Microstructure related to charge and orbital ordering in $Pr_{0.5}Ca_{0.5}MnO_3$

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We have investigated the microstructure related to the charge and orbital ordering in the manganites $Pr_{0.5}Ca_{0.5}MnO_3$ by transmission electron microscopy. Electron diffraction clearly shows the presence of the incommensurate structure in the paramagnetic insulator phase of $Pr_{0.5}Ca_{0.5}MnO_3$ between 180 and 260 K. Our experimental results clearly show that the incommensurate-to-commensurate (IC-to-C) charge-ordering transition was correspondent with the paramagnetic to antiferromagnetic transition around 180 K. Dark field images also revealed the motion of the discommensurations during the IC-to-C transition. A model of the IC structure which involves the presence of the partial orbital disordering and the complete charge ordering is proposed. [S0163-1829(99)11721-1]

The fascinating physical phenomena in manganites are dominated by the competition of two prominent ground state, namely ferromagnetic metallic and charge-ordered insulating phases. Recently an incommensurate charge ordered phase has been found to coexist with the ferromagnetic metallic phase in $La_{0.5}Ca_{0.5}MnO_3$ by electron and neutron diffraction experiments.[1,2] It was suggested that the physical origin of the incommensurate charge ordering could be due to the presence of the partial orbital disordering in spite of the complete charge ordering.[3] Hence, the degree of freedom of the e_g orbital is important to understand the nature of the incommensurate structure in the manganites.

It has been known that $Pr_{1-x}Ca_xMnO_3$ compounds do not show the ferromagnetic metallic properties in the entire range of Ca concentration, because $Pr_{1-x}Ca_xMnO_3$ has a smaller one-electron bandwidth than other manganites such as $La_{1-x}Sr_xMnO_3$.[4] In addition, $Pr_{1-x}Ca_xMnO_3$ has an orthorhombic structure (space group; Pbnm) in the whole Ca concentration (x). According to the previous work, $Pr_{1-x}Ca_xMnO_3$ for $0.3<x<0.75$ shows an insulating state characterized by the charge/orbital ordering at lower temperatures.[4–7] The wave vectors due to the charge ordering (δ) vary with the Ca concentration (x) for $0.5<x<0.75$, and for x less than 0.5, δ remains unchanged with $\delta=0.5a^*$. Note that a^* denotes a reciprocal lattice vector in the orthorhombic system. $Pr_{0.5}Ca_{0.5}MnO_3$ has been found to undergo a charge ordering transition at $T_{co}=260\,K$ and subsequently the paramagnetic-to-antiferromagnetic transition at $T_N=180\,K$. In this paper we reported microstructure related to the charge ordered state in $Pr_{0.5}Ca_{0.5}MnO_3$ by electron diffraction and high resolution electron microscopy. An incommensurate charge ordering is found to be present in the paramagnetic insulator state in the intermediate temperature region. The incommensurability (ε) characterizing the incommensurate charge ordering changes with respect to the temperature with a small thermal hysteresis. The incommensurate (IC) to commensurate (C) transition correlate well with the paramagnetic to antiferromagnetic transition around 180 K.

In this work both ceramic and single crystals of $Pr_{0.5}Ca_{0.5}MnO_3$ were used, where single crystals are prepared by floating-zone method. The observation was carried out by using JEM-2000FX and JEM-200CX equipped with the low temperature holder. High resolution lattice images were taken by including electron diffraction spots at large angle and so the main contribution to the contrast of the lattice fringes is due to the displacements of the individual atoms, not to charge distribution.[8] The samples in the electron microscope are under the magnetic field by the object lens with the magnitude of 2 T.

