Microscopy of magnetic transition in a layered manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.32$)

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Temperature-dependent magnetic structures in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.32$) are derived from real-space observation based on three-dimensional magnetization vector analysis using spin-polarized scanning electron microscopy. Below 80 K, a flux closure structure is formed at the *ab* surface, indicating ferromagnetic inter-bilayer coupling with magnetization along the *c* axis. The closure domains are turned into larger ones with irregular shapes above 80 K. The drastic domain reconstruction results from the change in inter-bilayer coupling to antiferromagnetic one, accompanied by the magnetization inclined toward the *ab* plane.

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Layered perovskite manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$[1,2] have attracted enormous interest because they exhibit intriguing magneto-electronic properties and also a variety of magnetic structures depending on the hole-doping level x. Especially at around $x=0.3$, the magnetic structure is extremely sensitive to the hole concentration, even accompanying spatial inhomogeneity, and hence the magnetic structures deduced from macroscopic methods are still controversial. So far, neutron diffraction studies have been performed by several groups. At $x\approx 0.30$, the structure has been reported to be a mixture of the major phase of a layered antiferromagnet and a minor phase of a ferromagnet[3,4] or solely a ferromagnet[5,6] at the ground state. At $x\approx 0.32$, the structure changes into a ferromagnet with the easy axis along *c* (Ref. 7) or one that has the easy axis lying in the *ab* plane.[5,6] Furthermore, the inclination of the easy axis toward the *ab* plane with increasing temperature is inferred from results of diffraction studies.[3–6] In turn, such a complex magnetic structure with possible spatial inhomogeneity may offer a challenging arena to test the state-of-art magnetic microscopy.[8] To settle the issue, we have taken a new approach, variable-temperature spin-polarized scanning electron microscopy (spin SEM), which enables the three-dimensional analysis as well as local probing of the magnetization direction over the wide range of temperature. Using this technique, we have reported on the real-space imaging of the layered antiferromagnetic structures formed as the major phase of the crystal with $x=0.30$.[8] This technique is surface sensitive with a typical probing depth of about 1 nm, and hence is quite suitable for probing the layered magnetic structures of this system. In this paper, we present the systematic study on the temperature dependence of the magnetic structures at $x=0.32$. Temperature-dependent phase transition with the drastic reconstruction of the magnetic domain is discussed.

A single crystal was prepared using a floating zone method as reported previously.[1] The crystal was first cooled down to 40 K on the sample stage in the spin SEM observation chamber with the base pressure of 3×10^{-10} Torr, and then cleaved along the *ab* plane to produce a clean surface. After stabilizing the temperature, the images of the secondary electron (SE) intensity as well as of the three magnetization-vector components at the cleaved surface plane were obtained simultaneously. Two of the components are parallel to the *ab* plane and make a right angle to each other. The other is perpendicular to the *ab* plane.

The crystallographic structure of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.32$) is schematically shown in the left drawing of Fig. 1. The basic crystallographic structure of the layered manganite is the alternate stacking of a nonmagnetic insulating $(La,Sr)_2O_2$ layer and a ferromagnetic metallic MnO_2 bilayer sheet along the *c* axis.[1] From the analysis of the magnetic domain structures, we have deduced the magnetic structure depicted in the right drawing of Fig. 1, as will be discussed in detail.

Figure 2 indicates the temperature dependence of the magnetic domain pattern at the cleaved *ab* surface. Figure 2(a) shows the SE intensity image of the observed region at 45 K. The magnetic images were observed while increasing temperature from (b) 45 K up to (h) 110 K. These images were obtained by the in-plane magnetization component parallel to the arrow in Fig. 2(h). The contrast in the magnetic image represents the magnitude of the magnetization component. The component normal to the surface was not detected at any temperature [for the normal component images, see the examples shown in Figs. 3(b) and 4(b), respectively]. Within the narrow band around the middle of the SE intensity image [a region indicated by the open arrows in Fig. 2(a)], the SE yield is partly changed, indicating difference in elemental composition at the surface layer.[9] Considering the reduced magnetic contrast in the corresponding region of the magnetic image, the topmost surface within the region would be the nonmagnetic insulating layer. As shown in the figure, the domain pattern is drastically changed at the temperature higher than, but close to 80 K. Below 80 K, the domain pat-

