Anomalous strain effect in La$_{0.8}$Ba$_{0.2}$MnO$_3$ epitaxial thin film: Role of the orbital degree of freedom in stabilizing ferromagnetism

Teruo Kanki, Hidekazu Tanaka, and Tomoji Kawai*

Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka, 567-00476 Japan

We achieved enhancement of colossal magnetoresistance at room temperature in a tensile strained La$_{0.8}$Ba$_{0.2}$MnO$_3$ thin film (52% at 297 K under an applied field of 0.8 T). Surprisingly, the tensile strain increased the Curie temperature T_C from 270 K in the bulk to 320 K in the thin film. While it is well known that tensile strain decreases T_C through a decrease of the transfer integral t_0 in (La, D)MnO$_3$ (D = Ca or Sr), this unprecedented anomalous strain effect in La$_{0.8}$Ba$_{0.2}$MnO$_3$ films could not be explained by t_0 alone; the orbital degree of freedom also needed to be considered. We successfully derived an equation for T_C including both effects in the strained thin films.

I. INTRODUCTION

Mn perovskite oxides [(La$_{1-x}M_x$)MnO$_3$ with M = Ba, Ca, Sr, etc.] have been attracting attention due to various physical phenomena. Among these phenomena, the colossal magnetoresistance (CMR) effect is not only greatly useful for various industrial applications, but also very interesting in physics. Their ferromagnetism with metallic conduction has been explained within the framework of a double-exchange mechanism[1] on the basis of Hund coupling between the localized t_{2g}^3 ($S_{t_{2g}} = \frac{3}{2}$) spins and the conductive e_g spins. The e_g electron hops while coupling ferromagnetically with the localized t_{2g} spins. It has consequently been recognized that the spin and charge degrees of freedom are important. In addition, the e_g electrons have to occupy either the $d_{x^2-y^2}$ orbital or the $d_{3z^2-r^2}$ orbital in the e_g orbital. As a recent result, the orbital degree of freedom has been acknowledged to be one of the most important factors of magnetic and transport properties. The appearance of various antiferromagnetic states owing to a large number of carriers occupied with either the $d_{3z^2-r^2}$ or $d_{x^2-y^2}$ orbitals has been confirmed by experiment[2-4] and theory.[5,6] In advanced ideas, the orbital degree of freedom should strongly relate to the phase-transition temperature in one magnetic state, including ferromagnetic state. The strained thin-film technique is greatly useful for controlling the degree of that freedom. From the viewpoint of the control of electron transfer, it has been reported in many papers that tensile strain generally induces a decrease in Curie temperature (T_C) in (La,Sr)MnO$_3$ (Refs. 7–9) and (La,Ca)MnO$_3$ (Refs. 10 and 11) thin films deposited on substrates with a different lattice constant. This is explained by a decrease in electron transfer due to stretched Mn-O bond lengths along the in-plane direction. However, we have found that T_C increases in tensile-strained La$_{0.8}$Ba$_{0.2}$MnO$_3$ (abreviated LBMO hereafter) thin films,[12] leading to a very large CMR effect at room temperature. It is not possible to explain this anomalous strain effect in LBMO thin films using just the transfer integral. It is necessary to consider a combination of both the transfer integral and the orbital degree of freedom for a satisfactory explanation.

In this paper, we report the discovery of enhanced ferromagnetism in tensile-strained LBMO films, including (La,Sr)MnO$_3$, (La,Ca)MnO$_3$, and (La,Ba)MnO$_3$, and systematically discuss the expanded theory on the change of T_C induced by a tensile-strain effect, making it clear that double-exchange ferromagnetism is greatly influenced by the orbital degree of freedom, especially in the (La,Ba)MnO$_3$ system.

