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<td><strong>Citation</strong></td>
<td>Physical Review B, 79(13), p.132405_1-132405_4</td>
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<td><strong>Text Version</strong></td>
<td>Publisher's Version</td>
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<tr>
<td><strong>DOI</strong></td>
<td><a href="https://doi.org/10.1103/PhysRevB.79.132405">https://doi.org/10.1103/PhysRevB.79.132405</a></td>
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X-ray absorption magnetic circular dichroism of (La,Ce)MnO$_3$ thin films

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(Received 28 May 2008; revised manuscript received 28 March 2009; published 22 April 2009)

Creating a bipolarity of semiconductors has been a key technology to develop recent advanced semiconductor devices. Such bipolarity for manganese oxides, of which “hole-doped manganites” exhibit a rich variety of electric transport and magnetic properties, has been of great importance. Although theoretical calculation predicts the presence of ferromagnetic “electron-doped manganites” with doping tetravalent cations [Q. Zhang and W. Zhang, Phys. Rev. B 68, 134449 (2003)], the ferromagnetic origin in experiments has been controversial due to the lack of direct experimental evidence. Here, we investigate the ferromagnetism in (La,Ce)MnO$_3$ thin films by measuring the magnetic circular dichroism in soft x-ray absorption (XMCD). Despite the presence of Mn$^{3+}$, i.e., electron doping for manganese, the Mn$^{3+}$ amount did not correlate with the Curie temperature, indicating the minor magnetic contribution of Mn$^{3+}$. More crucially XMCD measurements clarified that the ferromagnetism is not caused by the presence of Mn$^{3+}$ but by self-hole doping for manganese.

DOI: 10.1103/PhysRevB.79.132405 PACS number(s): 75.70.–i, 71.30.+h, 75.50.–y, 75.75.+a

I. INTRODUCTION

Hole-doped rare-earth manganites (R$_{1-x}$A$_x$MnO$_3$), in which the rare earth in the parent compound is partially replaced by a divalent cation such as Ba, Ca, Sr, and others, have been intensively investigated due to many interesting physical properties including colossal magnetoresistance (CMR), charge ordering (CO), and metal-insulator transition (MIT), as well as their potential for device applications.1–16 As to the hole doping in the parent compound LaMnO$_3$, a proportionate amount of Mn$^{3+}$ with the electronic configuration of $t_{2g}^2e_g^1$ is replaced by Mn$^{4+}$ resulting in holes in the $e_g$ band. The holes permit charge transport in the $e_g$ band, inducing ferromagnetism through double exchange interaction between Mn$^{3+}$ and Mn$^{4+}$. On the other hand, recent attempts to create electron-doped manganites with the $t_{2g}^2e_g^1$ and $t_{2g}^2e_g^1$ electronic configuration by doping tetravalent cations, including Ce,2–5 Sn,6 and Te,7 have attracted attention since the first report by Mandal and Das.2 The realization of such electron-doped manganites is very interesting not only for fundamental physics in the context of the emergence of ferromagnetism in that electronic configuration8 but also for the device application, e.g., the $p$–$n$ homojunctions of both hole- and electron-doped manganites would be possible and promising for unique functional spintronic devices in future.5 Although many investigations as for so-called electron-doped manganites with the $t_{2g}^2e_g^1$ and $t_{2g}^2e_g^1$ electronic configuration consistently reported the presence of MIT, ferromagnetic (FM) transition, and CMR effect,2–7 the stoichiometry of such tetravalent cation doped manganites, i.e., the phase pure nature, has been questioned.9–14 For example, fabricating a single phase of bulk Ce-doped LaMnO$_3$ system was found to be unfeasible using conventional solid-state reaction method due to the thermal stabilization of CeO$_2$.9 On the contrary, fabricating a single phase of Ce-doped LaMnO$_3$ showing no impurity phases in the x-ray diffraction (XRD) data was reported to be possible only in the form of thin film using a pulsed laser deposition (PLD) technique.3–5 Although the presence of Mn$^{2+}$ within the (La,Ce)MnO$_3$ thin films has been demonstrated,15,16 the magnetic contribution of Mn$^{2+}$, which is in fact crucial information, has not been clarified so far. Here, we present the valence specific magnetic information of (La,Ce)MnO$_3$ thin films by measuring the magnetic circular dichroism in soft x-ray absorption (XMCD).

