Introduction

La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) has attracted considerable attention over recent years due to not only its exotic chemical and physical properties in various complex phases but also its great potential for a variety of applications. LSMO is widely regarded as a useful material in practical areas such as spintronics and energy device materials because the perovskite manganite structure results in the colossal magnetoresistance (CMR) effect and half-metal properties with potential applications to magnetic memory devices.\(^1,2\) Furthermore, some hole-doped LSMO materials exhibit high Curie temperatures ($T_c$) above room temperature.\(^3\) LSMO also possesses a high conductivity and good thermal expansion coefficient, making it a suitable cathode material for commercial solid oxide fuel cells (SOFCs).\(^4,5\) In addition, the Jahn–Teller (JT) distortion forms polarons above the $T_c$ ($= 370 \text{ K}$), as changing the electronic and atomic structures is associated with the conductivity of materials.\(^6\) With respect to physical properties, the complex phases of hole-doped manganites have numerous different ground states caused by competing internal degrees of freedom and applied parameters such as temperature, electric field, magnetic field, and strain.\(^7,8\) The exotic phases include various magnetic and electronic phases, a hole-doping metal–insulator transition, and a Griffiths phase.\(^1,9,10\)

LSMO has complex electronic and magnetic ground states such as the paramagnetic insulating (PMI) phase, ferromagnetic metallic (FMM) phase, and ferromagnetic insulating (FMI) phase.\(^11,12\) In particular, the nature of the FMI phase is not well understood compared with that of the FMM phase, which can be described using the double-exchange model. Furthermore, the relationships between the applied parameters and the resulting magnetic states are not yet well established. To further investigate the FMI phase of La$_{1-x}$Sr$_x$MnO$_3$, the low-doping region ($x \leq 0.15$) is interesting since the exotic FMI phase is stabilized under these conditions. Thus, this material represents a very attractive model for exploring the correlation between the crystal structure and magnetism.

In an effort to elucidate the interplay between the crystal structure and magnetism of perovskite oxides, numerous studies have investigated the thickness dependence of the structural, electrical, and magnetic properties of epitaxial thin films such as BiFeO$_3$, LiFe$_5$O$_8$, and La$_{1-x}$Sr$_x$MnO$_3$.\(^11-14\) However, the FMI phase of La$_{0.88}$Sr$_{0.12}$MnO$_3$ has not been adequately investigated. Few studies were conducted partially with transport measurements.\(^11,17\)

In this work, we report on the exotic magnetic properties caused by substrate-effected strain from two distinct substrates with various experimental methods. Since the applied parameters can be conveniently used to tune the physical properties such as crystallographic structure and magnetism of epitaxial LSMO thin films,\(^6,7\) we performed structural characterization, X-ray spectroscopy, and magnetic measurements to observe the effects of substrate-effected strain on the films.

Strain-effected physical properties of ferromagnetic insulating La$_{0.88}$Sr$_{0.12}$MnO$_3$ thin films

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The functional perovskite La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) possesses various exotic phases owing to competing physical parameters and internal degrees of freedom. In particular, the nature of the ferromagnetic insulating phase (FMI) has not been adequately explored, resulting in a limited understanding of the relationship between crystal structure and magnetism. To investigate this structure–property relationship, epitaxial La$_{0.88}$Sr$_{0.12}$MnO$_3$ thin films were grown on two different substrates, (001) SrTiO$_3$ and (001) (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$, by pulsed laser deposition. Element-specific and surface-sensitive techniques were applied in conjunction with bulk magnetometry to investigate the inextricable link between the structures and magnetic properties of the films and the effects of tuning the strain. The results unambiguously demonstrate that structure–property relationship of a FMI LSMO tuned by strain has a crucial role for manipulating the properties in the FMI regime.