II. EXPERIMENT

The strained LBMO (d = 3.891 Å) films were fabricated on SrTiO$_3$(001) (d = 3.905 Å) (abbreviated STO hereafter) substrates or on a Sr$_{0.8}$Ba$_{0.2}$TiO$_3$ (d = 3.933 Å) (abbreviated SBTO hereafter) buffer layer for adjustment of lattice mismatch, using a pulsed laser deposition (PLD) technique (ArF excimer, λ = 193 nm). STO and SBTO gave a lattice mismatch of 0.3% and 1.0%, respectively, to the LBMO layer, to induce tensile strain. The target used was a sintered LBMO pellet prepared using a conventional solid reaction process. La$_2$O$_3$, Mn$_2$O$_3$, and BaO powders were mixed and calcined in air at 900 °C for 40 h and then reground and sintered at 1300 °C for 24 h.[13] LBMO was deposited at a substrate temperature of 750 °C in an O$_2$ gas pressure of 1.0×10^{-1} Pa. The film thickness was varied from 4000 to 200 Å. After formation, the films were annealed at 900 °C for 10–15 h in an O$_2$ atmosphere at 1 atm. The film structure was examined using x-ray diffraction and reflection high-energy electron diffraction (RHEED), and it was confirmed that films had been epitaxially grown with no additional impurity phase.[12] The temperature dependence of magnetization was measured using a superconducting quantum-interference device magnetometer (SQUID). The resistivity and magnetoresistance effect of the polycrystal and films were measured along the in-plane direction using the standard four-probe method under a magnetic field (H) of 8000 Oe. The magnetoresistance (MR) ratio is defined as [$R(0) - R(H)$]/$R(H) \times 100\%$.

III. RESULTS AND DISCUSSION

A. Thickness dependence of magnetic and electrical transport properties

Figure 1(a) shows the temperature dependence of magnetization (M-T curve) for bulk LBMO and the films of vari-
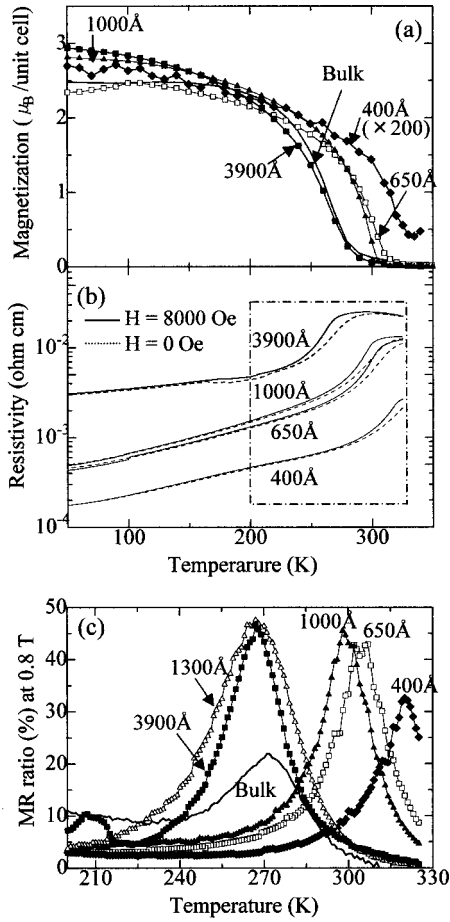
FIG. 1. (a) Temperature dependence of magnetization for the LBMO bulk sample and thin films on STO substrates with various thicknesses (0.3% tensile strain) at an applied magnetic field of 100 Oe, (b) resistivity of thin films under a field of 0 and 8000 Oe, and (c) the MR ratio at an applied field of 8000 Oe for the bulk and the films with ■, 3900 Å; △, 1300 Å; ▲, 1000 Å; □, 650 Å; and ◆, 400 Å thickness.
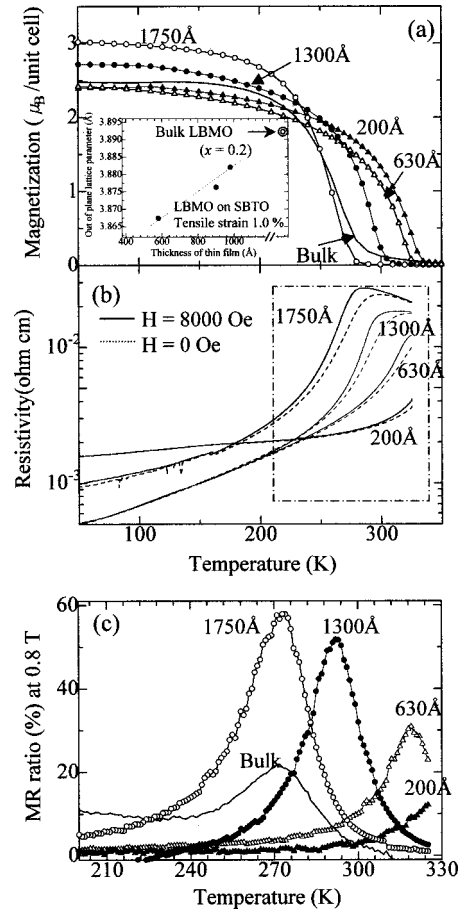

