Evidence for the charge-ordered state and phase separation at room temperature in half-doped $La_{0.5}Ca_{0.5}MnO_3$ films

S. Y. Park, Y. H. Hyun, and Y. P. Lee[a)]
Quantum Photonic Science Research Center, Hanyang University, Seoul 133-791, Korea and Department of Physics, Hanyang University, Seoul 133-791, Korea

V. L. Svetchnikov
National Center for HREM, TU Delft, 2628AL Delft, The Netherlands

K. W. Kim
Department of Physics, Sunmoon University, Asan, Choongnam 336-840, Korea

V. G. Prokhorov
Institute of Metal Physics, National Academy of Sciences of Ukraine, Kiev 03142, Ukraine

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The microstructure and the magnetotransport properties of $La_{0.5}Ca_{0.5}MnO_3$ films, prepared by rf magnetron sputtering on a $LaAlO_3$ substrate, have been investigated. The electron-diffraction and the high-resolution electron-microscopy studies reveal the coexistence at room temperature of double-period modulated (charge-ordered) and unmodulated (charge-disordered) phases. It is suggested that the high-temperature fragmentation of film results in the magnetic-phase-separated state at low temperatures. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2243340]

$La_{1-x}Ca_xMnO_3$ is a typical system, displaying a rich variety in the ground state when the concentration of Ca doping crosses 0.5.[1] The paramagnetic (PM) insulating, the ferromagnetic (FM) metallic, the antiferromagnetic (AFM) metallic or insulating, the charge-ordered (CO), and the orbital-ordered phases appear in this compound upon lowering temperature.[2] Moreover, the majority of these phases can coexist in a wide temperature range, resulting in the phase-separated state.[2–7] The most debatable question for the half-doped manganites is the origin for the CO phase. It was shown that the CO phase for $x=0.5$ is characterized by the appearance of superlattice spots on the electron diffraction (ED) patterns, with a wave vector $q=a^*/2$, where a^* is the reciprocal lattice vector along the a axis for the simple pseudocubic symmetry.[5,8,9] This corresponds to the real-space "stripes" with the doubled a axis period, parallel to the c axis, which are distinguishable on the cross-sectional high-resolution electron-microscopy (HREM) images.[5,9–12] However, most of the HREM studies were carried out on the bulk polycrystalline samples whose magnetic and transport properties differ drastically from those for the thin films.[13,14]

In this letter, we demonstrate that the double-period modulated phase, which is interpreted as a CO phase, exists in the half-doped $La_{0.5}Ca_{0.5}MnO_3$ film even at room temperature, and forms a phase-separated state with the charge-disordered (CD) phase. There is no sharp boundary between modulated and unmodulated regions. Instead, one phase is blended gradually with the other. The analysis of experimental results allows us to conclude that the CO state in the $La_{0.5}Ca_{0.5}MnO_3$ film occurs through the first-kind transition in a wide temperature interval.

The films were grown on a $LaAlO_3$ (001) single crystal (pseudocubic with $a\simeq 0.379$ nm) by rf magnetron sputtering, using the so-called "soft" (or powder) target.[15] The substrate temperature during deposition was 750 °C. The film thickness was about 200 nm. The θ-2θ x-ray diffraction (XRD) patterns were obtained using a Rigaku diffractometer with Cu $K\alpha$ radiation. The HREM studies were carried out using a Philips CM300UT-FEG microscope with a field emission gun operated at 300 kV. The resolution of the microscope was in the order of 0.12 nm. The cross-sectional specimens were prepared by the standard techniques using mechanical polishing followed by ion-beam milling at a grazing incidence. The resistance was obtained by using the four-probe method with dc density of $\simeq 1.0$ A/cm^2. The magnetization was taken with a Quantum Design superconducting quantum interference device magnetometer.