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**Experimental**

**Sample preparation**

Lightly doped manganite La$_{0.88}$Sr$_{0.12}$MnO$_3$ belongs to the space group $Pbnm$ and its lattice parameters are $a = 5.5425$ Å, $b = 5.5346$ Å, and $c = 7.7857$ Å. We grew epitaxial thin films of (001) orthorhombic La$_{0.88}$Sr$_{0.12}$MnO$_3$ on cubic (001) SrTiO$_3$ ($STO$, $a = 3.905$ Å) and (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT, $a = 3.868$ Å) single-crystal substrates by pulsed laser deposition (Q-switched pulsed Nd:YAG laser with $\lambda = 355$ nm). The laser fluence was 0.62 J cm$^{-2}$. We used a La$_{0.88}$Sr$_{0.12}$MnO$_3$ target from Toshiba, Japan. The growth conditions were 600°C at 100 mTorr of an oxygen partial pressure. We also optimized the growth process by using a 300 Torr oxygen partial pressure to remove oxygen vacancies upon cooling.

**Characterization of thin films**

To examine the crystal structural properties of the epitaxial LSMO thin films deposited on single-crystal STO and LSAT substrates, we performed X-ray reflectivity (XRR) and X-ray diffraction (XRD) measurements with a wavelength ($\lambda$) of 1.54 Å using a high-resolution X-ray diffractometer (HR-XRD, SmartLab, Rigaku). Fig. 1(a) and (b) show the XRR patterns for the epitaxial LSMO/STO and LSMO/LSAT films, respectively. The results revealed a well-defined film thickness of 17 nm on STO and 18 nm on LSAT, allowing a reasonable comparison to be made between the two films owing to their similar thickness. Fig. 1(c) and (d) show the XRD patterns, which clearly demonstrated that the films were epitaxial and free from impurities. Since the crystal structure of LSMO is orthorhombic, based on a pseudocubic model, the lattice constant for an LSMO thin film is 3.916 Å. As the lattice constants of the substrates are 3.905 Å for STO and 3.868 Å for LSAT, the lattice mismatches were $-0.28%$ for LSMO/STO and $-1.24%$ for LSMO/LSAT, where the negative sign indicates compressive strain.

To confirm the existence of substrate-effected strain in the LSMO films, we used the reciprocal space mapping (RSM) method. The RSM measurements were performed for the (103) STO and (103) LSAT substrates. Fig. 2(a) and (b) show the corresponding RSM images. The results clearly confirmed that the epitaxial LSMO films exhibited the same in-plane lattice constants for each substrate, indicating the presence of compressive substrate-effected strain in the epitaxial thin films.

**Results and discussion**

The temperature and field dependences of the magnetization were measured using a superconducting quantum interference device (SQUID) magnetometer. We used an applied magnetic field of 100 Oe and field cooling to clearly observe the $T_c$ in the temperature dependence of magnetization ($M$–$T$) curves for the epitaxial LSMO/LSAT and LSMO/STO thin films. The applied magnetic field is perpendicularly to the plane of thin films. Fig. 3(a) shows that the $T_c$ values were 170 K and 190 K for the LSMO/LSAT and LSMO/STO films, respectively. It should be noted that an anomaly of magnetization was observed for the LSMO/LSAT film, in that the magnetization initially increased up to $\sim$106 K and thereafter decreased. The low temperature behavior of LSMO on LSAT is reminding us of spin glass and/or cluster glass. However, in this work, we have focused on biaxial substrate-induced strain effect on magnetism. This indicates that charge-orbital ordering (COO) occurred in this film. Since the in-plane compressive strain reduces the bond distance of Mn$^{3+}$–O$^{2-}$–Mn$^{4+}$ by stretching the MnO$_6$ octahedra in the out-of-plane direction, the value of $T_c$ decreases owing to the stronger double exchange. Furthermore, elongation of the MnO$_6$ octahedra also stimulate the competition of the internal degrees of freedom and shift the $T_c$ to a lower temperature. This is caused by the stabilization of the $d_{3z^2}$ with reduced
ferromagnetic interaction in the $ab$ plane since $T_c$ links inex- 
tricably to delocalize the $e_g$ orbitals.$^{17,21}$

