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Phase-separated state in the bilayer manganite investigated by scanning-type resonant soft X-ray scattering

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Abstract. Phase separation between the CE-type charge-orbital ordered (CE) phase and the A-type antiferromagnetic ordered (A-AF) phase has been investigated in the bilayer manganite, $\mathrm{La}_{2-2x}\mathrm{Sr}_{1+2x}\mathrm{Mn}_2\mathrm{O}_7$ ($x = 0.51$), by resonant soft X-ray scattering (RSXS) at the Mn $L_{2,3}$ edge. The order parameters of CE and A-AF phases were measured at 1/4 1/4 0 and 0 0 1 reflections, respectively, and the phase separation was observed at the intermediate temperature region. Using a scanning-type RSXS with an X-ray focused by a Fresnel zone plate, the real-space images of domains for both the competing CE-phase and A-AF-phase were successfully observed. In the phase-separated state, we revealed that the domain of the CE phase forms a stripe pattern, and it seems to originate from the inhomogeneity of the chemical composition on sample.

1 Introduction

In strongly correlated electron system, giant physical responses, such as the colossal magnetoresistance (CMR) effect [1] and the gigantic magnetoelectric effect [2], have been discovered and have attracted much attention. The competition between electronically ordered phases is crucial for these giant responses, and the phase separation has been reported near the boundary between the competing phases [3]. Therefore, observing the domain distributions of the competing phases is essential for understanding the origin of giant response.

Resonant X-ray scattering (RXS) is a powerful tool for observing the spatial ordering of electronic degrees of freedom (i.e., charge, spin, orbital, and multipoles) [4]. Moreover, in the soft X-ray region, the RXS signal at the $L_{2,3}$ edge ($2p \to 3d$ transition) can directly probe the $3d$ electronic state, which is important in understanding the physical properties in $3d$ transition-metal compounds, and the strong RXS signals were reported in various kinds of materials. Thanks to the strong intensity, real-space imaging of the spin texture could be realized by the coherent diffraction imaging technique even at Photon Factory [5, 6], which is an old synchrotron radiation facility.

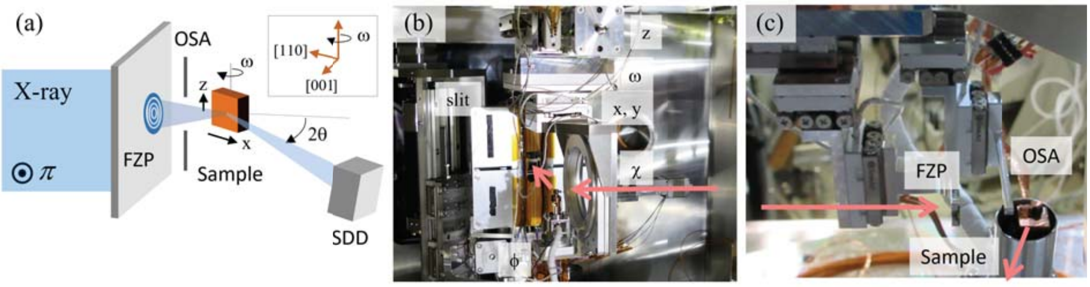

Figure 1: (a) Schematic view of diffractometer for a scanning-type resonant soft X-ray scattering. A Fresnel zone plate (FZP), order sorting aperture (OSA), sample, and silicon drift detector (SDD) are placed. Photographs of (b) four-circle diffractometer, and (c) experimental configuration to observe the signal at the 1/4 1/4 0 reflection.

The hole-doped bilayer manganite, La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$, is a well-known system exhibiting the CMR effect [1], and LaSr$_2$Mn$_2$O$_7$ ($x = 0.5$) exhibits the phase separation between the CE-type charge-orbital ordered (CE) phase and the A-type antiferromagnetic ordered (A-AF) phase [7, 8]. Moreover, it was reported that the order parameters of CE and A-AF phases can be observed by resonant soft X-ray scattering (RSXS) at 1/4 1/4 0 and 0 0 1 reflections, respectively [9]. Hence, it was selected as the first target to measure the spatial distribution of the domains. In this study, a scanning-type soft X-ray diffractometer has been developed by integrating a focusing optical system as shown in Fig. 1(a). Finally, we have succeeded in observing the domain distributions of both the competing CE-phase and A-AF-phase.