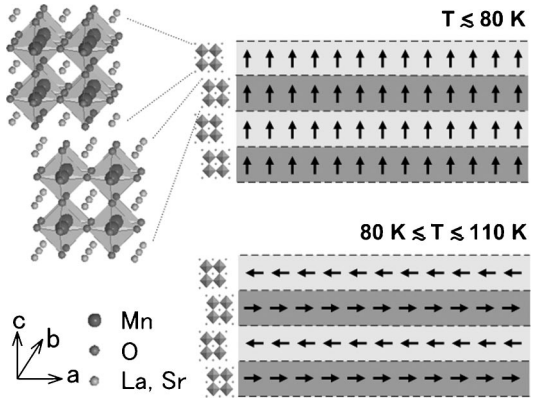

FIG. 1. The schematic diagram of the layered crystallographic structure of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.32$) (left). MnO_6 octahedra are shown in polyhedral representation. The arrows represent the crystallographic direction. Magnetic structures below 80 K (top right) and above 80 K (bottom right) are deduced from the present observation. Ferromagnetically coupled magnetizations within the MnO_2 bilayers are distinguished with different shading.

tern is made up of numerous fine domains with the size of several hundred nanometers. Those domains begin to expand and take round shapes at around 80 K, while keeping the domain structure. Above 80 K, the domains expand to over-micrometer size and take irregular shapes and sizes. The magnetic contrast finally vanishes at around 110 K. The domain reconstruction at around 80 K reflects the variation of the magnetic structure of the material. In the following, we will discuss the details of the characteristic domain structure formed in the respective temperature ranges.

A higher-magnification image was obtained at 65 K to investigate the domain structure developed below 80 K. Figure 3(a) indicates the distribution of the in-plane magnetization direction. The color wheel at the right side of the image represents the relation between the color and the magnetization direction. The similar complex patterns to those shown in Figs. 2(b) and 2(c) are observed ubiquitously also in the other regions examined (not shown). The perpendicular component image is also shown in Fig. 3(b). Since the magnetic contrast cannot be seen in the image, the magnetization in the surface region is completely parallel to the surface plane (*ab* plane). The observed characteristic domain pattern composed of numerous fine domains is typical of the closure domain structure which is produced at the surface of ferromagnetic materials with weak uniaxial magnetic anisotropy perpendicular to the surface.[10] As an example, the anticipated closure structure is schematically illustrated in Fig. 3(c) for the region represented by the white broken line in Fig. 3(a). The magnetization at the surface (thin arrows) is readily laid down to the surface plane due to a demagnetizing field overwhelming the uniaxial anisotropy, and connected to the internal domains with the magnetization perpendicular to the surface plane (thick arrows), forming the complete flux closure structure.[11,12] The magnetization at the surface is rotated by approximately 90 deg. The relatively weak in-plane magnetic anisotropy may originate from fourfold crystallographic anisotropy within the *ab* plane. While the developed closure domains increase the wall energy to some extent, the