Fig. 3(b) shows the magnetization as a function of the 
applied field ($M$–$H$ hysteresis loops), which was measured at 80 
K in the fully FMI phase for both substrates below their $T_c$. 
These loops revealed distinct differences in the saturated 
magnetic moments ($M_s$) of the two films. The magnetization of 
the epitaxial LSMO thin film grown on STO was smaller than 
that of the LSMO film grown on LSAT. This implies that 
a greater compressive strain leads to a higher $M_s$. This means 
that the in-plane compressive strain can control magnetic 
properties. It should also be noted that, as shown in the inset of 
Fig. 3(b), the coercive field was higher for LSMO/LSAT than for 
LSMO/STO. This may also be the result of the complex competi-
tion between the COO and JT interactions.

We also measured resistivity as a function of temperature as 
shown Fig. 3(c). These curves indicate that the thin films show 
indeed insulator behavior. Also, note that there are little humps, 
pointed by arrows, around 170 K on LSMO/LSAT and 190 K 
around on LSMO/STO. These present that there is the ferro-
magnetic phase transition which agrees well to the result of 
magnetization measurements in terms of temperature shown in 
Fig. 3(a).

To examine the influence of the substrate-e
 effic
ted strain on 
the magnetic properties of the films, we performed X-ray 
magnetic circular dichroism (XMCD) with X-ray absorption 
spectroscopy (XAS) on the 2A beamline of Pohang Accelerator 
Laboratory. The XAS and XMCD spectra were obtained in total 
electron yield mode using an elliptically polarized undulator. 
XAS and XMCD are very powerful techniques for studying the 
electronic and magnetic structures of transition-metal mate-
rials owing to their element-specific excitation.$^{22,23}$ XAS provides 
direct information concerning the valence states of transition-
metal materials such as Mn ions, because the core electrons 
in the 2p orbitals are excited to the 3d orbitals upon absorp-
tion.$^{22}$ XMCD is a unique tool for separately determining the 
spin and orbital magnetic moments for the element-specific 
moment.$^{24–26}$

For these experiments, the base pressure of the experimental 
chamber was maintained below $5 \times 10^{-10}$ Torr during the 
measurements. The applied temperature was 80 K for consis-
tency with the $M$–$H$ measurements. To obtain the XMCD 
spectra, an external magnetic field of $H \approx 0.7$ T was applied in 
the out-of-plane direction of the sample. The applied field 
direction is the same to the SQUID measurement. The field was 
flipped to be parallel ($\mu_+$) and antiparallel ($\mu_-$) to the circularly 
polarized photon helicity.$^{25,27}$ Then, the dichroism ($\Delta \mu = \mu_+ - 
\mu_-$) was calculated from the difference between the two values at 
each data point. The XAS spectra were normalized for compar-
ison of the XMCD results. Fig. 4 presents the obtained Mn $L_{2,3}$
edge spectra of the FMI LSMO thin films on the two substrates, 
illustrating the XAS and XMCD spectra of the Mn ions in the 
LSMO/STO and LSMO/LSAT thin films. From the XAS results, 
Mn $L_{2,3}$-edge spectra are roughly 641.95 eV. This confirms that 
our samples were well grown as La$_{0.88}$Sr$_{0.12}$MnO$_3$ since the $x$ of 
Sr in the thin films is 0.12 in good agreement with the spectra of 
various Sr concentrations studied by Abbate et al.$^{25}$

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Fig. 3 (a) Magnetization curves as a function of temperature, obtained 
at an applied magnetic field of 100 Oe. COO occurred in the epitaxial 
LSMO/LSAT thin film, as revealed by the anomalous increase in 
magnetization up to $\sim$106 K and subsequent decrease, which was not 
observed for the epitaxial LSMO/STO thin film. (b) Magnetic hysteresis 
loops of the LSMO films under different in-plane compressive strains 
at 80 K. The magnetization of LSMO/LSAT is greater than that of 
LSMO/STO, which implies that increased compressive strain reduces 
the magnetization. (c) Resistivity vs. temperature curves of LSMO thin 
films.
SQUID measurements expected. The Mn and neglected in this analysis.