2 Experiments

A high-quality single crystal of La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ was grown using the floating-zone method. Here, $x = 0.51$ was selected to achieve half doping, Mn$^{3.5+}$, due to the presence of oxygen vacancies. The lattice constants are $a = 0.387$ nm and $c = 2.003$ nm with the space group $I4/mmm$. The crystal was cleaved parallel to the ab-plane, and (1 1 0) surface cut and polished with a fine emery paper to detect the order parameters of the CE and A-AF phases. RSXS measurements were performed near the Mn $L_{2,3}$ edge at BL-16A [10] and BL-19B, Photon Factory, KEK. A π-polarized X-ray from the APPLE-II type undulator was used. The [110]-[001] plane became the scattering plane as shown in the inset of Fig. 1(a). Hence, the 1/4 1/4 0 and 0 0 1 reflections are observable by the ω-rotation, although we are unable to measure the same region of the sample for both reflections [11].

In order to measure a spatial distribution of the domains, we installed a focusing optics, four-circle

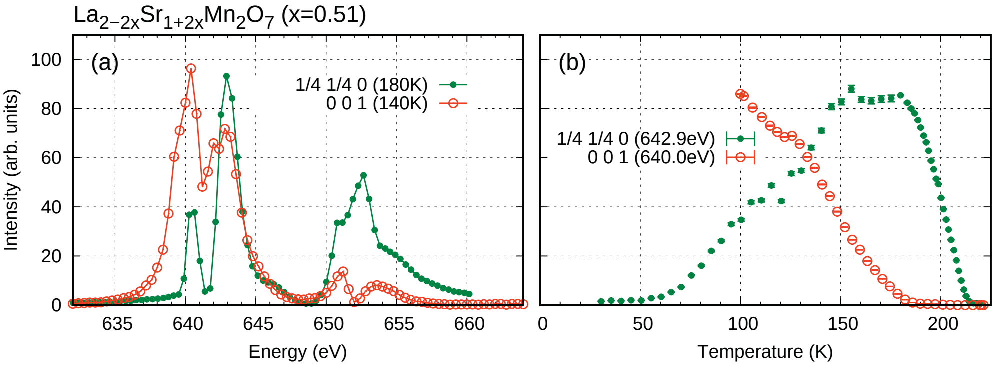

Figure 2: (a) Energy dependence and (b) temperature dependence of the scattering intensity at the 1/4 1/4 0 reflection (CE-phase; green closed circles) and at the 0 0 1 reflection (A-AF-phase; orange open circles).

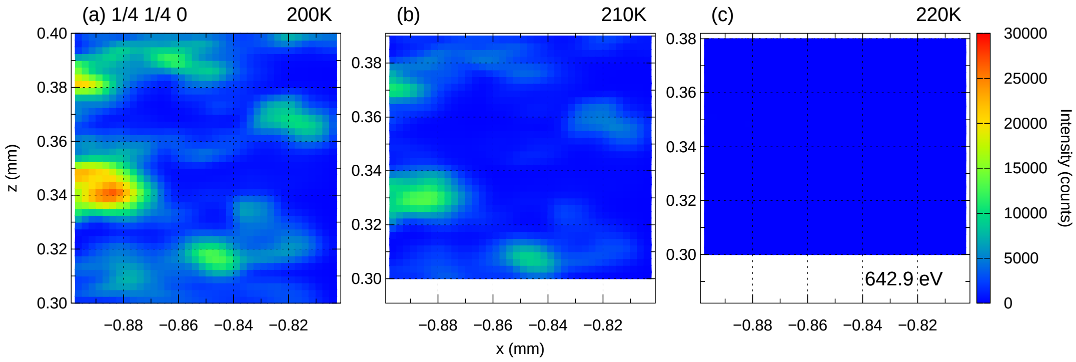

Figure 3: Spatial distribution of the scattering intensity of the 1/4 1/4 0 reflection (a) at 200 K, (b) at 210 K, and (c) at 220 K. The figure roughly compensates for the shift in the z-direction due to the thermal expansion of the cryostat.