The ED patterns, shown by Fig. 1, reveal the known orthorhombic crystal structure with a lattice parameter for the simple pseudocubic symmetry about 0.382 nm, which is almost identical to the XRD data (not shown). On the other hand, the well-defined superlattice spots are evident at the positions such as $(1/2,0,0)$ (indicated by white circles) in addition to the fundamental Bragg reflections. The similar superlattice spots in ED pattern were observed before for the bulk $La_{0.5}Ca_{0.5}MnO_3$ at $T=95$ K and treated as appearance of a charge ordering of the Mn^{4+} and the Mn^{3+} ions.[8] Surprisingly, the superlattice reflections in our case exist even at room temperature while the CO phase in the bulk appears at $T_{CO}\leqslant 150$ K.[2]

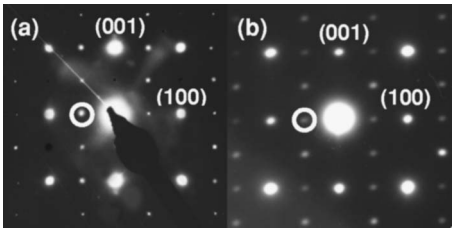

FIG. 1. [010] zone-axis electron diffraction patterns for the $La_{0.5}Ca_{0.5}MnO_3$ film prepared at (a) 300 and (b) 87 K, respectively. The fundamental Bragg peaks are indicated. The presence of superlattice spots with a modulation wave vector, similar to $(1/2,0,0)$, is evident.

[a)]Electronic mail: yplee@hanyang.ac.kr

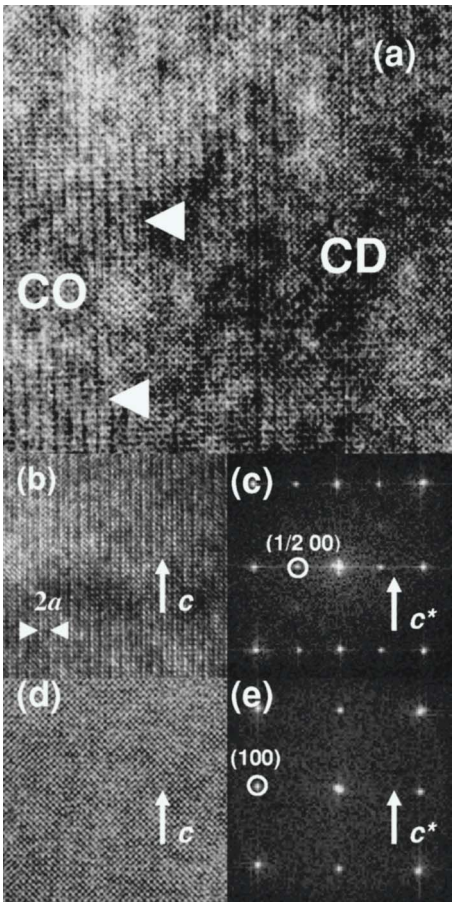

FIG. 2. (a) High-magnification cross-sectional HREM image at 300 K. The modulated (indicated by white arrows) and the unmodulated phases are denoted as CO and CD, respectively. (b) and (d) present these phases in detail, respectively. The modulated phase demonstrates the stripe structure with the doubled *a*-axis lattice period, parallel to *c*-axis direction. (c) and (e) present the corresponding fast Fourier transform (FFT) of these HREM images, respectively.

Figure 2(a) shows the high-magnification cross-sectional HREM image taken at 300 K. It is seen that the selected area of the film demonstrates the coexistence of the modulated (indicated white arrows) and the unmodulated phases. These phases do not have the sharp definite boundary and gradually replace each other. Figures 2(b) and 2(d) present these phases in detail. The modulated phase exhibits the stripe structure with the doubled *a*-axis lattice period, parallel to *c*-axis direction, which was already observed in this compound at 95 K.[8] The fast Fourier transform (FFT) of this HREM image, represented by Fig. 2(c), produces not only a rectangular pattern of the basic Bragg spots, which are typical for a regular pseudocubic crystal lattice, but also the additional superlattice reflections with a wave vector $q=a^*/2$ (one of them is indicated by white circle). It is excellently coincident with the ED data which result in $q/a^*=0.502$. On the contrary, the FFT of HREM image for the unmodulated phase [see Fig. 2(e)] demonstrates the rectangular pattern of the fundamental Bragg spots, only. The analysis of HREM images and FFT patterns reveals that both the unmodulated and the modulated phases have equal crystal lattices with a slight tetragonal distortion $c/a \simeq 1.02$ and an almost direct angle between *c* and *a* axes $\beta \simeq 90.3° \pm 0.2°$, which is identified as a weakly strained orthorhombic structure.