LSMO/LSAT

Fig. 4 Mn L$_{2,3}$-edge XAS and XMCD spectra of the epitaxial thin films of (a) LSMO/STO and (b) LSMO/LSAT. The XAS spectra were normalized to allow easier comparison of the XMCD results for the two samples. The dichroism is $\Delta \mu = \mu_+ - \mu_-$. Both spectra were recorded at 80 K in the presence of an external magnetic field of approximately 0.7 T.

According to the XMCD sum rules, the spin magnetic moment $M_{\text{spin}}$ and orbital magnetic moment $M_{\text{orb}}$ can be expressed as follows:

$$M_{\text{spin}} = -\frac{6p - 4q}{r} \times (10 - n_{3d}) \left(1 - \frac{7(T_2)}{2(S_2)}\right)^{-1}, \quad (1)$$

$$M_{\text{orb}} = -\frac{4q}{3r} \times (10 - n_{3d}), \quad (2)$$

where $p = \int \Delta u dE$, $q = \int_{L_1}^{L_2} \Delta u dE$, and $r = \int_{L_1}^{L_2} (\mu_+ + \mu_-) dE$.

$L_1$ and $L_2$ are the integration range, and $n_{3d}$ is the occupation number of 3d electrons in a Mn ion. The $(T_2)/S_2$ term can be neglected in this analysis. Here, we select $n_{3d} = 4$ since Mn$^{3+}$ is the dominant ion influencing the magnetic structure in La$_{0.88}$Sr$_{0.12}$MnO$_3$ films. For the LSMO/STO film, $M_{\text{spin}}$ and $M_{\text{orb}}$ were estimated to be 1.44 $\mu_b$/Mn and $-1.71 \times 10^{-2}$ $\mu_b$/Mn, respectively. These give $M_{\text{orb}}/M_{\text{spin}} = -1.19 \times 10^{-2}$. For the LSMO/LSAT film, $M_{\text{spin}}$ and $M_{\text{orb}}$ were estimated to be 1.50 $\mu_b$/Mn and $-1.51 \times 10^{-2}$ $\mu_b$/Mn, respectively. These give $M_{\text{orb}}/M_{\text{spin}} = -1.01 \times 10^{-2}$. The negative sign indicates that the spin and orbital moments are antiparallel to each other as a result of Hund’s rule. The spin magnetic moments are comparable to the results of the $M$–$H$ measurements and in the same order as expected. The $M_s$ values were approximately 1.06 $\mu_b$/Mn for the LSMO/STO film and 1.29 $\mu_b$/Mn for the LSMO/LSAT film. These are summarized in Table 1.

As demonstrated by the XMCD results, the different spin magnetic moments of the Mn ions on the two substrates correspond to the degree of compressive strain effected by the substrates. These are in good agreement with the SQUID results. With a bulk measurement of SQUID, the results of XMCD supports strongly to the structure–property relationship. Unlike the FMM of LSMO, the FMI cannot be explained simply by using the double-exchange interaction, as mentioned earlier in the text. Instead, the situation is more complicated as the long-range COO must be considered, since an epitaxial La$_{0.88}$Sr$_{0.12}$MnO$_3$ film on a substrate is a lightly doped manganite with lattice distortion. Previous studies reported that the COO of lightly doped La$_{1-x}$Sr$_x$MnO$_3$ is associated with lattice distortion and the result of a complex interplay between electron–electron correlation, double exchange, and JT distortion in the Mn$^{3+}$–O$^2$–Mn$^{4+}$ bond. This can apply to our material model in this work. The orbital configuration associated with the electronic structure is related to the competition between these factors in the FMI phase. This causes a change in the magnetic structure of the epitaxial thin film. Thus, our results indicate that a large compressive strain effected by a substrate presents the COO transition with the JT distortion and the structure deformation. Like the $M$–$H$ curves shown in Fig. 3(b), the XMCD results similarly demonstrated that the $M_{\text{spin}}$ of the LSMO/LSAT thin film was larger than that of the LSMO/STO film. In contrast, the opposite was true for the orbital magnetic moments, where the $M_{\text{orb}}$ of LSMO/LSAT was smaller than that of LSMO/STO (Table 1). A large in-plane compressive strain gives rise to distortion of the MnO$_6$ octahedra, resulting in different magnetic properties.