II. EXPERIMENT

La$_{0.7}$Ce$_{0.3}$MnO$_3$ epitaxial films were grown on [(LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$] (LSAT) (001) ($d$=3.868 Å) substrate by the PLD technique (ArF excimer, $\lambda$=193 nm) in an oxygen atmosphere. The thickness of the films fabricated was in the range of 1500–2000 Å. The oxygen pressure $P_O_2$, and the substrate temperature $T_s$, during depositions were 1 Pa and 700 °C, respectively.12,13 To investigate the effect of the transition temperature variation, several films were then annealed at 600 °C in flowing argon at atmospheric pressure for 10 h. The crystallinity was characterized by a four-axis XRD measurement, showing the film epitaxy to the substrate and also the absence of Ce-rich impurities on the XRD level12,13 (see also the inset of Fig. 1). The compositions of the films were measured using electron probe microanalyzer (EPMA) coupled with energy dispersion spectroscopy (EDS). The film composition was almost consistent with the nominal value within the resolution of EDS.13 The magnetic properties were evaluated using a superconducting quantum interference device (SQUID) magnetometer. We measured XMCD for thus well-defined thin films at BL23SU beamline of SPring-8 to identify the origin of ferromagnetism in La$_{0.7}$Ce$_{0.3}$MnO$_3$ films. The measurements were performed at 20 and 100 K under an applied magnetic field of 3 T, which was much higher than saturating magnetic field, along the surface normal of the sample. To prevent contamination, the samples had been capped with SrTiO$_3$ (1–2 nm thickness) without atmospheric exposure, which remained on the samples during the measurements. The XMCD spectra were measured by switching the photon he-
licity being parallel ($I_\parallel$) and antiparallel ($I_\perp$) to the fixed magnetization at each photon energy employing the total electron yield (TEY) mode with an energy resolution of 0.1 eV. The degree of circular polarization was better than 90%. We assume our XMCD measurements to be representative of entire LCeMO films because the probing depth of the TEY method is approximately 5 nm or deeper.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of magnetization for as-grown and annealed LCeMO thin films fabricated by PLD. The lack of impurities on the XRD level for the as-grown film can be seen in the inset XRD data. The variation in Curie temperature $T_C$ was found to range from 140 to 265 K, which is consistent with previous reports. In fact, such observed ferromagnetism has been frequently thought to be the evidence of electron-doped manganites. The as-grown film is insulating and the annealed film exhibits the metal-insulator transition, as reported elsewhere. However, subsequent reports have raised concerns about the suggested intrinsic nature of ferromagnetism in these materials due to the possibility of self-hole doping effects where cation vacancies and/or nanoscale impurities of doped cations are created under oxidizing atmosphere, providing charge carriers even for thin films. This situation clearly calls for more detailed studies of Ce-doped manganites to establish or refute the premise of the intrinsic nature in magnetism. One of the important criteria for electron-doped manganites to be intrinsic is suggested to be the observation of the presence of Mn$^{2+}$ by electron spectroscopy (XAS). It should be noted that in the context information not only about the valence state but also the contribution of Mn$^{2+}$ to ferromagnetism are crucial to identify the intrinsic origin of ferromagnetism observed in many electron-doped manganites. However, to the best of our knowledge investigating the magnetic contribution of each manganese valence state in Ce-doped manganites has not been reported at all so far. In Sec. IV, we present the XMCD in LCeMO epitaxial thin films since this technique provides spectral features only from those components that exhibit ferromagnetism.

Figure 2(a) shows the Mn 2p$_{3/2}$ XAS ($I_\parallel + I_\perp$) spectra of as-grown ($T_C = 145$ K) and annealed ($T_C = 255$ K) films of LCeMO in comparison with the spectra of lightly hole-doped manganites (La$_{0.88}$Sr$_{0.12}$MnO$_3$) and Ga$_{0.975}$Mn$_{0.025}$As as a reference of Mn$^{2+}$. The spectral shape for the annealed film was nearly identical to the previous results of LCeMO films with $T_C = 260$ K. Since it has been theoretically and experimentally found that Mn$^{2+}$ ion produces the distinct feature at around 640 eV, our spectra confirm the presence of Mn$^{2+}$ within the LCeMO films. Theoretical calculations also demonstrated that the major distinct feature at around 640 eV due to Mn$^{2+}$ is common even varying the crystal field, allowing the comparison between the perovskite manganese and Mn-doped GaAs. It is noted that XMCD measurements are representative of bulk LCeMO films rather than only the surfaces because of the deep probing depth of the method and the use of cap layer. The comparison of the spectral weight of Mn$^{2+}$ peak indicates that the as-grown films have higher Mn$^{2+}$ content than the annealed films. There should be certain relationship between the amount of Mn$^{2+}$ and the Curie temperature since within the framework of the double exchange interaction mechanism, the amount of Mn$^{2+}$, i.e., the carrier density in electron-doped systems, should increase with the Curie temperature. The comparison between films in terms of the $T_C$ and the Mn$^{2+}$ content indicates that the lower the Mn$^{2+}$ content is, the higher the Curie temperature is, as shown in the inset of Fig. 2(a). Therefore our results indicate that the Mn$^{2+}$ component does not increase the Curie temperature of LCeMO films. These XASs indicate that there is no clear evidence for the contribution of Mn$^{2+}$ to the ferromagnetism in LCeMO systems.

