Paired and Unpaired Charge Stripes in the Ferromagnetic Phase of $La_{0.5}Ca_{0.5}MnO_3$

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The mysterious coexistence of ferromagnetism and charge ordering in $La_{0.5}Ca_{0.5}MnO_3$ is found to result from an inhomogenous spatial mixture of incommensurate charge-ordered and ferromagnetic charge-disordered microdomains with a size of 20–30 nm. Furthermore, high resolution lattice images of the incommensurate charge-ordered microdomains indicate a charge-ordered state with a fine mixture of paired and unpaired Jahn-Teller distorted Mn^{3+} stripes. We propose that the unpaired Mn^{3+} stripes arise from disordering of the d_{z^2} orbitals. These results demonstrate a dramatic case of microscopic-scale electronic phase separation. [S0031-9007(98)07522-X]

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The rich physics of colossal magnetoresistive compounds with perovskite structure is dominated by the intriguing competition between ferromagnetic double exchange coupling and charge/orbital ordering [1–5]. Charge localization, prerequisite of charge ordering, is mutually exclusive with ferromagnetism in the double exchange mechanism which requires actual hopping of charge carriers. The general ground state of mixed valence manganites, e.g., $La_{1-x}Ca_xMnO_3$, is therefore either a ferromagnetic (FM) metal or an antiferromagnetic (AF) charge-ordered insulator. The $x = 0.5$ compound, which is located on the phase boundary separating these two competing ground states, provides a rare opportunity for studies of these competing interactions. Early reports have shown that $La_{0.5}Ca_{0.5}MnO_3$ first undergoes a FM transition at 240 K on cooling and then follows a first-order transition to an AF charge-ordered state at 135 K (185 K on warming) [6]. Recent electron diffraction experiment showed that the FM to AF transition actually coincides with an incommensurate (IC) to commensurate (CM) or nearly commensurate (NC) charge-ordering transition [7]. Furthermore, both electron and x-ray diffraction experiments have found the surprising coexistence of ferromagnetism and IC charge ordering in this narrow temperature window [7,8]. However, the detailed nature of this coexistence is still largely unknown. In this Letter, we report microstructures related to the FM-to-AF transition and the IC charge ordering in $La_{0.5}Ca_{0.5}MnO_3$ by both dark field and high resolution electron microscopy. It is shown that the FM phase is spatially inhomogeneous consisting of both the IC charge-ordered and the ferromagnetic charge-disordered microdomains with a size about 20–30 nm. The FM-to-AF transition is characterized by an evolution of the IC charge-ordered microdomains inside the FM domains. Recently, it has been shown that paired charge-ordered Mn^{3+} stripes are the fundamental building blocks of the charge-ordered states in the perovskite manganites [9]. Our high resolution lattice images observed in the IC charge-ordered phase, however, show the presence of both paired and unpaired charge-ordered Mn^{3+} stripes. We propose that complete orbital ordering does not occur simultaneously with charge ordering in the incommensurate phase, and the presence of unpaired Mn^{3+} stripes is a direct consequence of the orbital disordering in the charge-ordered stripes.

Samples, both poly- and single-crystalline, for electron diffraction were prepared by mechanical polishing followed by ion milling at liquid nitrogen temperature. The experiment was carried out using a JEOL 2000FX electron microscope equipped with a low temperature sample stage and a 14-bit charge-coupled array detector. In particular, high resolution images were taken under the condition in which the objective aperture size is large enough to include electron diffraction spots at large scattering angles corresponding to a spacing up to 1.9 Å in real space. The contrast in the image is, therefore, mainly due to the atomic displacement, not due to charge distribution [10].