FIG. 2. (a) Temperature dependence of magnetization for LBMO bulk sample and thin films on SBTO buffer layers with various thicknesses (1.0% tensile strain) at an applied magnetic field of 100 Oe. The inset shows out-of-plane lattice parameters for LBMO/SBTO/LSAT thin films as functions of thickness. (b) Resistivity of thin films under a field of 0 or 8000 Oe. (c) The MR ratio at an applied field of 8000 Oe for the bulk and the thin films with ○, 1750 Å; ●, 1300 Å; △, 630 Å; and ▲, 200 Å thickness.

ous thicknesses. The T_C values of the bulk, 3900-Å, 1000-Å, 650-Å, and 400-Å thick films were found to be 271, 267, 298, 307, and 320 K, respectively. Figure 1(b) shows the temperature dependence of resistivity for each film. The LBMO thin films have two noticeable characteristic features. The first is that the MR effect is over twice as large as that of polycrystal bulk, as shown Fig. 1(c) (21% at 271 K in the polycrystal bulk, 48% at 267 K in the 3900-Å thick film). The low grain boundary and fine magnetic homogeneity in the thin films induce enhancement of the MR effect. The second and most important feature is that T_C (and the maximum MR temperature T_{MR}) systematically increases with decreasing thickness of the LBMO layer (from 267 K at 1300–3900 Å to 320 K at 400 Å). It is construed that the 0.3% lattice mismatch between the STO substrate and LBMO layer induces an increase of T_C through the deformation of the LBMO lattice structure. We fabricated large strained LBMO thin films with a tensile strain of up to 1.0% on a SBTO buffer layer on a STO substrate in order to verify the effect of strain on the increase in T_C. Figure 2(a) shows the M-T curve for the LBMO thin film with a tensile strain

of 1.0%. It was also found that T_C increases with decreasing thickness of the LBMO layer. Figure 2(b) shows the temperature dependence of resistivity. The metal-insulator transition temperature increases and resistivity decreases with decreasing thickness. Figure 2(c) shows the temperature dependence of the MR ratio at 0.8 T. It was also found that the MR ratio was enhanced for thin films and T_{MR} increased with decreasing thickness (from 273 K at 1750 Å to 329 K at 200 Å).

B. Anomalous strain effect on the LBMO thin films

Figure 3 shows the dependence of T_C on the thickness of LBMO layers with different tensile strains (0.3% and 1.0%). T_C of the 1.0% tensile-strained films is higher than that of 0.3%, compared to both strained films for the same degree of thickness. The tensile-strain effect is therefore the essential factor in the increase of T_C. In the enhancement of T_C by a combination with tensile strain, the Gong *et al.* result in (La,Ca)MnO$_3$/SrRuO$_3$ superlattice is interesting.[14] However,

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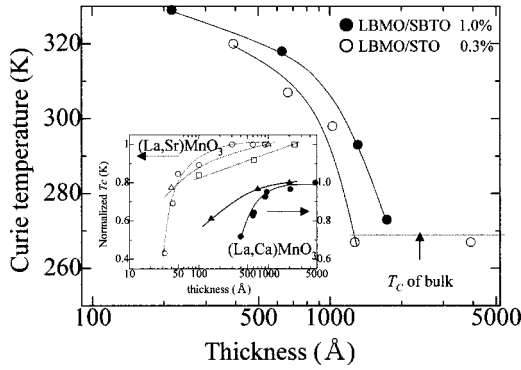
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FIG. 3. T_C of LBMO thin films deposited on STO and LBMO thin films deposited on SBTO on STO as a function of thickness. The inset shows T_C of (La$_{1-x}$Sr$_x$)MnO$_3$ [□, $x = 0.1$ (Ref. 7); ○, $x = 0.25$ (Ref. 8); and △, $x = 0.4$ (Ref. 9)] and (La$_{1-x}$Ca$_x$)MnO$_3$ [●, $x = 0.33$ (Ref. 11) and ▲, $x = 0.33$ (Ref. 10)] thin films with tensile lattice strain as a function of thickness.