diffractometer, and xyz-stages into our in-vacuum diffractometer [12]. Here, the piezo stages were used to scan the sample position on a nanometer resolution as shown in Fig. 1(b). Unfortunately, the z-stage was motor-driven due to weight limitation in this measurement, which limited the resolution to 500 nm. However, we plan to replace it with a high-load piezo stage in the near future. A small cryostat that can be placed on this small diffractometer was also developed, and the lowest temperature is 30 K. A Fresnel zone plate (FZP) is utilized as the focusing optics, and the diameter is 320 μm with the center stop diameter 100 μm. The focal length is $f = 16.5$ mm at 640 eV to maintain a large working distance around the sample, even though the order sorting aperture (OSA) exists in the radiation shield of the cryostat as shown in Fig. 1(c). We selected the size of virtual light source upstream of FZP to efficiently detect the signal by the silicon drift detector (SDD). However, the focused beam size depends on the virtual source size. As a result, the focused beam size was about 3 μm when measuring the CE phase (Fig. 3), and it was about 300 nm when measuring the A-AF phase (Fig. 4). The beam size was estimated by a wire-scan. However, it was difficult to put the sample exactly at the focal point. Hence, the spatial resolution of the intensity map is worse than the beam size.

3 Results and discussion

RXS signals were searched at the 1/4 1/4 0 and 0 0 1 reflections near the Mn $L_{2,3}$ edge, and the energy spectra were measured as shown in Fig. 2(a). The spectra are consistent with the previous report [9], although there are differences in some details. The temperature dependence of the scattering intensity of the 1/4 1/4 0 reflection was observed at 642.9 eV with the cooling process as shown in Fig. 2(b). The signal appears below 215 K and it almost saturates around 180 K. Then, the intensity gradually reduces with decreasing temperature, and almost vanishes at around 50 K. The temperature dependence of the scattering intensity of the 0 0 1 reflection was observed at 640.0 eV with the heating process. The signal disappears at around 180 K ($= T_N^A$). It indicates that the growth of the A-AF phase causes a collapse of the CE phase. Namely, the phase separated state between the CE phase and A-AF phase is expected to emerge in the temperature range of 50 K to 180 K.

In the manganite system, it is noteworthy that the phase-separated state is expected to emerge electronically without any inhomogeneity in the chemical composition on sample [13]. To detect such the electronic competition, we first noted the creation of the CE phase. The spatial distribution of the scattering intensity of the 1/4 1/4 0 reflection was measured at 642.9 eV as shown in Fig. 3. Domains of several tens of micrometers in size could be observed clearly at 200 K. With increase temperature, the intensity become weak uniformly, though the domain position shifts in the z direction due to the thermal expansion of the cryostat. The signal completely disappears at 220 K in this intensity scale. Then the domain distribution was measured with the cooling process. However, we observed nearly the same spatial distribution of domains, although a different domain pattern was expected for each thermal process.

Next, the spatial distribution of the scattering intensity of the 0 0 1 reflection was measured at 640.0 eV as shown in Fig. 4. The signal was strong at the 0 0 1 reflection; therefore, a small pin-hole was used as the virtual light source. Hence, the spatial resolution is better than that of Fig. 3. As the observation region, the large domain of the A-AF phase was selected at 50 K. With increasing temperature, the intensity become weak, and the stripe pattern along the x-direction emerges as shown in Fig. 4(b). In the stripe region at $z \sim 0.03, 0.05$, the intensity almost disappears, namely the A-AF phase is strongly

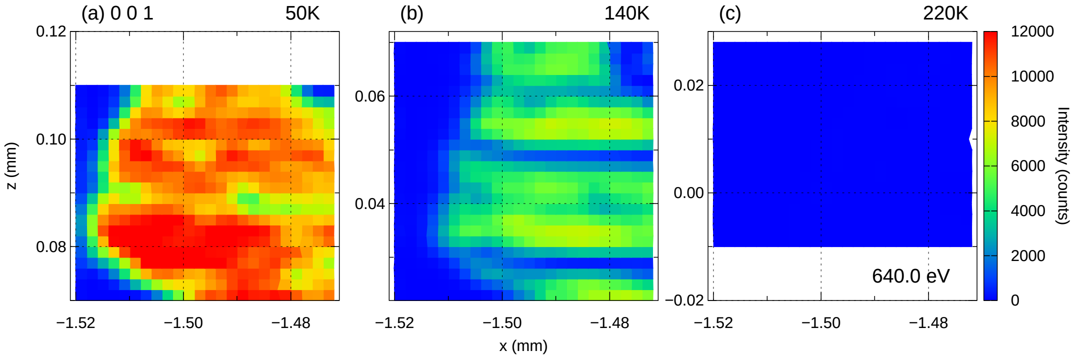

Figure 4: Spatial distribution of the scattering intensity of the 0 0 1 reflection (a) at 50 K, (b) at 140 K, and (c) at 220 K. The figure roughly compensates for the shift in the z-direction due to the thermal expansion of the cryostat.

