Anisotropic O 2p-Mn 3d unoccupied states in La$_{1-x}$MnO$_3$: an X-ray absorption spectroscopy study

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Abstract

We have studied La$_{1-x}$MnO$_3$ thin films, which show the metal–insulator transition similar to La$_{1-x}$Ca$_x$MnO$_3$. The transport and magnetic properties are measured. X-ray absorption spectroscopy is employed to investigate the electronic structure. Surprisingly, the electronic structure of La$_{1-x}$MnO$_3$ shows large anisotropy. Our results suggest that La$_{1-x}$MnO$_3$ is unique among manganites.

Keywords: CMR; XANES

Colossal magnetoresistance (CMR) manganites have generated much interest of research and potential applications recently. From scientific point of view, these compounds belong to a novel strongly correlated system in which phonons, carriers, and magnetism strongly interact with each other. For example, the coexistence of ferromagnetic transition and the metal–insulator transition is conventionally explained by the mechanism of double exchange (plus polarons). To further investigate these interesting and profound phenomena in this system, the understanding of the electronic structure is definitely indispensable. Recently, XANES studies on CMR manganites have provided valuable information of the electronic states in this system [1,2]. These studies suggest that the CMR manganites are charge-transfer materials. The transport properties are closely related to the carriers with a significant O 2p character.

Self-doped La$_{1-x}$MnO$_3$ shows the metal–insulator transition similar to the well-known La$_{1-x}$Ca$_x$MnO$_3$. This metal–insulator transition and the associated magnetic ordering are supposed to be due to the La deficiency in the lattice [3]. It is presumed that the mechanism for the magnetic ordering and the metal–insulator transition is the same in both La$_{1-x}$MnO$_3$ and La$_{1-x}$Ca$_x$MnO$_3$. However, the electronic structure of La$_{1-x}$MnO$_3$ is actually much less investigated. Therefore, we have conducted studies of La$_{1-x}$MnO$_3$ to shed light on its electronic structure.

La$_{0.8}$MnO$_3$ and La$_{0.7}$MnO$_3$ targets with nominal compositions were made by the standard solid state reaction method. Thin films were deposited on LaAlO$_3$ (100) substrates by laser pulsed ablation. A KrF excimer laser was employed. The substrate temperature was kept at 750°C during deposition and the oxygen partial pressure was 250 mTorr. Thickness of both films is about 300 nm. X-ray diffraction patterns of 2θ scan in Fig. 1 show that both films are highly textured. This allows the studies of the crystalline direction dependence of the electronic structure by the polarized X-ray absorption near edge structure (XANES). The XANES in florescence mode is a powerful tool to investigate the unoccupied (hole) electronic states in complex materials and is bulk sensitive. In particular, polarized XANES can give information about the anisotropy of the electronic structure. Energy resolution of the monochromator is about 0.1 eV for the O K-edge energy range. The saturation (or “self-absorption”) effects were corrected for all measured spectra. The spectra were...
taken at room temperature, and normalized to the tabulated standard absorption cross section in the energy range from 600 to 620 eV.

Both La$_{1-x}$MnO$_3$ thin films show the metal–insulator transition and the associated ferromagnetic ordering. The temperature of the maximum resistivity $T_p$ is 267 and 282 K for $x = 0.2$ and 0.3, respectively. Fig. 2 shows both resistivity $\rho$ and magnetization $M$ for La$_{0.8}$MnO$_3$. It can be seen that $T_p$ and the Curie temperature $T_C$ is nearly identical. The same correlation was observed in La$_{0.7}$MnO$_3$. This identification between $T_p$ and $T_C$ is curious since La$_{1-x}$MnO$_3$ is considered as a disorder system due to La deficiency. In disordered manganite, $T_p$ is usually significantly lower than $T_C$. [4].

The spectra of O K-edge XANES in Fig. 3 show another intriguing results. These spectra correspond to O 2p character mixed with the conduction band. The main peaks are assigned to be associated with O 2p-Mn 3d, O 2p-La 5d, and O 2p-Mn 4sp hybridization around 530, 535, and 543 eV, respectively. The spectrum with $E_{\parallel}ab$ or $E_{\parallel}c$ provides the information of the crystalline dependence of the electronic structure. As shown in Fig. 3, the spectra show certain degree of anisotropy. Especially, the O 2p-Mn 3d band, which is presumably responsible for the transport and magnetic properties, is

- **Fig. 1.** 20 X-ray diffraction patterns show well oriented (001) La$_{1-x}$MnO$_3$ thin films.

- **Fig. 2.** The metal–insulator transition in La$_{1-x}$MnO$_3$ is associated with a ferromagnetic ordering. The applied field for magnetization measurements is 10 Oe.

- **Fig. 3.** XANES of La$_{1-x}$MnO$_3$ for both $E_{\parallel}ab$ and $E_{\parallel}c$. (a) $x = 0.2$; (b) $x = 0.3$. 


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highly anisotropic. Although the spectra cannot resolve whether there are changes of the shape of the peak around 530 eV, the intensity for $E||c$ is clearly larger. Naively, it can be interpreted as that there are more hybridized unoccupied states along the “c-axis” direction. This is surprising. Though with a rhombohedral structure in the bulk form [3], $\text{La}_{1-x}\text{MnO}_3$ is thought to be cubic when deposited into thin films [5,6]. Actually, even for pseudocubic or rhombohedral $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (and other manganites), the electronic structure are considered to be isotropic since the $\alpha$ angle for the rhombohedral structure of all these manganites is very close to 60°. Detailed structure studies of our $\text{La}_{1-x}\text{MnO}_3$ thin films are currently underway. X-ray absorption near edge structure was also measured for a $\text{LaMnO}_3$ thin film (not shown). Indeed, nearly identical spectra were observed. It is likely that the anisotropic electronic structure of $\text{La}_{1-x}\text{MnO}_3$ is due to the lattice distortion induced by the La deficiency. When the lattice is distorted, the bond angle of Mn–O–Mn becomes smaller. However, the decrease in the bond angle along $ab$ is faster than that along $c$, thus leads to the anisotropy of the electronic structure. It would be interesting to see if the anisotropy manifests itself in the magnetotransport anisotropy. This work is currently underway.

To conclude, we have investigated the properties of $\text{La}_{1-x}\text{MnO}_3$ by magnetic, transport, and XANES measurements. Especially, XANES reveals the anisotropic electronic structure in $\text{La}_{1-x}\text{MnO}_3$. This anisotropy, together with other properties, suggests that $\text{La}_{1-x}\text{MnO}_3$ is probably unique among manganites.

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References