Consequently, this implies that a large compressive strain can afford unconventional properties with the electron configuration dependent on the complex interactions between the COO, JT distortion, and structural deformation. The consistent experimental results obtained from the bulk measurements and the surface-sensitive techniques support the idea that lattice distortion is intrinsically linked to magnetism in the FMI phase of La$_{0.88}$Sr$_{0.12}$MnO$_3$ as a result of the complex interactions discussed above.

**Conclusions**

In summary, we have used X-ray spectroscopy and magnetic measurements to examine the magnetic structures of FMI La$_{0.88}$Sr$_{0.12}$MnO$_3$ thin films, which are a potential model for the

| Lattice mismatch | $M_s$ ($\mu_b$/Mn) | $M_{\text{spin}}$ ($\mu_b$/Mn) | $M_{\text{orb}}$ ($\mu_b$/Mn) | $M_{\text{orb}}/M_{\text{spin}}$ |
|-----------------|-------------------|---------------------|---------------------|---------------------|
| LSMO/STO        | -0.28%            | 1.06                | 1.44                | -1.71 $\times 10^{-2}$ |
| LSMO/LSAT       | -1.24%            | 1.29                | 1.50                | -1.51 $\times 10^{-2}$ |

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FMI phase of LSMO at low temperature. The structural deformation of the epitaxial thin films grown on two different substrates effected changes in the magnetic properties. Our results indicate an inextricable link between crystal structure and physical properties, particularly magnetic properties. In the epitaxial LSMO thin films, a large compressive strain caused displacement of the MnO$_6$ octahedra in the out-of-plane direction and suppressed it in the in-plane direction. Distortion of the MnO$_6$ octahedra influenced the double-exchange interaction in Mn$^{3+}$-O$^-$-Mn$^{4+}$ via a complex interplay with COO and JT distortion. This structural deformation links degrees of freedom such as spin, charge, and orbital in the lightly doped La$_{1-x}$Sr$_x$MnO$_3$. The correlation between the structural, electrical, and magnetic properties can be explained by the competition between the COO, JT distortion, and double-exchange interaction. This study provides an opportunity to improve our understanding of the nature of the FMI phase of LSMO. There are no conflicts of interest to declare.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 A. P. Ramirez, J. Phys.: Condens. Matter, 1997, 9, 8171.
2 J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh and T. Venkatesan, Nature, 1998, 392, 794.
3 A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido and Y. Tokura, Phys. Rev. B: Condens. Matter Mater. Phys., 1995, 51, 14103.
4 S. P. Jiang, J. Mater. Sci., 2008, 43, 6799.
5 J. Sacanell, J. H. Sánchez, A. E. R. López, H. Martinelli, J. Siepe, A. G. Leyva, V. Ferrari, D. Juan, M. Pruneda, A. M. Gómez and D. G. Lamas, J. Phys. Chem. C, 2017, 121, 6533.