We found the presence of the incommensurate structure in the paramagnetic insulator state of $Pr_{0.5}Ca_{0.5}MnO_3$ and the incommensurability (ε) changes in the cooling and subsequent heating process with a small thermal hysteresis. It should be noticed that in some grains the temperature dependence of ε occasionally shows a relatively large thermal hysteresis. The wave vector characterizing the incommensurate structure can be written as $\delta=(1/2-\varepsilon)a_o^*$, where ε is defined as the deviation of the position of the superlattice reflection spot from its commensurate position in the reciprocal space. First of all, we will show the typical temperature dependence of ε obtained in $Pr_{0.5}Ca_{0.5}MnO_3$ during the cool-

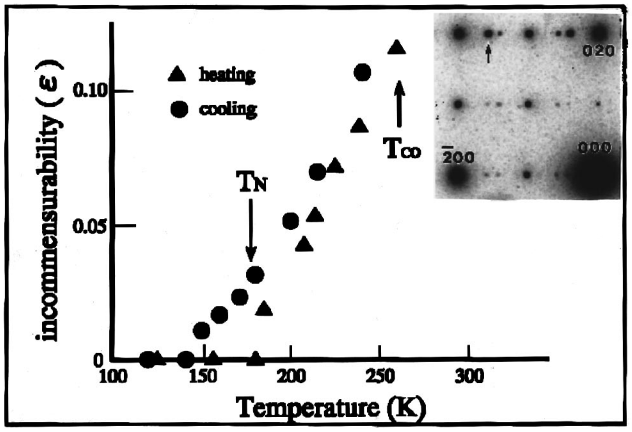

FIG. 1. Changes in the incommensurability (ε) characterizing the incommensurate charge ordering with respect to the temperature. Closed triangles and circles represent values of ε obtained from electron diffraction experiment at each temperature on warming and cooling, respectively. (Inset) Electron diffraction pattern taken at 200 K in the paramagnetic insulator state of $Pr_{0.5}Ca_{0.5}MnO_3$, which shows clearly the presence of the incommensurate structure.

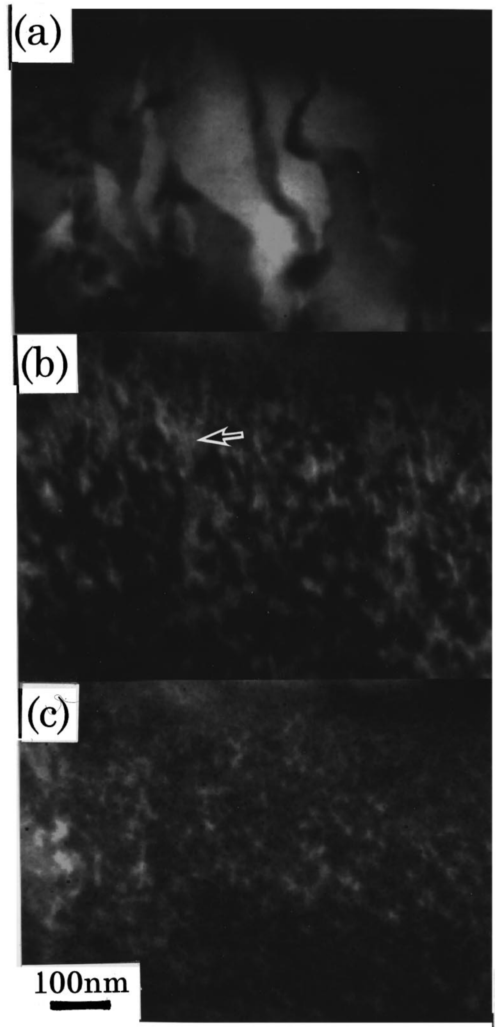

FIG. 2. Changes in microstructure related to the charge ordered state on warming from 95 K. The images are taken at (a) 95 K, (b) 200 K, and (c) 240 K by using the satellite spots due to the charge ordering, respectively.

ing and subsequent warming process. As clearly seen in Fig. 1, ε has a finite value of 0.11 at the transition temperature of 260 K and decreases gradually with decreasing temperature. Finally ε reaches zero around 150 K and the charge ordered state becomes commensurate and is characterized by the wave vector of $\delta = 1/2 a_o{}^*$ at lower temperature, as has already reported in the previous work.[5–7,9] On the other hand, on warming ε remains zero until around 180 K and reaches a value of $\varepsilon = 0.11$ around 260 K. It should be noted that the temperature dependence of ε in $Pr_{0.5}Ca_{0.5}MnO_3$ exhibits a small thermal hysteresis, although in the case of $La_{0.5}Ca_{0.5}MnO_3$ the temperature dependence of ε has a large thermal hysteresis.[1] The transition temperature (180 K) of the IC-to-C structural transition coincides with the paramagnetic to antiferromagnetic one obtained by magnetic and resistivity measurements.[4]

