Little volume change in orbital ordering transition in manganite thin films

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Abstract. We have investigated the structural feature of orbital-ordering manganite thin films fabricated on the perovskite (011) substrates by means of synchrotron x-ray diffraction technique. Like bulk manganites, these films show large jumps in lattice parameters at the orbital ordering transition temperature, which clearly show the transitions are first order. However, the magnitude of the volume change at the transition temperature for the films is much smaller than that for the orbital ordering transition in bulk manganite. This difference is understood by taking into account the stress from the substrate.

1. Introduction
Many transition metal oxides show various properties that can be used for devices, and thin films made of them are therefore extensively studied with a view to device application. Among the oxides, manganites are one of the most promising materials because of their metal-insulator switching controlled by temperature, magnetic field[1, 2, 3], and photo-irradiation[4, 5]. These properties are known to be related to the orbital occupancy of the 3d electrons, and in manganites, the orbital occupancy is closely related to the lattice strain. Therefore, the property of the epitaxial film is different than that of bulk crystals. The most well studied system is the films fabricated on perovskite (001) substrates[6, 7, 8, 9, 10]. In these systems, metal-insulator transitions are suppressed and, in many cases, the transitions are reported in films whose in-plane lattice parameters are relaxed from the substrates. When we change the orientation of the substrate from (001) to (011), the property changes drastically[11]. The film shows clear first-order metal-insulator transition at almost the same temperature with bulk system. Such orientation dependence of the property is reported in ref.[12]. Only films made on (011) substrate show clear metal-insulator transition, and no clear transitions are observed in films fabricated on (001) or (111) substrates.

The orbital occupancy of the manganites characterized by a periodicity longer than 11Å is best studied by the soft x-ray resonant scattering technique using Mn L-absorption edge[13],

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and ferro-ordering of the orbital occupancy is studied by linear dichroism around Mn $L$-edge, while ordering characterized by an intermediate wavelength cannot be observed through $L$-edge resonance. Because of this limitation in periodicity, an arrangement of the orbital occupancy (orbital ordering) with unknown periodicity is often studied through Jahn-Teller (JT) mode lattice distortion. Nevertheless, detailed structure refinement of the film system is, unlike bulk systems[14, 15], not very simple[16]. Instead of making structure analyses, one can estimate the magnitude of the JT distortion based on the position of the Bragg reflections and characteristic superlattice reflections, together with utilizing the $K$-edge resonant x-ray scattering[17], which is known to reflect the local structure around the Mn ions[16]. Based on such structural studies, it has been clarified that the origin of the substrate-orientation dependent property is the fact that the JT distortion in films on (001) substrate is the elongation mode while that in films on (011) substrate is the shear mode [18], as shown in Fig.1. In the films on (001) substrates (panel (a)), the JT mode distortion for $e_g$ electrons involves a large volume change, while that in films on (011) substrates does not (panel (b)). In this paper, we present the little volume change in the orbital ordering transition in three manganite films fabricated on (011) surfaces of the [(LaAlO$_3$)$_{0.3}$(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$] (LSAT) substrate. LSAT has the cubic perovskite structure with the lattice parameter of 3.87Å, and all the films we used in this study have in-plane lattice parameters locked into the substrate.

![Figure 1. Schematic view of the JT mode lattice distortion in films on (a) (001)-substrate and (b) (011)-substrate. Shear mode strain in films on (011) substrate is a JT mode, while that in films on (001) substrate is not.](image)

2. Experiment

Epitaxial films of Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ (PSMO), Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ (NSMO), and Pr$_{0.55}$(Ca$_{0.8}$Sr$_{0.2}$)$_{0.45}$MnO$_3$ (PCSMO) were grown on (011) surfaces of LSAT substrates using the pulsed laser deposition method[11, 12]. The typical thickness of the samples was 80 nm. X-ray diffraction experiments were carried out on the BL-4C at the Photon Factory, KEK, Japan and on the X22C at the National Synchrotron Light Source, Brookhaven National Laboratory, USA. The beamlines are equipped with four-circle diffractometers connected to closed-cycle refrigerators. The temperature dependence of the lattice parameters was measured for all the samples with x-rays having energies of 9.5keV (Photon Factory) or 6.5keV (NSLS).
3. Results

Temperature dependences of the lattice parameters $a$, $b$ and $c$ in pseudo-cubic notation of the films are shown in Fig. 2. For comparison, those of bulk manganite $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (bulk NSMO) are also shown in panel (d).