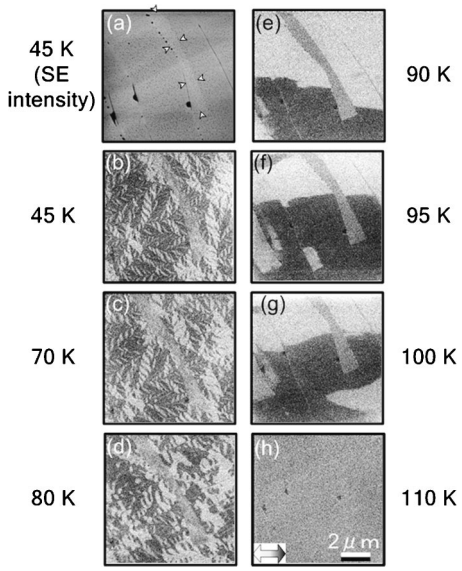

FIG. 2. (a) Secondary electron (SE) intensity and (b)–(h) magnetic images at the cleaved *ab* surface of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.32$) observed by the variable-temperature spin SEM. The images were obtained at temperatures of (a, b) 45 K, (c) 70 K, (d) 80 K, (e) 90 K, (f) 95 K, (g) 100 K, and (h) 110 K, respectively. The magnetic images were recorded with the magnetization component parallel to the arrow in the image (h). The magnetic contrast indicates the magnitude of the magnetization component. Open arrows in (a) represent the nonmagnetic surface region that appeared accidentally upon the cleaving procedure. See text and also compare with the corresponding region observed in the magnetic images, (e)–(g).

domain structure is magnetostatically stable. This is because the structure strictly keeps the continuity of magnetic flux and hence saves the considerable demagnetizing energy. These observations show that the magnetizations within the adjacent MnO_2 bilayers are coupled ferromagnetically across the nonmagnetic $(La,Sr)_2O_2$ layer and aligned along the *c* axis in this temperature range.[13]

As previously shown in Fig. 2, the domain structure drastically changes above 80 K. The domain size increases to over several micrometers. The disappearance of the flux closure structure at the overall surface indicates that the magnetization direction within the internal domain becomes parallel to the surface. These facts mean that the easy axis aligned along the *c* axis below 80 K inclines toward the *ab* plane with increasing temperature. However, an anticipated local flux-closure character within the *ab* plane is not observed at all above 80 K. Such a breaking in flux continuity is more evident in the picture displayed in Fig. 4. Figure 4(a) indicates distribution of the in-plane magnetization direction observed at lower magnification. The region shown in Fig. 2 and its surroundings are included in this picture. The image was obtained at 85 K in another heating run. The color wheel at the right side of Fig. 4(a) represents the magnetization direction. The magnetization is completely parallel to the *ab* plane: no contrast is seen in the perpendicular component image presented in Fig. 4(b). Especially in a single-crystal surface with fourfold crystallographic anisotropy, the local flux closure structure would be expected to consist of the