their superlattice was composed of two ferromagnetic materials so that neighboring magnetic order through the interface strongly influenced the magnetic property of (La,Ca)MnO$_3$, as already reported in several papers.[15-17] The interface magnetic interaction between Ru and Mn is ferromagnetic, judging from the work in Ref. 18 on the (La,Ca)(Mn,Ru)O$_3$ solid solution, leading to enhancement of T_C in the superlattice. On the other hand, there are many reports showing that tensile strain reduces ferromagnetism in (La,Sr)MnO$_3$ and (La,Ca)MnO$_3$ (Refs. 7–11) by using nonmagnetic counterparts. Therefore, enhancement of T_C by tensile strain alone in LBMO thin films is extremely unique. We also show a lattice change through strain on LBMO thin films. The inset in Fig. 2(a) shows the thickness dependence of the c-axis lattice parameter of LBMO films deposited on the SBTO buffer layer/LSAT [(LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$] ($d = 3.868$ Å) substrate (1.0% lattice mismatch). It was found that the c axis decreases with decreasing thickness, which indirectly means extending the lattice parameter in the in-plane (x-y) direction and indicates an increase of the tensile-strain effect. Normally, the tensile-strain effect induces a decrease of T_C in the (La,Sr)MnO$_3$ (Refs. 7–9) and (La,Ca)MnO$_3$ (Refs. 10 and 11) films as shown in the inset of Fig. 3. T_C of these films decreases with decreasing thickness (i.e., increasing effective tensile strain). This is caused by a decrease of the transfer integral on in-plane e_g electrons. A theory considering only the transfer integral cannot possibly explain this anomalous strain effect on LBMO thin films. We therefore developed a theory including not only the transfer integral but also the orbital degree of freedom, which occupies either the $d_{x^2-y^2}$ orbital or the $d_{3z^2-r^2}$ orbital.

C. Mechanism of T_C enhancement by the tensile-strain effect

According to Zener,[1] T_C in double-exchange ferromagnetism is proportional to the transfer integral between neighboring Mn ions through the oxygen pass. Considering the orbital degree of freedom T_C is given as follows:

TABLE I. d-d transfer intensities $[\alpha(\gamma)\alpha(\gamma')]$ for the x-y direction and z direction. γ is the transfer from the d orbital to the p orbital and γ' is the transfer from the p orbital to the d orbital. $|x^2-y^2\rangle$ and $|3z^2-r^2\rangle$ show e_g orbitals occupied with the focused carrier.

γ \ γ'	Out-of-plane (z direction)		In-plane (x-y direction)	
	$|x^2-y^2\rangle$	$|3z^2-r^2\rangle$	$|x^2-y^2\rangle$	$|3z^2-r^2\rangle$
$|x^2-y^2\rangle$	0	0	3/4	$\sqrt{3}/4$
$|3z^2-r^2\rangle$	0	1^a	$\sqrt{3}/4$	1/4

^{a}A definition as regulation value.

$$T_C \propto t_{d\text{-}d} = \sum_{\langle i,j \rangle} \alpha(\gamma_i)\alpha(\gamma'_j)t_0 \quad (t_0 \propto V_{pd}^2). \quad (1)$$

Here, $\alpha(\gamma)$ is the intensity of the e_g electron transfer from the d_γ orbital in Mn ion ($\gamma = |x^2-y^2\rangle$ or $\gamma = |3z^2-r^2\rangle$) to oxygen p orbital, and $\alpha(\gamma')$ is that from the oxygen p orbital to the d_γ orbital in the neighboring Mn ion ($\gamma' = |x^2-y^2\rangle$ or $\gamma' = |3z^2-r^2\rangle$). The intensities $\alpha(\gamma)\alpha(\gamma')$ are given in Table I. V_{pd} is the matrix element between p and d orbitals, and according to Harison[19] is proportional to $d_{\text{Mn-O}}^{-7/2}$.