We have carried out an *in situ* observation in the temperature range between 250 and 95 K in order to examine the changes in microstructure associated with the FM to AF transition in $La_{0.5}Ca_{0.5}MnO_3$. Figure 1 shows the microstructural changes of the transition during the cooling process. Note that the transition temperature (T_N) determined by the magnetic measurement is about 135 K on cooling [4]. Figure 1(a), which is taken at 142 K by using one of the satellite spots due to charge ordering, shows a typical microstructure in the FM phase of $La_{0.5}Ca_{0.5}MnO_3$. In this so-called dark-field image, we can see clearly bright specklelike contrasts due to the charge-ordered microdomains with size about 20–30 nm. On the other hand, the regions with dark contrast should be regarded as normal lattice structure with no charge ordering, i.e., FM charge-disordered regions. On further cooling below T_N, as shown in a similar image taken at 124 K [Fig. 1(b)], the size of the charge-ordered microdomains has grown to be ~50–60 nm at the expense of the FM charge-disordered domains and at the temperature of 95 K [Fig. 1(c)] charge-ordered domains cover basically the entire region. The rapid decrease of the incommensurability on cooling [7,8], occurs

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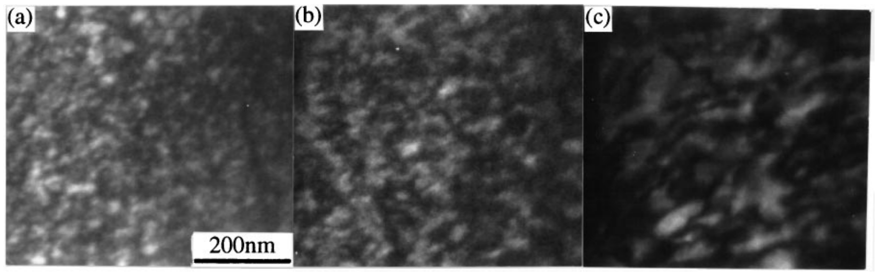

FIG. 1. (a), (b), and (c) are dark-field images obtained on cooling from a charge ordering superlattice reflection at temperatures of 142, 124, and 95 K, respectively. As the temperature is lowered, the charge-ordered domains with bright contrast grow in size at the expense of the ferromagnetic charge-disordered domains with dark contrast. The charge-ordered domain in (c) is nearly commensurate as indicated by electron diffraction and residual discommensurations (wavy dark lines) with 70 nm spacing are visible, which considerably darken the contrast of the domain.

simultaneously as the IC charge-ordered microdomains grow at the expense of the FM charge-disordered domains. On warming above T_N (180 K), images similar to that shown in Fig. 2(a) are also seen. From the dark-field images in the FM phase, it is now clear that the FM phase of $La_{0.5}Ca_{0.5}MnO_3$ is characterized by a fine mixture of the two competing ground states, namely, the AF charge-ordered and the FM charge-disordered microdomains. We emphasize that the fine mixture of the two electronically different phases at low temperatures is not due to chemical composition inhomogeneities. Our samples are characterized to be chemically homogeneous by *in situ* electron microprobe analysis using x-ray fluorescence with a spatial resolution of 20 nm.

In order to elucidate details of the IC charge ordering in the FM phase, high resolution lattice images were first carefully investigated around 200 K. Figure 2(a) is a high resolution lattice image along the [001] zone axis obtained at 206 K on cooling. Electron diffraction study shows that the charge ordering is incommensurate with a wave vector of $(1/2 - \varepsilon, 0, 0)$ and incommensurability $\varepsilon = 0.085$. The lattice fringes corresponding to a 5.5 Å planar spacing are clearly resolved in Fig. 2(a). The most striking feature in the image is the presence of the clusters with an average size of $\sim$10–20 nm, in which quasiperiodic paired lattice fringes with a significant lattice contraction ($\sim$8%) can be seen clearly. Fourier transform from these clusters shows incommensurate superlattice peaks consistent with the electron diffraction results. The clusters could be identified as the IC charge-ordered microdomains, which was seen as bright contrast speckles in the dark-field image shown in Fig. 1(a). The paired lattice fringes with enhanced dark contrast have been previously ascribed to the Jahn-Teller distorted stripes (JTS) of the $Mn^{3+}O_6$ octahedra, and the characteristic pairing of JTS's with large lattice contractions have also been found to be the fundamental building blocks in the charge-ordered states of the manganites [9]. In addition, there are regions of similar sizes in which only regular lattice fringes with 5.5 Å spacing can be seen, without the presence of any quasiperiodic pairs JTS's. We identify these regions as the FM charge-disordered microdomains, which show up as the dark speckles in Fig. 1(a). High resolution lattice images are, therefore, totally consistent with the results of dark-field images shown in Fig. 1(a).

