Studies on the cluster sizes in the mixed-phase thin films

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Based on the phase separation scenario, by simulating the resistivity of $La_{0.33}Pr_{0.34}Ca_{0.33}MnO_3$ film with the known coexisting-phase sizes, the authors have obtained the theoretical ferromagnetic (FM) cluster sizes of $La_{2/3}Ca_{1/3}MnO_3$ film, showing around 0.6 μm near T_c. Subsequently the insulator-metal transition occurs when the cluster grows up to 0.7 μm, and the abrupt drop in resistivity occurs when the size is around 0.9 μm. Furthermore, the FM cluster sizes grow with the magnetic field. The obtained results indicate that the model and method can be used to predict the critical size of the clusters at the phase transition for the mixed-phase materials. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2432945]

Perovskite manganites have attracted considerable attention due to the rich strong-correlated effects, such as colossal magnetoresistance effect[1] and phase separation phenomenon.[2] Experimentally, phase separation tendencies with intrinsic inhomogeneities have been confirmed in many manganite systems and those observed separated phases are on the different scales. It is found that the nanometer clusters exist in $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ (Ref. 3) and $(La,Pr,Ca)MnO_3$ materials.[4] Furthermore, the separated paramagnetic (PM) and ferromagnetic (FM) phases on a large submicrometer scale have been observed in $La_{0.73}Ca_{0.27}MnO_3$ thin film just below T_c.[5] In $La_{0.33}Pr_{0.34}Ca_{0.33}MnO_3$ thin film, the FM and PM regions coexist on the micrometer scale, which has been observed by using the magnetic force microscope (MFM).[6] The transport investigation indicates that the variation of the cluster sizes with the temperature T plays a crucial role in the phase transition.[7] So the revealing of the real size of the coexisting clusters is becoming a very important issue for the physics properties in the phase-separated system. However, as far as we know, though some experimental work has been done to obtain the cluster sizes of these kinds of materials, few theoretical studies have been carried out on the calculation of the FM cluster sizes and their evolution under the external conditions. Previously, based on the percolation theory, we have studied the transport properties of the mixed-phase manganites with metal-insulator transitions accompanied by FM to PM phase transition.[7,8] Our obtained results indicate that the transport behaviors are strongly related to the percolation mode, showing that the cluster percolation is important to determine the abrupt character of resistivity in the thin film.

In this letter, we report our calculated sizes and their evolution with temperature and the applied magnetic field under the phase separation system of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) thin film. To obtain the size of each lattice in the network of our model, the simulation of the transport properties of the system was carried out to compute with the experimental data.

The description of the random network model is that the system of an $N \times N$ matrix is composed of FM metallic region with resistance $R_M(T)$ and PM insulating region with resistance $R_I(T)$.[8,9] The total effective resistance R_{eff} is determined by the parallel connection of $R_M(T)$ and $R_I(T)$. A quantity f, defined as f=(the number of FM lattices)/(the number of total lattices), represents the fraction of FM metallic sites ($0 \leqslant f \leqslant 1$). It should be noticed that f increases with the decreased T and changes rapidly near T_c, similar to the T-dependent magnetization.[9] To calculate $R_M(T)$ and $R_I(T)$, we assume $\rho_m(T)=\rho_{m0}+\rho_{m1}T^2+\rho_{m2}T^{4.5}$ and $\rho_i(T)=\rho_{i0}\exp[E_0/(k_BT)]$ are the T-dependent resistivities for each FM site and PM site, respectively. ρ_{m0} is the low-T residual resistivity, the T^2 term indicates the electron scattering,[10] and the $T^{4.5}$ term denotes the magnon scattering.[11] ρ_{i0} is the high-

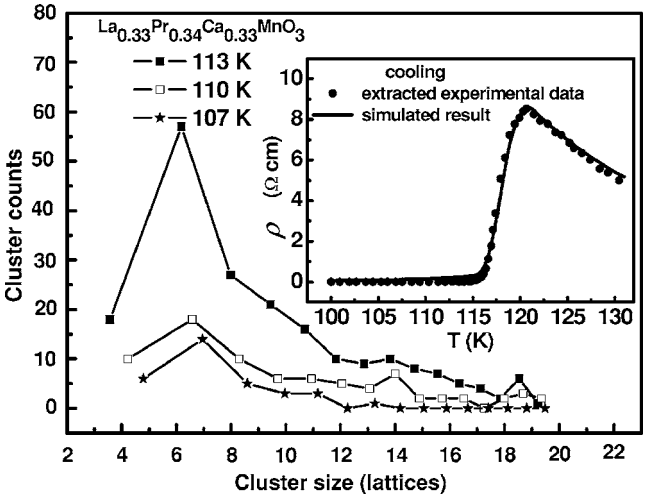

FIG. 1. Calculated cluster counts of the FM cluster sizes in the $La_{0.33}Pr_{0.34}Ca_{0.33}MnO_3$ thin film at 113, 110, and 107 K. The inset is the simulated T-dependent resistivity curve (solid line) of $La_{0.33}Pr_{0.34}Ca_{0.33}MnO_3$ thin film on cooling with the extracted experimental data (full circles) from Ref. 6.