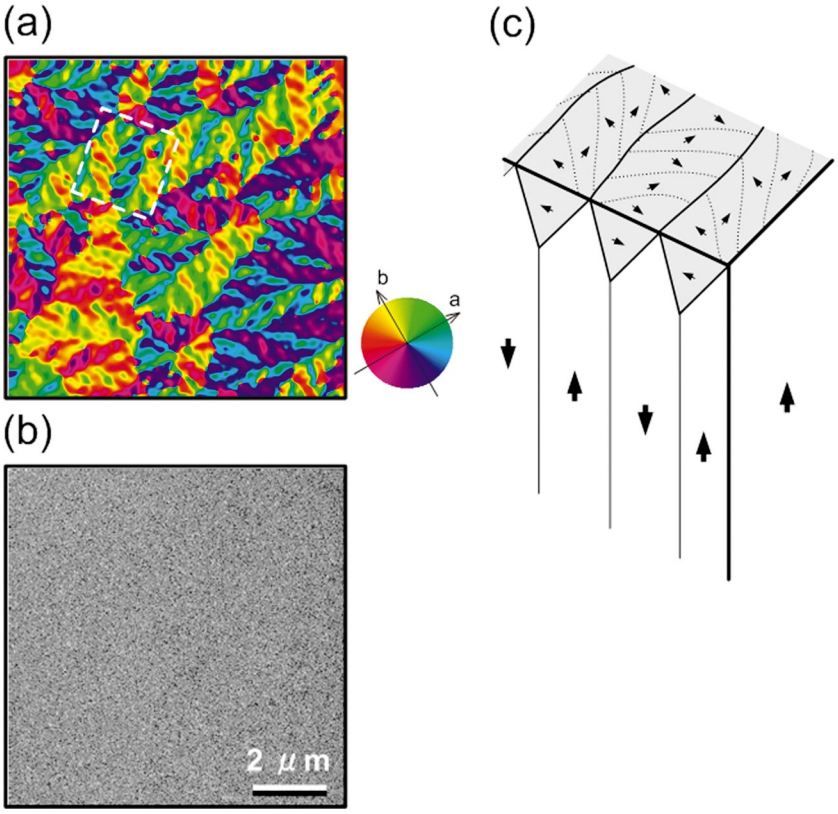

FIG. 3. (Color) (a) In-plane and (b) perpendicular magnetization component images observed at 65 K. The in-plane component image indicates the distribution of the magnetization direction. The color wheel represents the relation between the color and the magnetization direction. The crystallographic axes are indicated in the wheel. (c) Schematic diagram of the observed domain structure toward the bulk inside for the region indicated by the white broken line in (a). Thin and thick arrows in the figure represent the magnetization in the surface and internal regions, respectively.

magnetization aligned along four preferred axes.[11] In reality, however, heads or tails of magnetization meet at the domain boundaries without exhibiting any flux-closure features, as shown in Fig. 4(a). In addition, the domain walls wind, forming domains with irregular shapes and sizes. These peculiar features are observed ubiquitously also in the other regions (not shown). Such an apparently puzzling behavior of the magnetic domain can be elucidated in terms of the layered antiferromagnetic structure, as argued in the following.

Since magnetization is parallel to the surface plane, if the

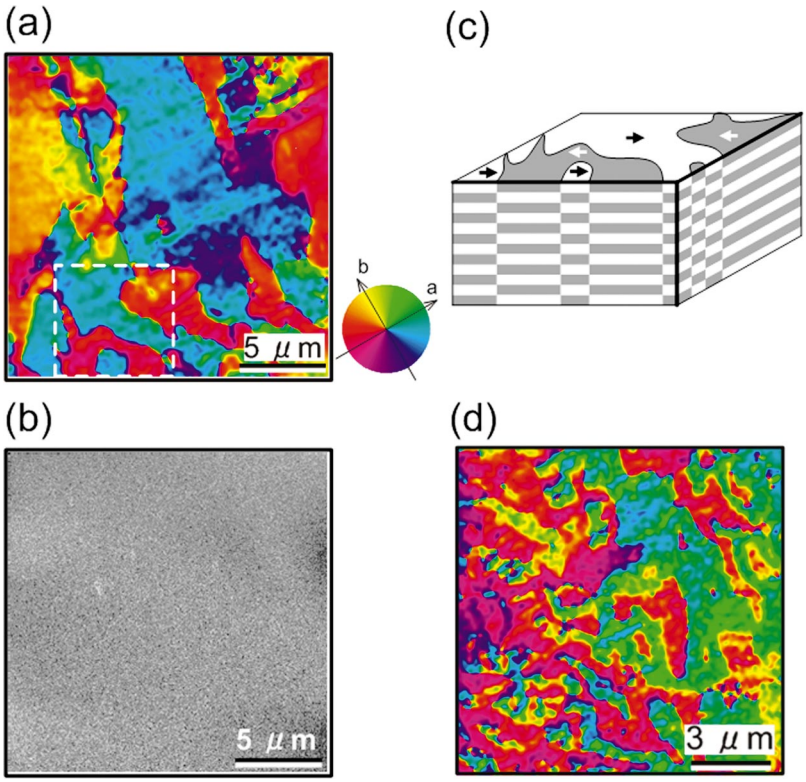

FIG. 4. (Color) (a) In-plane and (b) perpendicular magnetization component images at lower magnification observed at 85 K in a heating run different from that in Fig. 2. The observed area includes that shown in Fig. 2 and its surroundings. The in-plane component image indicates the distribution of the magnetization direction. The color wheel represents the relation between the color and the magnetization direction. The crystallographic axes are indicated in the wheel. (c) The schematic domain structure toward the bulk inside for the region represented by the white broken line in (a). The shading indicates the direction of the magnetization within the MnO_2 bilayers. The magnetization directions are represented by the arrows drawn on the surface plane of the sketch. (d) The distribution of the in-plane magnetization direction in the irregular patch pattern observed in another region at around 90 K. The magnetization direction is indicated by the color wheel at the right side of (a).