Figure 3 shows that the $La_{0.5}Ca_{0.5}MnO_3$ film undergoes the PM to FM transition at $T_C \lesssim 250$ K, which is coincident

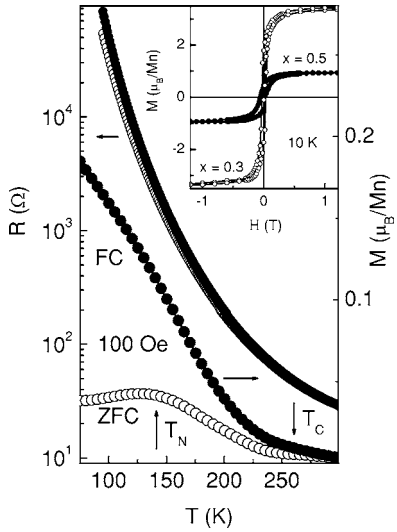

FIG. 3. Temperature dependence of resistance without (solid symbols) and with (open symbols) an applied magnetic field of 5 T, and the in-plane FC (solid symbols) and ZFC (open symbols) magnetizations in an applied magnetic field of 100 Oe. The inset displays the in-plane hysteresis loops at 10 K for the $La_{0.5}Ca_{0.5}MnO_3$ (solid symbols) and $La_{0.7}Ca_{0.3}MnO_3$ (open symbols) films. The lines are guides for the eyes.

with that for the bulk.[1,2] The Curie point was identified from the onset increase of the field-cooled (FC) and the zero-field-cooled (ZFC) magnetization with the decreasing temperature, $M(T)$. The $M(T)$ curves were obtained in the in-plane applied magnetic field of 100 Oe. The observed decrease of the ZFC magnetization at $T_N \lesssim 140$ K is treated as an appearance of the AFM phase. On the other hand, the AFM phase transition in the bulk is accompanied by a significant decrease in the magnetization with decreasing temperature, indicating that the AFM phase is formed from the FM one.[1,2,7,8] On the contrary, the FC $M(T)$ for the films does not present the similar peculiarity below T_N. Consequently, in our case, both FM and the AFM transitions take place independently, and the films contain the two kinds of magnetic phases at low temperatures. In addition, the temperature-dependent resistance, $R(T)$, without (solid symbols) and with (open symbols) an applied magnetic field of 5 T, manifests an exponential behavior in the whole temperature range with a negligible sensitivity to the applied magnetic field. Therefore, no evidence for the metal-insulator (MI) transition was found in the $La_{0.5}Ca_{0.5}MnO_3$ film, which is typical for the bulk materials. The inset in Fig. 3 presents the in-plane magnetic hysteresis loops, $M(H)$, at 10 K. Even though the film experiences the FM transition at $T_C \lesssim 250$ K, it is not clear how much of the volume still remains in the FM state below T_N. For comparison, the $M(H)$ dependence for a $La_{0.7}Ca_{0.3}MnO_3$ film (open symbols) is shown as well. It is seen that the saturated magnetic moment of $La_{0.7}Ca_{0.3}MnO_3$ film ($\simeq 3.2\mu_B$/Mn) is very close to the theoretical effective magnetic moment for the fully FM sample ($\mu_{\text{eff}} \simeq 3.5\mu_B$/Mn). However, the saturated magnetic moment of the $La_{0.5}Ca_{0.5}MnO_3$ film does not exceed $0.95\mu_B$/Mn. Taking into account that the whole volume of $La_{0.7}Ca_{0.3}MnO_3$ film becomes ferromagnetic at low temperatures, one can suggest that only 30% of the film volume belongs to the FM phase, which is almost coincident with the published results for the bulk.[7] Therefore, in the half-doped $La_{0.5}Ca_{0.5}MnO_3$ film both FM and AFM phases coexist at

low temperatures, indicating a magnetic-phase-separated state. It is reasonable to suggest that the observed magnetic separation arises from the high-temperature fragmentation of the film onto the CO (modulated) and the CD (unmodulated) regions. With cooling, the CO phase undergoes the PM to AFM transition at $T_N \lesssim 140$ K, while the CD one becomes ferromagnetic at $T_C \lesssim 250$ K, and is being in this state up to low temperatures. Because the volume of the FM phase ($\simeq 30\%$) is smaller than the threshold value for a percolation,[16] the MI transition is not observed in this film. The appearance of the CO state at high temperatures in the films is triggered probably by a ferroelastic phase transition in the $LaAlO_3$ substrate at $T=544\ ^\circ C$,[17] which leads to the generation of a lattice strain and an inhomogeneous distribution of charges.