suppressed. In this temperature region, the phase separation between the CE phase and A-AF phase occurred. Hence, we can think that the A-AF phase changes into the CE phase in the stripe region with increasing temperature from 50 K to 140 K. On the other hand, the scattering intensity of the 0 0 1 reflection monotonically decreases towards T_N^A in the other region. The signal completely disappears at 220 K as shown in Fig. 4(c). Then, with the cooling process, we observed nearly the same spatial distribution of domains again including the stripe pattern. Therefore, these results reveal that the phase-separated pattern at this size scale is independent of the thermal process. A similar stripe structure was reported in the bilayer manganite, and the stripe run perpendicular to the crystal-growth direction [14]. It was discussed to originate from the modulation of chemical compositions or lattice parameters frozen in the process of crystal growth. In present case, the stripes also run perpendicular to the crystal-growth direction. Hence, the observed stripe pattern seems to originate from the inhomogeneity of the chemical composition on sample. To elucidate a purely electronic phase-separated state, it is important to investigate within a stripe region, where the CE phase and A-AF phase compete with each other at the intermediate temperatures.

In conclusion, we have developed a scanning-type soft X-ray diffractometer to investigate the spatial distributions of the domains. Utilizing the RSXS technique, the CE phase and the A-AF phase in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.51$) could be observed at the 1/4 1/4 0 and 0 0 1 reflections, respectively. Moreover, we succeeded in observing the spatial distributions of the domains of the CE and A-AF phase by the scanning-type RSXS. The domain of the CE phase forms the stripe pattern, and consistently appears in the same position on the sample. This may be caused by inhomogeneity in the chemical composition of the sample. Further studies are desired to understand the phase-separated state as a key of the giant responses.

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References

[1] Moritomo Y, Asamitsu A, Kuwahara H and Tokura Y 1996 *Nature* **380** 141

[2] Kimura T, Goto T, Shintani H, Ishizuka K, Arima T and Tokura Y 2003 *Nature* **426** 55

[3] Tokura Y 2006 *Rep. Prog. Phys.* **69** 797

[4] Matsumura Y, Nakao H and Murakami Y 2013 *J. Phys. Soc. Jpn.* **82** 021007

[5] Ukleev V, Yamasaki Y, Morikawa D, Kanazawa N, Okamura Y, Nakao H, Tokura Y and Arima T 2018 *Quantum Beam Sci.* **2** 3

[6] Ukleev V, Yamasaki Y, Morikawa D, Karube K, Shibata K, Tokunaga Y, Okamura Y, Amemiya K, Valvidares M, Nakao H, Taguchi Y, Tokura Y and Arima T 2019 *Phys. Rev. B* **99** 144408

[7] Kubota M, Yoshizawa H, Moritomo Y, Fujioka H, Hirota K and Endoh Y 1999 *J. Phys. Soc. Jpn.* **68** 2202

[8] Wilkins S B, Hatton P D, Prabhakaran D and Boothroyd A T 2003 *Phys. Rev. Lett.* **90** 187201

[9] Wilkins S B, Stojic N, Beale T A W, Binggeli N, Hatton P D, Bencok P, Stanescu S, Mitchell J F, Abbamonte P and Altarelli M 2006 *J. Phys: Condens. Matter* **18** L323

[10] Amemiya K, Sakamaki M, Koide T, Ito K, Tsuchiya K, Harada K, Aoto T, Shioya T, Obina T, Yamamoto S and Kobayashi Y 2013 *J. Phys.: Conf. Ser.* **425** 152015

[11] In RSXS measurements, we can only observe the surface of the sample, because the penetration depth is quite shallow in the soft X-ray region.

[12] Nakao H, Yamasaki Y, Okamoto J, Sudayama T, Takahashi Y, Kobayashi K, Kumai R and Murakami Y 2014 *J. Phys.: Conf. Ser.* **502** 012015

[13] Moreo A, Yunoki S and Dagotto E 1999 *Science* **283** 2034

[14] Tokunaga Y, Tokunaga M and Tamegai T 2005 *Phys Rev. B* **71** 012408