In the tensile-strained perovskite film on STO(001) substrate, the Mn-O bond length along [100] and [010] orientations (in-plane direction, d_{in}) becomes longer and that along the [001] orientation (out-of-plane direction, d_{out}) becomes shorter, as shown in Fig. 4(a). Considering four Mn-O bonds along the in-plane direction, the two bonds along the out-of-plane direction, and the ratio of electron occupancy in each e_g orbital ($n_{x^2-y^2}$ for the $d_{x^2-y^2}$ orbital, $n_{3z^2-r^2} = 1 - n_{x^2-y^2}$ for the $d_{3z^2-r^2}$ orbital), Eq. (1) is expanded as follows:

$$T_C \propto t_{d\text{-}d} \propto \frac{1}{6}(4\{n_{x^2-y^2}\alpha(\gamma = |x^2-y^2\rangle)[\alpha(\gamma' = |x^2-y^2\rangle)$$
$$+ \alpha(\gamma' = |3z^2-r^2\rangle)]\} + (1-n_{x^2-y^2})\alpha(\gamma = |3z^2-r^2\rangle)$$
$$\times [\alpha(\gamma' = |x^2-y^2\rangle) + \alpha(\gamma' = |3z^2-r^2\rangle)]d_{\text{in}}^{-7} + 2$$
$$\times (1-n_{x^2-y^2})\alpha(\gamma = |3z^2-r^2\rangle)\alpha(\gamma' = |3z^2-r^2\rangle)d_{\text{out}}^{-7}). \quad (2)$$

Using the intensities of electron transfer depending on the type of orbital in Table I, we are able to develop the following equation on the assumption of constant cell volume of $2d_{\text{out}} = V_0/(2d_{\text{in}})^2$:

$$T_C \propto t_{d\text{-}d} \propto \left\{ (1+\sqrt{3}+2n_{x^2-y^2})d_{\text{in}}^{-7} \right.$$
$$\left. + 2(1-n_{x^2-y^2})\left(\frac{V_0}{8d_{\text{in}}^2}\right)^{-7} \right\}\frac{1}{6}. \quad (3)$$

The electron occupancy ($n_{x^2-y^2}$) is a function of lattice structure (d_{in}), and we examined its relationship by a molecular orbitals calculation using discrete variational $X\alpha$-
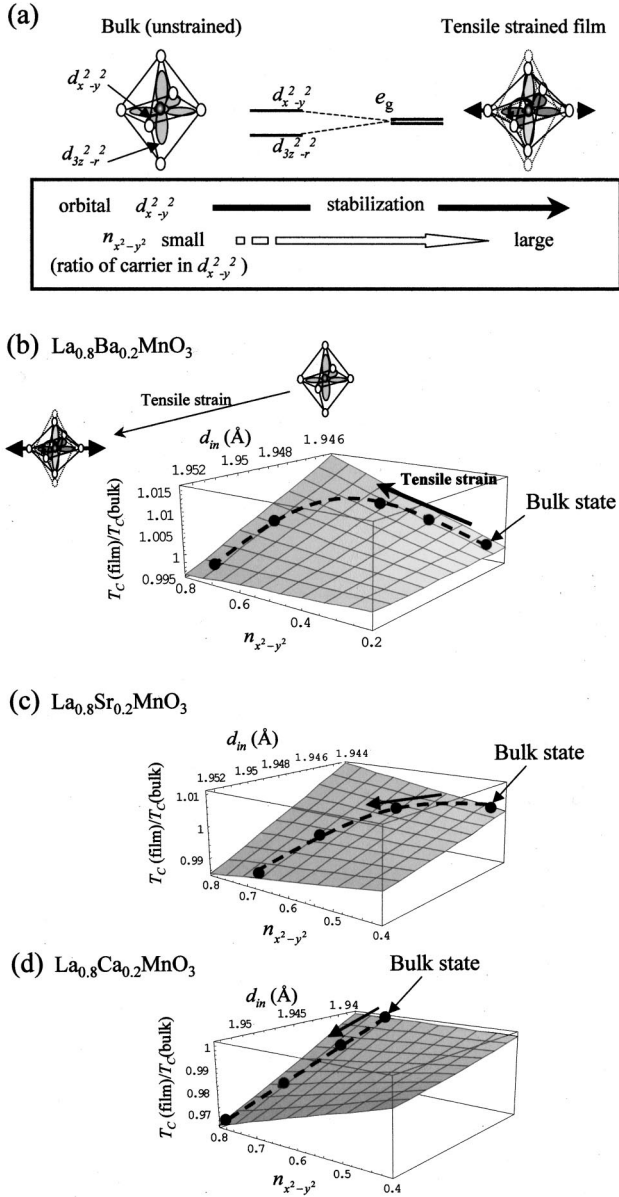
TABLE II. Lattice parameters for each bulk Mn perovskite oxides. The Mn-O bond lengths are given as $d_{in} = a^*/2$ and $d_{out} = c/2$.