In order to elucidate changes in microstructure related to the charge ordered state in $Pr_{0.5}Ca_{0.5}MnO_3$, an *in situ* observation was carried out in the temperature range between room temperature and 95 K on cooling and warming. As shown in Fig. 1, the presence of an incommensurate structure in the temperature range between 180 and 260 K is found in the electron diffraction experiment. Figure 2 shows changes in microstructure related to the charge ordered state on warming from 95 K. Note that all images shown in Fig. 2 were taken by using the superlattice reflection spots due to the charge ordering and then the bright contrast regions in Fig. 2 correspond to ones where the charge ordering occurs. At lower temperature of 95 K the charge ordered state is seen as a large domain structure with a long coherence of >100 nm, as shown in Fig. 2(a). Note that dark contrast lines in Fig. 2(a) are mainly due to the antiphase boundaries in the commensurate structure. On warming from 95 K, we found the presence of the discommensuration structure which has a close relationship to the incommensurate structure around 200 K. Figure 2(b) is a dark field image taken at 200 K by using the satellite reflection spot. As shown by an arrow in the image, dark line contrasts which should be identified as the discommensuration with a phase slip of π can be clearly seen. It should be noted that average distance between two neighboring dark line contrasts is about 12 nm, which is consistent with that estimated from the incommensurability (ε) obtained experimentally, where ε is 0.045 at 200 K on warming. The similar dark line contrasts due to the DC's were seen in the nearly commensurate phase of $La_{0.5}Ca_{0.5}MnO_3$.[1] On further warming to the transition temperature of 260 K, the size of the microdomains due to the charge ordered state has shrunk down to the size of about 10–20 nm, as shown in Fig. 2(c) taken at 260 K, and finally disappear above the transition temperature of about 260 K. These images shown here revealed that the incommensurate structure is characterized by the presence of the DC's with a phase slip of π. It is expected that the C-to-IC transition will proceed with the creation and annihilation processes of the DC's on warming. We examined change in microstructure

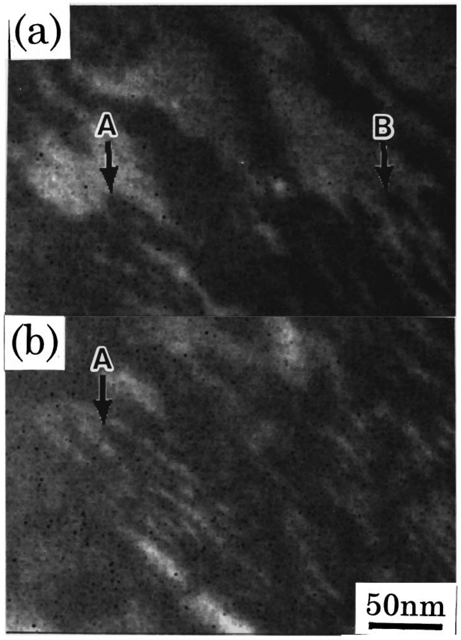

FIG. 3. Dynamical motion of the DC's during the C-to-IC structural transition in $Pr_{0.5}Ca_{0.5}MnO_3$. Paired DC's can be seen, as shown by arrows *A* and *B* in the figure.

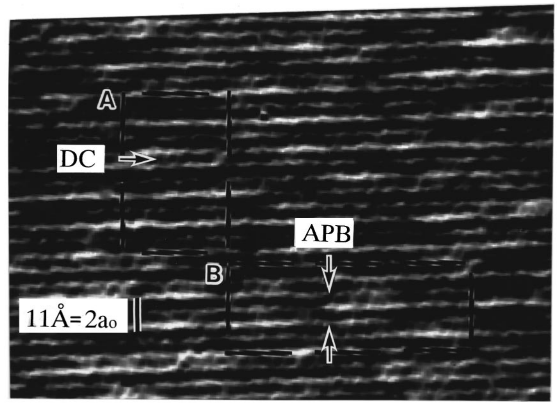

FIG. 4. High resolution lattice fringes taken in the charge ordered state at 95 K. The incident beam is almost parallel to the [001] direction. Two types of the defect structures, antiphase boundaries and discommensurations, can be seen, as shown in the rectangular regions *A* and *B*, respectively.