Close examinations of the charge-ordered microdomains in Fig. 2(a), moreover, reveal that single (unpaired) JTS occasionally exists between two paired JTS's, as indicated by an arrow in Fig. 2(a). The coexistence of unpaired and paired JTS's is very interesting since the pairing tendency of JTS's is known to be very strong as reported previously [9]. We first note that the spacing between two unpaired JTS's is about 30 Å on average in this case, which coincides with that of discommensurations estimated from the incommensurability of $\varepsilon = 0.085$. This strongly suggests that unpaired JTS's should serve as discommensurations in the IC charge-ordered microdomains. In order to learn more about the unpaired JTS in the IC phase, we have cooled the sample between 130 K to a NC charge ordered [7,8]. Figure 3 displays a high resolution lattice image obtained from the NC phase at 95 K. It is clear that, in the NC phase, most of the JTS's are now paired with a $2a_0$ periodicity and only very few unpaired JTS's still remain. This is consistent with the rapid decrease of incommensurability from the IC phase to the NC (or CM) phase. One of the remaining unpaired JTS's is highlighted by an arrow in the boxed area B as shown in Fig. 3. The appearance of the unpaired JTS's in the NC phase is very similar to that observed in the IC phase as shown in Fig. 2(a), and these are the residual discommensurations in the NC phase at low temperatures. Another feature indicated in the boxed area A can be identified as antiphase boundary of the paired JTS's where the pairing order of JTS's is completely out of phase across the antiphase boundary. To clearly show the phase relationship of the paired JTS's on either side of the antiphase boundary, we show in the inset of Fig. 3 intensity profiles from the immediate regions separated by the antiphase boundary. The phase relationship of the paired JTS across the antiphase boundary is differed by π; i.e., they are shifted by 5.5 Å. We note from Fig. 3 that the antiphase boundary is usually quite short $\sim$30–40 Å in length and the paired JTS's on either side of the antiphase boundary eventually become