Lattice parameter	$a/\sqrt{2}$	$b/\sqrt{2}$	c	V_0	c/a^{*a}
$La_{0.8}Ba_{0.2}MnO_3$	3.8904	3.8907	3.9267	59.4360	1.0093
$La_{0.8}Sr_{0.2}MnO_3$	3.8780	3.8958	3.9137	59.1278	1.0069
$La_{0.8}Ca_{0.2}MnO_3$	3.8725	3.8795	3.8795	58.2831	1.0009

$^a a^* = (a+b)/2\sqrt{2}$.

Table II. Remarkably, the calculated T_C of $La_{0.8}Ba_{0.2}MnO_3$ also increases with an increase of the in-plane bond length d_{in}, whereas that of $La_{0.8}Sr_{0.2}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$ decreases. Equation (3) shows good agreement with experimental results on strain effect. Bulk LBMO has a relatively large c/a ratio, so electron occupancy in the $d_{3z^2-r^2}$ orbital is larger than that in the $d_{x^2-y^2}$ orbital. With increasing tensile strain, the $d_{x^2-y^2}$ orbital with a large transfer intensity is gradually stabilized, and then the electron occupancy $n_{x^2-y^2}$ becomes large, leading to an increase of T_C. Conversely, the decrease in the transfer integral itself induces a decrease in T_C ($\propto d_{in}^{-7}$). Nevertheless, judging from the $\Delta T_C \propto -\Delta d_{in}/d_{in}^8$ equation, the magnitude of the decrease is relatively small in the $(La,Ba)MnO_3$ system with a larger bond length in comparison with $(La,Sr)MnO_3$ and $(La,Ca)MnO_3$. The elongation of the in-plane bond length, which corresponds to the tensile strain, induces a decrease of T_C in the case of $La_{0.8}Sr_{0.2}MnO_3$ and remarkably in the case of $La_{0.8}Ca_{0.2}MnO_3$, as shown in Figs. 4(c) and 4(d). In both these cases, the effect of the decrease in the transfer integral is more dominant. Consequently, it is quite reasonable to assert that the T_C of LBMO increases with tensile strain in terms of the orbital degree of freedom.

IV. CONCLUSION

We discovered an anomalous tensile-strain effect that causes a remarkable increase in T_C of $La_{0.8}Ba_{0.2}MnO_3$ thin films, and additionally acquired the valuable result of enhancement of CMR at room temperature (52% at 297 K and 0.8 T). It was found that the orbital degree of freedom is the important factor in determining T_C, showing the influence of the anomalous strain effect in strained LBMO thin films compared with that of $(La,Sr)MnO_3$ and $(La,Ca)MnO_3$ systems.

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FIG. 4. (a) Schematic illustration of the deformation of crystal structure by tensile strain. Tensile strain in the in-plane direction stabilizes the $d_{x^2-y^2}$ orbital, leading to an increase in $n_{x^2-y^2}$. The relationship between the stabilization of the $d_{x^2-y^2}$ orbital and the increase in $n_{x^2-y^2}$ can be quantitatively decided on a one-to-one correspondence. This relationship may be calculated using discrete variational $X\alpha$ techniques (Ref. 20). In the calculation, the Mn-O-Mn bond angle is assumed to be 180°. The calculated T_C are shown on the track of broken lines in the bond length $(d_{in})-n_{x^2-y^2}$ plane of (b) LBMO, (c) $La_{0.8}Sr_{0.2}MnO_3$, and (d) $La_{0.8}Ca_{0.2}MnO_3$ by using Eq. (3). The $n_{x^2-y^2}$ value is obtained with the discrete variational $X\alpha$ method.

techniques.[20] Figures 4(b)−4(d) show the tensile-strain dependence of T_C for $La_{0.8}Ba_{0.2}MnO_3$, $La_{0.8}Sr_{0.2}MnO_3$, and $La_{0.8}Ca_{0.2}MnO_3$ thin films, respectively, using Eq. (3). The structural data of bulk state used in calculation are shown in

*Corresponding author. E-mail address: kawai@sanken.osaka-u.ac.jp

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