn^{2+} and Mn^{3+} . Although there are a number of reports on the $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ films, the direct evidence of electron doping is the results of Hall resistivity and x-ray absorption (XAS) spectrum. We found that the XAS data of LaMnO_3 , which has been used as a reference for the analyses of the $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ film, changes from literature to literature. For example, the Mn-L3 XAS peak of LaMnO_3 varies from 641.8 eV,²³ to 642.5 eV,⁷ and to 644 eV.²⁴ It should be noted that the difference in the binding energy for Mn^{2+} , Mn^{3+} , and Mn^{4+} is subtle (< 2 eV), and a small shift can result in a completely different conclusion, noting the fact that electron doping has been postulated based on the difference of the two XAS spectra of LaMnO_3 and LCEMO.⁷ These results manifest the possibility of experiment uncertainty.

IV. SUMMARY

In summary, resistive behavior and Hall effect of the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_{3+\delta}$ film with different oxygen content, which is believed an electron-doped manganite, have been experimentally studied. A low temperature-shift of the metal-to-semiconductor transition, accompanying an increase of the overall resistivity, are observed with the decrease of the oxygen content in the film. This is a behavior usually occurring in a hole-doped manganite. The holelike character of the charge carriers is further confirmed by the discovery of positive normal Hall coefficient in the temperature range below the resistive transition. This means that the dominative electronic process in the present sample is that between Mn^{3+} and Mn^{4+} , different from that previously believed. It is possible that the presence of excessive oxygen or, equivalently, cation vacancies in the film, which may occur accompanying tetravalent ion doping, counteracts the effects of tetravalent ion substitution, resulting in the hole-doping effect. Removing excessive oxygen can drive the system into the electron-doping state, however, the resistivity increases monotonically with oxygen loss, and the metal-to-semiconductor

transition typical for a hole-doped manganite disappears. These results suggest the determinative role of hole doping for the resistive and magnetic transitions in our LCEMO films.

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