material had a ferromagnetic structure, the observed wall bending and flux discontinuity would produce magnetic charges on the wall planes, disfavoring such a domain structure.[14] It is known, however, that the irregular domain is often produced in layered-structure systems where adjacent ferromagnetic layers are coupled antiferromagnetically through the medium of a thin nonmagnetic layer inserted between them.[15–18] In this case, because magnetic charges can be compensated at every point of the domain walls, domain shape and size are not determined by the flux continuity principle, leading to irregular domain patterns. We attribute the irregular magnetic domain structure appearing in Fig. 4(a) to the layered antiferromagnetic structure which is produced by the switching of the inter-bilayer coupling to the antiferromagnetic type. The anticipated magnetic domain structure toward the bulk inside for the region indicated by the white broken line in Fig. 4(a) is illustrated in Fig. 4(c). In fact, the domain pattern appearing in Fig. 4(a) exhibits neither geometrical regularity nor flux continuity. In addition, extremely irregular patches observed in another region at around 90 K [Fig. 4(d)] coincide with those observed often in other layered antiferromagnetic systems,[15,16,18] supporting the present interpretation.

These findings show that the magnetic phase of the material transforms with increasing temperature, as summarized in Fig. 1. Below 80 K, magnetization couples ferromagnetically between the adjacent MnO_2 bilayers and aligns along the *c* axis (top drawing). As the temperature is increased, the inter-bilayer magnetic coupling becomes antiferromagnetic, accompanied by the inclination of the easy axis toward the *ab* plane (bottom drawing). As for the ground state magnetic structure, two different models have so far been proposed from the neutron diffraction experiments: ferromagnetic inter-bilayer coupling with the magnetization parallel to the *c* axis (by Mitchell *et al.*[7]) or otherwise the *ab* plane (by Kubota *et al.*[5,6]). The present result is in accord with the former. Kubota *et al.*[5,6] have also reported the temperature dependence of the magnetic structures of their crystal with $x=0.30$. The reported transition from a ferromagnetic to layered antiferromagnetic phase in their $x=0.30$ crystal is similar, and hence perhaps related, to the present result on our $x=0.32$ crystal, although the transition temperature of 70 K (Ref. 19) slightly differs from that of the present ferromagnetic phase. The present analysis based on microscopy reveals that the ferromagnetic phase at low temperatures transforms into the layered antiferromagnetic one with increasing temperature. The magnetic structure in the layered manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ is extremely sensitive to hole-doping level around $x=0.3$ and hence perhaps to the sample off stoichiometry. Our analysis indicates that there is a magnetic phase distinct from both of those for $x=0.30$ and $x>0.32$ (ferromagnetic inter-bilayer coupling with the magnetization parallel to the *ab* plane[5–7]). Considering the presence of the lattice striction anomaly at around the present transition temperature of 80 K in the $x=0.32$ crystal from the same batch,[20] the present magnetic transition is likely related to the lattice structural change associated with temperature variation of the orbital character of the conduction electrons.

In summary, the temperature-dependent domain reconstruction of the layered manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.32$) has been investigated in the temperature range from 45 K up to 110 K using the variable-temperature spin-polarized scanning electron microscopy. From the real-space observation based on the quantitative magnetization-vector analysis, it is fully revealed that the crystal undergoes the novel magnetic transition at around 80 K. The closure structure of the magnetic flux is formed at the *ab* surface below 80 K. The development of the closure domains confirms that ferromagnetic bilayer sheets with the magnetization parallel to the *c* axis are coupled ferromagnetically. Above 80 K, the closure domains abruptly transform into larger ones without exhibiting flux continuity. The irregular-shape domain structure indicates the antiferromagnetic inter-bilayer coupling with the magnetization parallel to the *ab* plane.

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