In summary, the coexistence of double-period modulated (charge-ordered) and unmodulated (charge-disordered) phases was found in the half-doped $La_{0.5}Ca_{0.5}MnO_3$ film at room temperature. Both phases demonstrate a weakly strained orthorhombic crystal structure, without sharp interboundaries. Instead, one phase mixed with the other gradually. This implies that the CO state is formed through the first-kind transition in a wide temperature interval. With decreasing temperature the $La_{0.5}Ca_{0.5}MnO_3$ film reveals firstly the PM to FM transition at $T_C \lesssim 250$ K, and then the appearance of AFM phase at $T_N \lesssim 140$ K. It was shown that the volume of FM phase does not exceed 30% at 10 K and coexists with the AFM one at low temperatures. We suggest that the FM and the AFM phases are formed independently of each other in the different (CD and CO) regions of film. The film manifests an exponential temperature dependence of resistance in the whole temperature range without evidence for the MI transition. This is explained by the insufficient FM phase for the formation of infinite percolating cluster.

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[1] P. Schiffer, A. P. Ramirez, W. Bao, and S.-W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).
[2] P. G. Radaelli, D. E. Cox, M. Marezio, and S.-W. Cheong, Phys. Rev. B **55**, 3015 (1997).
[3] G. Adolli, R. De Renzi, F. Licci, and M. W. Pieter, Phys. Rev. Lett. **81**, 4736 (1998).
[4] J. Dho, I. Kin, and S. Lee, Phys. Rev. B **60**, 14545 (1999).
[5] S. Mori, C. H. Chen, and S.-W. Cheong, Phys. Rev. Lett. **81**, 3972 (1998); Nature (London) **392**, 473 (1998).
[6] W. Tong, Y. Tang, X. Liu, and Y. Zhang, Phys. Rev. B **68**, 134435 (2003).
[7] J. C. Loudon, N. D. Mathur, and P. A. Midgley, Nature (London) **420**, 797 (2002); J. Magn. Magn. Mater. **272-276**, 13 (2004).
[8] C. H. Chen and S.-W. Cheong, Phys. Rev. Lett. **76**, 4042 (1996).
[9] C. H. Chen, S.-W. Cheong, and H. Y. Hwang, J. Appl. Phys. **81**, 4326 (1997).
[10] J. C. Loudon and P. A. Midgley, Phys. Rev. B **71**, 220408 (2005).
[11] J. C. Loudon, S. Cox, A. J. Williams, J. P. Attfield, P. B. Littlewood, P. A. Midgley, and N. D. Mathur, Phys. Rev. Lett. **94**, 097202 (2005).
[12] J. Tao, D. Niebieskikwiat, M. B. Salamon, and J. M. Zuo, Phys. Rev. Lett. **94**, 147206 (2005).
[13] E. B. Nyeanchi, I. P. Krylov, X.-M. Zhu, and N. Jacobs, Europhys. Lett. **48**, 228 (1999).
[14] M. Malfait, I. Gordon, V. V. Moshchalkov, Y. Bruyneraede, G. Borghs, and P. Wagner, Phys. Rev. B **68**, 132410 (2003).
[15] V. G. Prokhorov, G. G. Kaminsky, V. A. Komashko, J. S. Park, and Y. P. Lee, J. Appl. Phys. **90**, 1055 (2001).
[16] Y. Xiong, S.-Q. Shen, and X. C. Xie, Phys. Rev. B **63**, 140418 (2001).
[17] S. Bueble, K. Knorr, E. Brecht, and W. W. Schmahl, Surf. Sci. **400**, 345 (1998).