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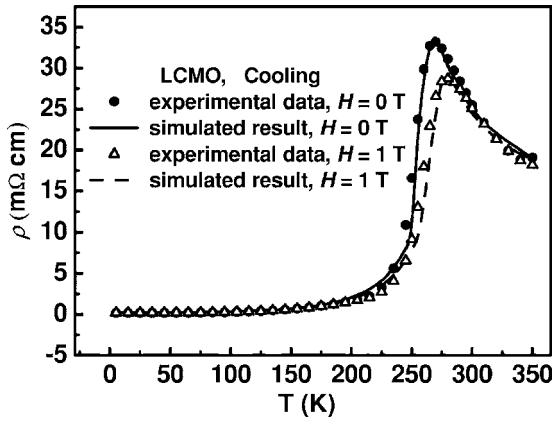

FIG. 2. Simulated T-dependent resistivities of LCMO thin film in the cluster percolation mode on cooling with (dashed line) and without (solid line) H.

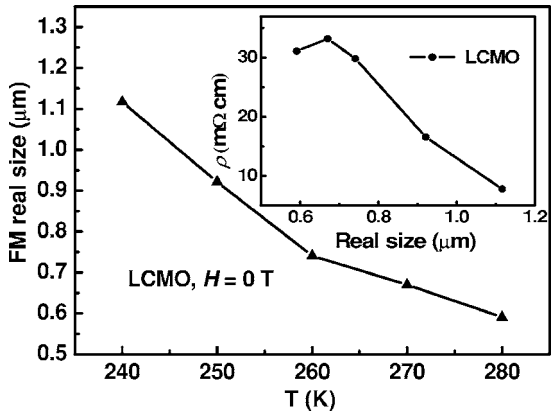

FIG. 3. Calculated T-dependent real size of the FM clusters in LCMO. The inset is a curve of the influence of FM cluster size on the resistivity.

T residual resistivity, E_0 is the activation energy, and k_B represents the Boltzmann constant.[12,13] In fact, ρ_{m0} and ρ_{i0}, which vary with the different materials, can be obtained by fitting the experimental data of the low-T and high-T regions, respectively. So in the simulation procedure, those two parameters remain unchanged and only three other parameters need to be adjusted. Using the breadth-first traversal algorithm,[14] we can find the path lengths of the FM metallic and PM insulating domains, respectively, to derive $R_M(T)$ and $R_I(T)$, then the total effective resistivity can be obtained according to the size of the sample.

From the T-dependent MFM images of $La_{0.33}Pr_{0.34}Ca_{0.33}MnO_3$ thin film in Ref. 6, we can find that the isolated FM domains start to grow and merge at the insulator-metal transition (IMT) temperature, leading to a steep drop in resistivity, and continue to grow far below the IMT temperature. The phase transition and separation mainly occur in the temperature range from ~100 to ~120 K. The scanned area is 6×6 μm^2 for all cooling images. By using the cluster percolation mode and methods mentioned above, we have simulated the T-dependent resistivity of $La_{0.33}Pr_{0.34}Ca_{0.33}MnO_3$ thin film upon cooling on a 300×300 matrix, as presented in the inset of Fig. 1, exhibiting an agreement with the extracted experimental data.

To obtain the relation between the real size in the sample and the simulated cluster size in the network, we have calculated the lattice number of the FM cluster areas and obtained the cluster counts at three temperatures. Furthermore, we use the cluster radius as its size, which can be computed from the cluster area by using the formula of $D=\sqrt{4\times\text{area}/\pi}$, as presented in Fig. 1. It can be found that the three curves exhibit the different maximum count sizes at 113, 110, and 107 K, respectively. The calculated result indicates the maximum count size increases with the decreased T, suggesting the FM cluster grows when T is decreased. According to the MFM images scanned on the area of 6×6 μm^2, we roughly consider that the real size of FM cluster is ~1 μm at 107 K. By dividing the radius size of about seven lattices at the maximum count, we have obtained each lattice in the network represents the real size of around 0.14 μm.

Next we analogize the cluster size in another mixed-phase material of LCMO thin film, which is grown by facing-target sputtering technique.[15] The fabrication and the measurements of LCMO film are reported elsewhere.[16] Applying the simulation methods, we have obtained the calculated resistivities, which agree with the experimental data on cooling with and without H, as shown in Fig. 2. The corresponding parameters used in simulation are listed in Table I.