during the C-to-IC transition carefully. Figure 3 shows changes in microstructure related to the C-to-IC transition obtained around 180 K. As shown by arrows *A* and *B* in Fig. 3(a), pairs formed by two DC lines can be seen clearly. Figure 3(b) was taken at 144 K several minutes later after Fig. 3(a) was taken at the same temperature. Paired DC lines indicated by arrows in Figs. 3(a) and 3(b) proceed forward into the large charge ordered domain and the regular arrangement of the DC lines can be seen in the incommensurate structure. This dynamical process of the DC during the C-to-IC structural transition is a characteristic of the incommensurate structure found in the charge ordered manganites. The motion of the DC's during the IC-to-C transition has been reported in many materials undergoing the IC-to-C transition such as $2H\text{-}TaSe_2$, alloys and ferroelectric insulators.[10–13] These experimental results strongly demonstrate the presence of the incommensurate structure in the paramagnetic insulator state of $Pr_{0.5}Ca_{0.5}MnO_3$.

Thus, in order to examine detailed microstructure related to the charge ordered state in $Pr_{0.5}Ca_{0.5}MnO_3$ at lower temperature, we took some high resolution lattice images in the charge ordered state at 95 K. Figure 4 is a high resolution lattice image with the incidence beam parallel to [001]. In the image, lattice fringes with the separation of 5.5 A corresponding to the lattice parameter along the [100] direction can bee seen clearly. One of the most striking features of the image is the presence of doublet enhanced dark fringes with the periodicity of 11 Å $(=2a_o)$. The regular arrangement of doublet dark enhanced fringes in the CO state of $Pr_{0.5}Ca_{0.5}MnO_3$ has already reported by Barnabe *et al.*[9] As we have already reported in Ref. 14, the origin of the enhanced dark contrast is mainly due to the displacement of the distorted $Mn^{3+}O_6$ octahedra by Jahn-Teller effect. Paired Jahn-Teller stripes is a fundamental building block of the charge ordered state in $Pr_{0.5}Ca_{0.5}MnO_3$, as in $La_{0.5}Ca_{0.5}MnO_3$.[14] The other feature is the presence of defect structures such as discommensuration (DC) and antiphase boundary (APE), which are shown in the rectangular regions (*A*) and (*B*), respectively. As has already discussed in Ref. 3, the presence of these types of defect structures in the HR images play an important role to the transition process from the IC structure to the C one.

In the case of $La_{0.5}Ca_{0.5}MnO_3$, the IC charge ordering is found to coexist with the ferromagnetic metallic state in a spatially inhomogeneous configuration with microdomains with the size of 20–30 nm.[3] In $Pr_{0.5}Ca_{0.5}MnO_3$, the IC charge ordering, however, is found in the insulator state. Note that we have to take into account two types of degree of freedom, charge and orbital, in examining the origin of the IC charge ordering in the manganites. In the case of $Pr_{0.5}Ca_{0.5}MnO_3$, we have to consider only the e_g orbital degree of freedom to understand the nature of the incommensurate structure. As evident in the IC structure of $La_{0.5}Ca_{0.5}MnO_3$, the IC charge ordering is characterized by the presence of the unpaired JTS between paired JTS's.[3] What causes the unpaired JTS is due to the partial disordering of e_g orbitals. In particular, by considering that the IC structure found in $Pr_{0.5}Ca_{0.5}MnO_3$ is characterized as the paramagnetic insulator state, we strongly proposed that the incommensurate charge ordering should be caused by the partial disordering of the d_{3z2-r2} orbitals with the charge ordering with the periodicity of $2a_o$.

In conclusion, electron diffraction and dark field images clearly show the presence of the incommensurate charge ordering in the paramagnetic insulator state of $Pr_{0.5}Ca_{0.5}MnO_3$, which is important to understand the role of the e_g orbitals in the charge ordered state of the manganites. We are now examining the influence of the ionic size in the *A* site of the perovskite structure on the IC charge ordering, in order to elucidate the nature of the e_g orbitals in the charge ordered state.

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