The lattice parameters of PSMO shown in panel (a) were obtained from 002, 102, and 012 Bragg reflections in a heating run. This figure shows sudden jumps in $b$ and $c$ lattice parameters around 125 K. Since there was no superlattice reflection, this transition was found to be a ferro-orbital ordering transition\cite{18}. Similarly, there is a clear transition in the lattice parameter of NSMO shown in panel (b). This transition is also a ferro-orbital ordering transition, while the ground state of this film is CE-type orbital ordered structure\cite{18}. The lattice parameters of PCSMO are shown in panel (c). Superlattice reflections corresponding to $\sqrt{2} \times \sqrt{2}$ structure indicates that this transition is antiferro-orbital ordering transition\cite{19}. Panel (d) shows the temperature dependence of the lattice parameters of another antiferro-orbital ordering material, bulk NSMO reported in ref.\cite{20}. Note that in the cubic notation, the lattice parameters $a$ and $b$ are the same because they are the length of the diagonal line for the rectangle defined by $a$ and $b$ for the orthorhombic Pbnm setting. All of the films as well as the bulk NSMO show clear jumps in their lattice parameters by 0.6% to 2% at the orbital ordering temperatures.

![Figure 2](image)

**Figure 2.** Temperature dependence of the lattice parameters of (a) PSMO, (b) NSMO, (c) PCSMO films as well as (d) bulk NSMO\cite{20}. NSMO film has no clear hysteresis, and orbital ordered and disordered phases coexist in this film within a wide temperature range.

Figure 3 shows the temperature dependence of the cell volumes of the films and bulk NSMO in cubic notation. One can obtain extremely precise cell volume for the film system from the
peak position of 011 Bragg reflection, because the in-plane lattice parameters are locked into the substrate. The experimental error of the peak position for PCSMO is the smallest, because the distance between the 011 Bragg reflections for the film and the substrate is the largest, which makes the analysis easier. Only the bulk NSMO shows a clear volume jump at the transition temperature, and the amount is 0.1%. Since all the transitions are first order, finite volume jump is expected at the transition points. However, no noticeable amount of the volume jumps were observed in the three films, while the bulk crystal system show finite volume jump as expected. Therefore, there must be a mechanism to suppress the volume jump in the film system. We discuss the origin of this lack of the volume jump in the film systems in the next section.

Figure 3. Temperature dependence of the cell volume of PSMO, NSMO, PCSMO films as well as bulk NSMO[20].

4. Discussion
As mentioned above, the origin of the orientation dependent properties is that the JT distortion is the shear mode in films on (011) substrate[18]. The orbital ordered state is stabilized by a large JT mode distortion, which are called $q_2$ or $q_3$ modes presented in Fig.4. Other modes of distortion are, at least to the first order, decoupled from the orbital occupancy; From energetic point of view, they only contribute to an elastic energy. The volume change is the distortion having $A_{1g}$ symmetry, in other words, breathing mode or $q_1$ mode distortion. The $q_1$ mode distortion decouples from JT mode distortion in films on (011) substrates. This makes the transition easier. By contrast, the $q_1$ mode distortion couples with JT mode in the films on (001) substrate in order to lock the in-plane lattice parameter to the substrate; The same amount of $q_1$ distortion with $q_3$ mode is required to keep the in-plane lattice parameters constant. This strong coupling makes the transition very hard. Despite this difficulty, one exception is recently reported: narrow-bandwidth material Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ film on LSAT(001) substrate[21]. This transition was attributed to the similarity of the LSAT lattice parameter with $a$ and $b$ of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ in ordered phases, and treated as an example of a strain assisted ordered structure.