The contribution of Mn$^{2+}$ to the ferromagnetism in LCeMO system was further studied by the MCD ($I_\parallel - I_\perp$) spectra as shown in Fig. 2(b). Although there is a significant difference in the Mn$^{2+}$ content, the shapes of the XMCD spectra of the LCeMO thin films were very similar to each other, and almost no characteristic signatures around 640 eV expected for Mn$^{2+}$ component were observed, demonstrating no significant magnetic contribution of Mn$^{2+}$ to the ferromagnetism of LCeMO systems in both as-grown and annealed films. In addition, the MCD spectra of LCeMO thin films were similar to that of (La, Sr)MnO$_3$ (LSMO) (spin-aligned Mn$^{3+}$ and Mn$^{4+}$). Further comparisons are shown in Fig. 2(c) as the difference between LCeMO and LSMO in the MCD spectra. Clearly the subtracted spectra were not consistent with the spectra of (Ga, Mn)As, which is the MCD reference of Mn$^{2+}$ induced ferromagnetism. Since above MCD measurements were performed at 100 K relatively near $T_C$ around 150 K, the MCD measurement at 20 K well below $T_C$ was performed for as-grown LCeMO film. The MCD
spectra were shown in Fig. 2. It can be seen that the major trend of MCD was independent of the temperature for MCD measurements. This suggests that the major origin of ferromagnetism in the LCeMO films is due to the double exchange interaction between Mn$^{3+}$ and Mn$^{4+}$ even in the presence of Mn$^{2+}$. Chang et al. discussed experimentally and theoretically the hole-type nature of LCeMO ferromagnetism even with the proper Ce doping. In addition to their interpretations based on the magnetotransport, XAS spectra, and optical reflectance data, our present XMCD data gave the direct experimental evidences to support the hole-type nature of the LCeMO ferromagnetism even in the presence of Mn$^{2+}$. We can thus conclude that the magnetic contribution of Mn$^{2+}$ to the ferromagnetism is rather negligible, considering all the observed facts including (i) the absence of correlation between the amount of Mn$^{2+}$ in the XAS spectra and the Curie temperature

FIG. 2. (Color online) Mn 2p$^{3/2}$ XAS and XMCD spectra of LCeMO films. (a) XAS spectra of LCeMO films in comparison with the spectra of (Ga,Mn)As film as the Mn$^{3+}$ reference and LSMO single crystal as the reference of hole-doped manganites. The inset shows the relationship between the relative intensity of Mn$^{2+}$ at the photon energy around 640 eV and the Curie temperature $T_C$. (b) XMCD spectra of LCeMO films, (Ga,Mn)As film, and LSMO single crystal. The photon energy around 640 eV, corresponding to the magnetic contribution of Mn$^{2+}$, is shown as the line for the comparison. The inset shows the relationship between the relative intensity of Mn$^{2+}$ at the photon energy around 640 eV and the Curie temperature $T_C$. (c) Difference between LCeMO films and LSMO in the MCD spectra. The significant discrepancy between the subtracted spectra and the spectra of (Ga,Mn)As film as the Mn$^{2+}$ reference was seen. (d) Comparison of MCD spectra measured at 20 and 100 K using as-grown LCeMO film. The spectra showed the same trend even at 20 K well below the Curie temperature $T_C$. 
temperature, (ii) no characteristic signatures of the presence of Mn\(^{2+}\) in the XMCD spectra, and (iii) the similarity of the XMCD spectra with those of hole-doped mananites. Thus this study gives the direct experimental evidence for the speculation in some previous investigations,\(^{10-14}\) which the formation of Ce-rich nanoclusters, the resultant La-deficient La\(_{1-x}\)MnO\(_3\), and/or overoxidized La\(_{1-x}\)MnO\(_3\)\(_{2+y}\) (Ref. 23) are responsible for the ferromagnetism of LCeMO films. The ferromagnetism arising from the self-hole doping effects on LaMnO\(_3\) is well known phenomena.\(^{19}\) The experimental findings in the present XMCD measurements highlight that such self-hole doping is crucial on emerging ferromagnetism in LCeMO systems. In addition the robustness of the Mn\(^{3+}\) and Mn\(^{4+}\) network even in the presence of Mn\(^{2+}\) is also indicated, in contrast to the theoretical calculation\(^8\) that predicts the existence of ferromagnetism based on a double exchange interaction between Mn\(^{2+}\) and Mn\(^{3+}\). In order to explore such mechanism, investigating an experimentally ideal system, in which the self-hole doping, i.e., Mn\(^{2+}\), is negligible as the theoretical prediction assumed, is essential to clarify the role of Mn\(^{2+}\) on the magnetism.

IV. CONCLUSION

We have investigated the ferromagnetism in LCeMO systems by measuring both XAS and XMCD. The XAS spectra clearly demonstrated the presence of Mn\(^{2+}\) within the films, while the amount of Mn\(^{2+}\) did not correlate to the Curie temperature. More crucially XMCD measurements showed no characteristic features due to Mn\(^{2+}\), indicating the minor contribution of Mn\(^{2+}\) on the ferromagnetism. These experimental findings highlight that the origin of ferromagnetism in LCeMO is a double exchange interaction between Mn\(^{3+}\) and Mn\(^{4+}\) due to self-hole doping effects even in the presence of Mn\(^{2+}\).