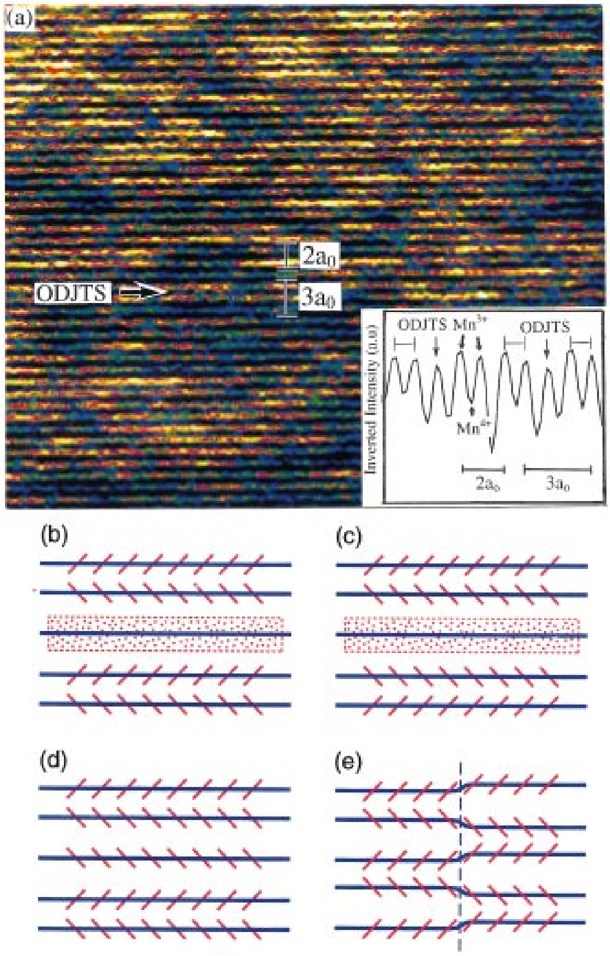

FIG. 2(color). (a) High resolution lattice image in the FM phase at 206 K showing fine mixture of IC charge-ordered and FM charge-disordered microdomains. An unpaired JTS sandwiched between paired JTS's is indicated by an arrow. An inverted intensity profile of this configuration is shown as the inset in (a). (b) and (c) show in-phase and out-of-phase configurations, respectively, of the paired JTS surrounding the orbital-disordered JTS. Blue lines represents Mn^{3+} JTS and the d_{z^2} orbital ordering (disordering) is indicated by the slanted red slashes (random-dotted red strip). For clarity, rows of nondistorted $Mn^{4+}O_6$ sandwiched between the Mn^{3+} JTS's are now shown here. (b) and (c) transform into residual discommensuration (d) and antiphase boundary (e), respectively, in the commensurate phase where complete orbital ordering is realized. The lattice contraction between the paired JTS is exaggerated in (e) to highlight the phase difference of π on either side of the antiphase boundary indicated by a dashed line.

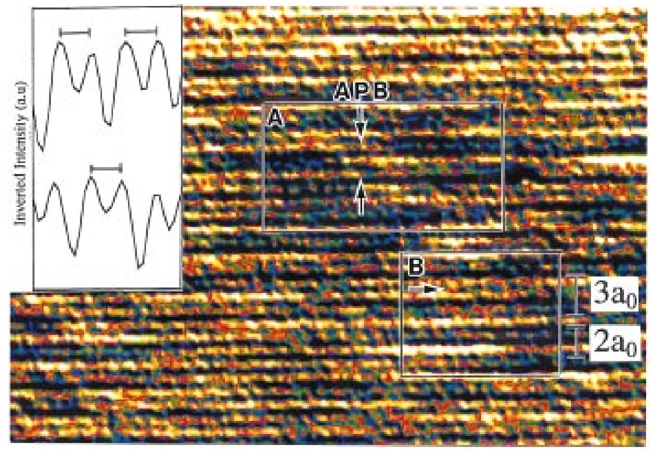

FIG. 3(color). High resolution lattice image of nearly commensurate charge ordering at 95 K showing the residual discommensurations (indicated by an arrow in area A) and antiphase boundaries of paired JTS's (highlighted in boxed area B). Inset shows intensity scans of two immediate regions of paired JTS's separated by an antiphase boundary showing a phase shift of π. Paired JTS's are also indicated.

in phase again with the presence of discommensurations in its immediate neighborhood.

From the above observations, we can see that most of the unpaired JTS's in the IC phase transform into paired JTS's at lower temperatures, and new ordering defects of antiphase boundaries occur as a result of this transformation. We now propose a model involving disordering of d_{z^2} orbitals which is consistent with our observations. Let us first examine the origin of the contrast of the unpaired JTS's in the IC phase. An inverted intensity trace perpendicular to the stripes in the IC charge-ordered microdomains is shown as the inset of Fig. 2(a), which shows an unpaired JTS (as indicated by an arrow) is sandwiched between the two paired JTS's. It is noted that the intensity of the unpaired JTS is nearly as strong as that of the paired JTS. Since the enhanced dark contrast of the paired JTS's is attributed to the JT distortion of the $Mn^{3+}O_6$ octahedra and orbital ordered JTS's have a strong tendency to form pairs [9], it is reasonable to interpret the enhanced dark contrast of the single unpaired JTS also as due to the JT distorted $Mn^{3+}O_6$ octahedra, but with no long-range orbital ordering along the stripe. A schematic description of the IC charge ordering is shown in Fig. 2(b). The configuration of JTS in Fig. 2(b) can be derived by the introduction of an orbital disordered JTS (ODJTS) into the regular arrangement of paired JTS. We should note that *charge* ordering remains intact in this situation despite the orbital disordering in ODJTS. We will therefore distinguish *charge* (in italics) ordering and orbital ordering hereafter. (The general phenomenon of "charge ordering" including orbital's degree of freedom will continue to be inferred with nonitalic form.) Two possibilities exist for the phase relationship of the orbital ordering of the two paired JTS on either side of the ODJTS. Namely, they can be either in phase or out of phase, as shown, respectively, in Figs. 2(b) and 2(c). High resolution lattice images as shown in Fig. 2(a), of course, cannot distinguish these two possibilities. It is noted that Fig. 2 actually describes a charge-ordered state with commensurate *charge* ordering and incommensurate orbital ordering.