Next, we focus on the little volume change in the orbital ordering transition. The decoupling of the $q_1$ and JT mode distortions in films on (011) substrate itself does not explain the little volume change. The strain energy $\Delta E$ is written as $1/2 \cdot \sum_i K Q_i^2$, where $K$ is the elastic constant.
and $Q_i$ is the magnitude of the lattice distortion corresponding to the mode $q_i$. Although $Q_2$ and $Q_3$ are very small in the orbital disordered phase, $Q_1$ is large in the orbital disordered phase in the film system. For example, film NSMO has larger volume than bulk NSMO by 0.6%. This volume difference is a good measure of $Q_1$ in the orbital disordered phase. At the transition temperature, the volume can be changed by the first order transition. The $\Delta E$ caused by this volume change is related to the specific latent heat of this transition. The amount of the volume change of the bulk NSMO is 0.1% from zero strain. The magnitude of $\Delta E$ corresponding to this strain is comparable to the $\Delta E$ caused by the volume change from 0.6% to 0.61%, which is too small to be observed by our experiment. This is the reason why the film systems do not show any volume jump in the transition. In conclusion, the little volume change at the first order transition is caused by the large lattice strain in the high temperature phase.

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References

[1] Tokura Y, Urushibara A, Moritomo Y, Arima T, Asamitsu A, Kido G and Furukawa N 1994 J. Phys. Soc. Jpn. 63 3931
[2] Tokura Y and Nagaosa N 2000 Science 288 462
[3] Dagotto E 2005 New J. of Phys. 7 67
[4] Miyano K, Tanaka T, Tomioka Y and Tokura Y 1997 Phys. Rev. Lett. 78 4257
[5] Kiryukhin V, Casa D, Hill J P, Keimer B, Vlgliante A, Tomioka Y and Tokura Y 1997 Nature 386 813
[6] Prellier W, Simon C, Haghiri-Gosnet A M, Mercey B and Raveau B 2000 Phys. Rev. B 62 R16337
[7] Prellier W, Haghiri-Gosnet A M, Mercey B, Lecoeur P, Hervieu M, Simon C and Raveau B 2000 Appl. Phys. Lett. 77 1023
[8] Ogimoto Y, Izumi M, Manako T, Kimura T, Tomioka Y, Kawasaki M and Tokura Y 2001 Appl. Phys. Lett. 78 3505
[9] Biswas A, Rajeswari M, Srivastava R C, Venkatesan T, Greene R L, Lu Q, de Lozanne A L and Millis A J 2001 Phys. Rev. B 63 (2001) 184424
[10] Buzin E R, Prellier W, Simon C, Mercone S, Mercey B, Raveau B, Sebek J and Hejtmanek J 2001 Appl. Phys. Lett. 79 647
[11] Ogimoto Y, Nakamura M, Takubo N, Tamraru H, Izumi M and Miyano K 2005 Phys. Rev. B 71 060403(R)
[12] Nakamura M, Ogimoto Y, Tamraru H, Izumi M and Miyano K 2005 Appl. Phys. Lett. 86 182504
[13] Wilkins S B, Spencer P D, Hatton P D, Collins S P, Roper M D, Prabhakaran D and Boothroyd A T 2003 Phys. Rev. Lett. 91 167205
[14] Radaelli P G, Cox D E, Marezio M and Cheong S-W 1997 Phys. Rev. B 55 3015
[15] Okuyama D, Tokunaga Y, Kumai R, Taguchi Y, Arima T and Tokura Y 2009 Phys. Rev. B 80, 064402
[16] Wakabayashi Y, Sawa H, Nakamura M, Izumi M and Miyano K 2004 Phys. Rev. B 69 144414
[17] Materlik G, Sparks C J and Fischer K 1994 Resonant anomalous x-ray scattering: theory and applications (Amsterdam)
[18] Wakabayashi Y, Bizen D, Kubo Y, Nakao H, Murakami Y, Nakamura M, Ogimoto Y, Miyano K and Sawa H 2008 J. Phys. Soc. Jpn. 77, 014712
[19] Wakabayashi Y, Takubo N, Miyano K and Sawa H 2009 Eur. Phys. J. Special Topics 167 67
[20] Shimomura S, Tajima K, Wakabayashi N, Kobayashi S, Kuwahara H and Tokura Y 1999 J. Phys. Soc. Jpn. 68 1943
[21] Okuyama D, Nakamura M, Wakabayashi Y, Itoh H, Kumai R, Yamada H, Taguchi Y, Arima T, Kawasaki M and Tokura Y 2009 Appl. Phys. Lett. 95, 152502