Analogically, the calculated curve of the T-dependent real sizes without H is given in Fig. 3. It can be concluded that the FM cluster sizes in LCMO increase with the decreased T, exhibiting the intrinsic inhomogeneity in this system. Furthermore, we can predict that the FM cluster size obtained theoretically is around 0.6 μm near T_c (~280 K). This indicates that the PM-FM phase transition takes place when the cluster size of FM clusters reaches about 0.6 μm. Those results are consistent with the observation of the coexisting PM and FM phases on the submicrometer scale in $La_{0.73}Ca_{0.27}MnO_3$ thin film just below T_c.[5] In addition, we find that the IMT occurs when the FM cluster grows up to about 0.7 μm (at ~270 K), and the abrupt drop in resistivity occurs when the cluster keeps increasing to about 0.9 μm (at ~250 K) on cooling. The relation between the resistivity and the FM cluster size is shown in the inset of Fig. 3. The existing peak in the curve reveals it is not always true that the resistivity increases with the decreased FM cluster size. When the FM cluster size is lower than a critical value, the PM cluster size is large enough to connect each other and induces the drop in resistivity. This result indicates that we should not analyze the physics process only by FM cluster or PM cluster evolution. The phase competition in the phase-mixed system is very important to determine the transport property. Moreover, if the bulk is the single crystal, the result will be identical with the thin film. However, for the polycrystalline bulk, the influence of grain boundaries is considerable, as discussed in Ref. 7. To enlarge the clusters around the grain boundaries, additional energy is required to overcome the grain boundaries, which is not energy favorable. Therefore, we believe that the size of cluster in polycrystalline bulk is correspondingly small compared with that in the thin film material.

TABLE I. Parameters used in simulation for LCMO thin film on cooling with and without H.

H (T)	ρ_{m0} (mΩ cm)	ρ_{m1} (mΩ cm K^{-2})	ρ_{m2} (mΩ cm $K^{-4.5}$)	ρ_{i0} (mΩ cm)	E_0/k_B (K)
0	0.19	9.0×10^{-6}	3.2×10^{-11}	7.5	327
1	0.18	8.7×10^{-6}	3.0×10^{-11}	7.5	310

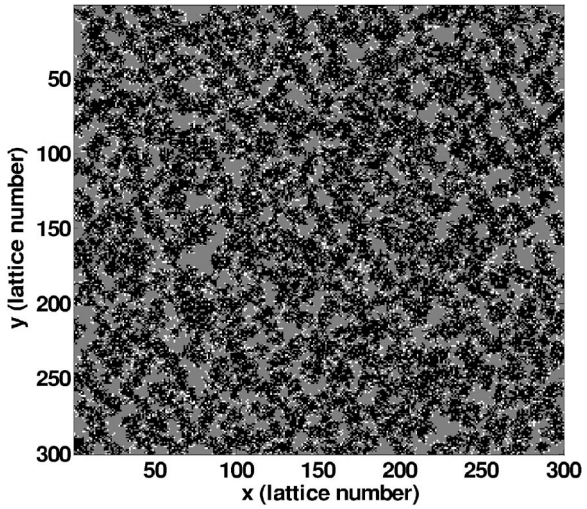

FIG. 4. Simulated result for H-induced enhancement in the FM cluster sizes at $T \sim 250$ K under H of 1 T. Black and gray denote the FM and PM regions, respectively, and white represents the PM state without H that turns into the FM state with H.

Now consider the influence of H on the FM cluster sizes. It is pointed out that the random spin disorder around T_c can be removed partially under H.[5,6,17] Hence, a fraction of PM insulating regions can be converted into FM metallic regions. Similar to the H-dependent magnetization, we believe that H can increase FM fraction f, leading to the growth in cluster size but the decrease in cluster number. In our presented model, the influence of the magnetic field is introduced from the formula of FM fraction f, which increases with the IMT temperature. The quantitative expression of f employed can refer to our previous work.[8] After applying H, due to the reason mentioned above, the IMT temperature will move to a higher value, causing the increase in f in our simulation. Figure 4 demonstrates the simulated result of the H-induced effect on the FM cluster sizes at $T \sim 250$ K under H of 1 T on a 300×300 matrix. From the figure, we can find that the percolation paths of the FM metallic phase have been enhanced due to connection of those size-increased clusters under H, inducing some drop in resistivity. These conclusions are consistent with the observation in some experiments.[3,5]

In summary, by simulating the resistivity of $La_{0.33}Pr_{0.34}Ca_{0.33}MnO_3$ thin film with the known coexisting cluster sizes, we have calculated the real size to which each lattice in the random network corresponds. Then the FM cluster sizes in LCMO thin film are analogically obtained, showing the size increases with the decreased T and becomes larger under H. The theoretical results predict that in LCMO thin film the phase transition occurs when the FM cluster size is about 0.6 μm, the IMT occurs when the size is around 0.7 μm, and the rapid drop in resistivity occurs when the cluster grows up to about 0.9 μm. All the results suggest that the coexisting cluster sizes are important in determining the transport properties of the phase-separated materials. The real sizes of the FM clusters in LCMO thin film still need the further experimental verification.

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