6 N. Mannella, A. Rosenhahn, C. H. Booth, S. Marchesini, B. S. Mun, S.-H. Yang, K. ibrahim, Y. Tomioka and C. S. Fadley, Phys. Rev. Lett., 2004, 92, 166401.
7 M. B. Salamon and M. Jaime, Rev. Mod. Phys., 2001, 73, 583.
8 M. Uehara, S. Mori, C. H. Chen and S. W. Cheong, Nature, 1999, 399, 560.
9 J. Deisenhofer, D. Braak, H.-A. Krug von Nidda, J. Hemberger, R. M. Eremina, V. A. Ivanshin, A. M. Balbashov, G. Jug, A. Loidl, T. Kimura and Y. Tokura, Phys. Rev. Lett., 2005, 95, 257202.
10 M. Paraskevopoulos, F. Mayr, J. Hemberger, A. Loidl, R. Heichele, D. Maurer, V. Müller, A. A. Mukhin and A. M. Balbashov, J. Phys.: Condens. Matter, 2000, 12, 3993.
11 Y. Endoh, K. Hirota, S. Ishihara, S. Okamoto, Y. Murakami, A. Nishizawa, T. Fukuda, H. Kimura, H. Nojiri, K. Kaneko and S. Maekawa, Phys. Rev. Lett., 1999, 82, 4328.
12 H. Nojiri, K. Kaneko, M. Motokawa, K. Hirota, Y. Endoh and K. Takahashi, Phys. Rev. B: Condens. Matter Mater. Phys., 1999, 60, 4142.
13 D. S. Rana, K. Takahashi, K. R. Mavani, I. Kawayama, H. Murakami, M. Tonouchi, T. Yanagida, H. Tanaka and T. Kawai, Phys. Rev. B: Condens. Matter Mater. Phys., 2007, 75, 060405.
14 R. Prasad, H. K. Singh, M. P. Singh, W. Prellier, P. K. Siwach and A. Kaur, J. Appl. Phys., 2008, 103, 083906.
15 R. Zhang, M. Liu, L. Lu, S.-B. Mi and H. Wang, J. Mater. Chem., 2015, 3, 5598.
16 P. Dey, T. K. Nath and A. Taraphder, Appl. Phys. Lett., 2007, 91, 012511.
17 L. Hu, Z. Sheng, X. Hu, R. Zhang, B. Wang, W. Song and Y. Sun, J. Phys. D: Appl. Phys., 2012, 45, 175002.
18 D. E. Cox, T. Iglesias, E. Moshipolou, K. Hirota, K. Takahashi and Y. Endoh, Phys. Rev. B: Condens. Matter Mater. Phys., 2001, 64, 024431.
19 E. Dagotto, New J. Phys., 2005, 7, 67.
20 B. Dabrowski, X. Xiong, Z. Bukowski, R. Dybzinski, P. W. Klamut, J. E. Siewenie, O. Chmaissem, J. Shaffer, C. W. Kimball, J. D. Jorgensen and S. Short, Phys. Rev. B: Condens. Matter Mater. Phys., 1999, 60, 7006.
21 A. Sadoc, B. Mercey, C. Simon, D. Grebille, W. Prellier and M.-B. Lepetit, Phys. Rev. Lett., 2010, 104, 046804.
22 F. M. F. de Groot, J. C. Fuggle, B. T. Thole and G. A. Sawatzky, Phys. Rev. B: Condens. Matter Mater. Phys., 1990, 42, 5459.
23 M. Abbate, F. M. F. de Groot, J. C. Fuggle, A. Fujimori, O. Strebels, F. Lopez, M. Domke, G. Kaindl, G. A. Sawatzky, M. Takano, Y. Takeda, H. Eisaki and S. Uchida, Phys. Rev. B: Condens. Matter Mater. Phys., 1992, 46, 4511.
24 B. T. Thole, P. Carra, F. Sette and G. van der Laan, Phys. Rev. Lett., 1992, 68, 493.
25 C. T. Chen, Y. U. Idzerda, H.-J. Lin, N. V. Smith, G. Meigs, E. Chaban, G. H. Ho, E. Pellegrin and F. Sette, Phys. Rev. Lett., 1995, 75, 152.
26 Y. Teramura, A. Tanaka, B. T. Thole and T. Jo, J. Phys. Soc. Jpn., 1996, 65, 3056.
27 J.-Y. Kim, T. Y. Koo and J.-H. Park, Phys. Rev. Lett., 2006, 96, 047205.
28 S. Uhlenbruck, R. Teipen, R. Klingeler, B. Büchner, O. Friedt, M. Hücke, T. Kierspel, T. Niemöller, L. Pinsard, A. Revcolevschi and R. Gross, Phys. Rev. Lett., 1999, 82, 185.