As the sample is cooled toward the IC-NC transition, the transformation of unpaired JTS's into paired JTS's requires long-range orbital ordering within the unpaired

ODJTS. Orbital ordering along ODJTS for the in-phase configuration [Fig. 2(b)] is frustrated and can adopt an orientation parallel to one of its nearest JTS's. As a result, there is a phase shift of π for the orbital ordering across the newly ordered, but unpaired, JTS [Fig. 2(d)]. Naturally, this type of new defects will serve as discommensurations in the NC (or CM) phase. In fact, an identical configuration of discommensurations has been proposed as a result of neutron scattering experiment [7]. For the out-of-phase configuration of ODJTS [Fig. 2(c)], on the other hand, there is a preferred orbital ordering that will lead to pairing tendencies with its nearest JTS and give rise to antiphase boundaries [Fig. 2(e)] perpendicular to stripes. If only out-of-phase ODJTS's exist in the IC phase, then we will expect the low temperature phase should be truly commensurate with $\varepsilon = 0$, since antiphase boundaries do not contribute to incommensurabilities in this case. However, if there are a significant number of in-phase ODJTS's in the IC phase, charge ordering at low temperatures will be nearly commensurate ($\varepsilon \cong 0$) due to the presence of these defects as discommensurations. This could explain why we often observe a mixture of grains showing either CM or NC charge ordering at low temperatures. In view of the two possible evolution paths of the ODJTS during the transition to the commensurate phase, namely, either antiphase boundaries or residual discommensurations, the rapid decrease of incommensurability (ε) as temperature is lowered can be easily understood.

The quasiperiodic fine mixture of paired JTS's and unpaired ODJTS for the IC charge ordering in $La_{0.5}Ca_{0.5}MnO_3$ as shown in Fig. 2(a) is similar to the IC structure of long-period superlattice observed in alloys such as Cu_3Pd and Ag_3Mg [11,12]. In these alloys, the incommensurability arises from the fine mixture of several distinct long-period superlattice with different characteristic cell dimensions which are multiples of the basic unit cell. The configuration of a single ODJTS sandwiched between two paired JTS's found in the IC phase will break the regular $2a_0$ paired JTS modulation and create locally a new spacing of $3a_0$ between them. However, it should be noted that the $3a_0$ configuration in this case is different from the $3a_0$ paired JTS's observed in $La_{0.33}Ca_{0.67}MnO_3$ [9], although their appearances in high resolution lattice images are quite similar. In the case of $La_{0.33}Ca_{0.67}MnO_3$, the single dark stripe between the $3a_0$ paired JTS is associated with the $Mn^{4+}O_6$ octahedra which exhibit no Jahn-Teller distortions. Therefore, the intensity of the stripe due to the $Mn^{4+}O_6$ octahedra is much weaker than that of the distorted $Mn^{3+}O_6$ octahedra [9].

The presence unpaired JTS in the IC phase as revealed in our high resolution lattice images may provide the first experimental indication in manganites which suggests a *charge* ordering can occur without complete orbital ordering. All the experimental evidences of charge ordering in manganites including 2D systems [13,14] have shown or suggested that *charge* ordering and orbital ordering occur simultaneously and orbital ordering is automatically assumed when the term "charge ordering" is used. However, there are no apparent reasons why these two degrees of freedom should order concomitantly. It is important to distinguish these two degrees of freedom, and our data are totally consistent with the scenario that total *charge* ordering with incommensurate orbital occurs in the IC phase at higher temperatures and commensurate orbital ordering finally takes place during the transition into the CM phase at lower temperatures.

In conclusion, it is shown clearly that the ferromagnetic phase is characterized by a fine mixture of the AF incommensurate charge-ordered and the FM charge-disordered microdomains. This coexistence in the narrow temperature region provides a remarkable example of microscopic-scale electronic phase separation. As the temperature is further decreased, the system eventually becomes an electronically homogeneous AF commensurate charge-orbital–ordered state. Our observation indicates that distinction between *charge* ordering and orbital ordering is necessary, and *charge* ordering with incommensurate orbital ordering occurs in the FM phase and the FM to AF transition is characterized by an IC to CM ordering transition of the orbital degree of freedom.

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