Percolative phase separation induced by nonuniformly distributed excess oxygens

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The zero-field $^{139}$La and $^{55}$Mn nuclear magnetic resonances were studied in $La_{0.8}Ca_{0.2}MnO_3$ (LCMO) [1], many theoretical and experimental works have been done to find the physical mechanism of CMR effect because of their interesting physical properties and application potential. The first explanation of the most interesting physical property of LCMO, the simultaneous occurrence of the paramagnetic to ferromagnetic and insulator to metal transitions, was the simple double exchange model given by Zener in 1951 [2]. However, Millis pointed out that the resistivity of Sr-doped manganites cannot be fully explained by double exchange alone in 1995 [3]. Thereafter, several theories have been proposed to describe the physical properties of CMR materials more completely, one of which is phase separations (PS).

In the low doping range ($x \leq 0.2$), the magnetic phase of LCMO is not homogeneous. The existence of magnetic PS was verified by the simultaneous observation of ferromagnetic and antiferromagnetic nuclear magnetic resonance (NMR) signals at low temperature [4]. Since the ferromagnetic metallic regions are embedded in the antiferromagnetic insulating regions, LCMO in this range shows ferromagnetic insulating behavior macroscopically. Since then, PS has been suspected as one of the possible mechanisms of CMR effect. On the other hand, PS has been also observed near phase transition temperature in LCMO for $0.2 < x < 0.5$, which are homogeneous ferromagnetic metals well below phase transition temperature [5]. These two kinds of PS are thought to be originated from different mechanisms, because the PS observed in the low doping range is the ground state and stable in a wide temperature range, while the PS observed for $0.2 < x < 0.4$ occurs only near phase transition temperature. In this report, we will focus our discussion on the PS in low doped LCMO.

Theory predicts two different types of PS in low doped LCMO. One is the charge segregation type and the other is the electroneutral type. Yunoki [6] studied the 2-orbital Kondo model including the classical Jahn-Teller phonons and found that PS is induced by the orbital degree of freedom. In such a case, the charge density of $e_g$ electron is not stable at a special value of chemical potential, resulting in two regions with different charge densities. The size of both regions is expected to be very small, about the order of nanometer, due to the extended Coulomb interaction. Recently, Uehara presented TEM images of $La_{5/8-x}Pr_{x}Ca_{3/8}MnO_3$ [7] which shows the mixture of the charge ordering phase of $La_{0.5}Ca_{0.5}MnO_3$ type and ferromagnetic phase at low temperature. The sizes of both regions are about 0.5 $\mu m$, which is too large to be explained by the charge segregation type PS. On the other hand, Nagaev paid attention to the PS induced by nonuniformly distributed oxygens [8]. He pointed out that the regions enriched with oxygen have an enhanced hole density and the holes establish local ferromagnetic ordering, whereas the remained regions are poorly conductive and antiferromagnetic due to the electron-hole recombination. In this case, PS is the electroneutral type because the densities of holes and excess oxygens are same in a given region, and the region sizes can be much larger than those of the charge segregation type PS. Several reports have supported the existence of PS, but it still remains unclear which scenario is more correct in low doped LCMO. There have been many works which showed that oxygen plays an important role in determining electromagnetic properties of LCMO [9,10], but its effects on PS have never been studied. In this work, we report that the electroneutral percolative PS is formed in low doped LCMO by excess oxygens. Experimental results provide an evidence for the fact that the PS in the low doping range is one source of CMR.

Two polycrystalline samples of $La_{0.8}Ca_{0.2}MnO_{3+\delta}$ with different $\delta$ values were synthesized by the conventional solid state reaction method. The starting materials were $La_2O_3$, $MnCO_3$, and $CaCO_3$. Calcining and sintering with intermediate regrinding were repeated in the temperature range of 1000 °C - 1350 °C for four days. Sample 1 was obtained by annealing in air at 1100 °C
for two days, and sample 2 was obtained by additional grinding, sintering and annealing of a part of sample 1 in oxygen flow (200 cc/min) at the same temperatures with sample 1. The crystal structures were examined by x-ray powder diffraction with Cu Kα radiation. Both samples were single phase and orthorhombic. The lattice parameters of sample 1 and 2 were \( a_1 = 5.489 \) Å, \( b_1 = 5.496 \) Å, \( c_1 = 7.765 \) Å, and \( a_2 = 5.502 \) Å, \( b_2 = 5.507 \) Å, \( c_2 = 7.777 \) Å, respectively. Resistivity was measured using the conventional four-probe method, and magnetization was measured by a commercial SQUID magnetometer. Zero field NMR spectra were obtained by using a spin-echo technique.

Fig. 1 shows the temperature dependence of magnetization at 1 Tesla. The paramagnetic Curie temperatures (\( T_C \)) of sample 1 and 2 are 191.5 K and 192.2 K, respectively. The difference of \( T_C \) values less than 1 K indicates that the difference between \( \delta \) values of sample 1 and 2 is less than 0.02 [10]. The magnetizations of sample 1 and 2 at low temperature were almost same, and the magnetic field dependences of the magnetizations were almost same either.

Though the macroscopic magnetic properties of two samples are very similar quantitatively, local magnetic environments are quite different as seen in the \(^{139}\text{La} \) NMR spectra obtained at 78 K (Fig. 2). In the figure, two differences are noticeable between the spectra of sample 1 and 2. First, the signal intensity of sample 2 is about five times that of sample 1, and second, the resonance frequency of sample 2 is higher and the linewidth is much broader, especially in the high frequency side. We discuss about the difference of signal intensity first.

The NMR signal intensity of a ferromagnet in zero field is proportional to \( \eta V H_L / T \), where \( \eta \) is the enhancement factor, \( V \) is the volume of the ferromagnetic region of a sample, and \( H_L \) is the local field at the nuclei of interest. Since magnetization which is proportional to \( V \) does not change, the NMR signal intensity change at a given temperature and a frequency by extra oxygens is due to the change of the enhancement factor. Fig. 3 provides experimental evidences for this claim. Fig. 3(a) shows that sample 2 gives the maximal signal at the much lower rf power than sample 1, meaning that rf field is more enhanced in sample 2 than in sample 1. The rf enhancement factors of sample 1 and 2 are about 22 and 105, respectively.

Fig. 3(b) shows the normalized NMR signal intensity vs. external magnetic field obtained at the fixed rf power which makes the maximal signal in zero field. In this figure, we notice that the signal of sample 2 decays almost to zero while that of sample 1 decays slowly approaching the saturation field, about 3 koe. These are the typical responses of single and multi-domain ferromagnets, respectively. The signal of sample 1 decays a little because the enhancement factor decreases with external field. On the other hand, the drastic signal decay of sample 2 means that domain walls disappear approaching the saturation field. Therefore, these results show that sample 2 has domain walls while sample 1 does not. The NMR signal of sample 2 comes mostly from domain walls because the enhancement factor is usually orders of magnitude larger in domain walls than in domain in general [12]. The size of ferromagnetic clusters embedded in the antiferromagnetic host of sample 1 is not large enough to form multi-domain state. The local ferromagnetic orderings generated by excess oxygens connect some of these ferromagnetic clusters and domain walls are formed on them.

In fact, these connected ferromagnetic clusters make also percolative conduction paths as shown in Fig. 4 displaying the temperature dependence of resistivity. The resistivity of sample 1 shows an insulating behavior except a small bending near phase transition, while that of sample 2 shows a broad peak in the temperature range of 170 K - 140 K and a metallic behavior below 140 K. The metallic behavior of sample 2 at low temperature implies that electric transport paths are formed by excess oxygens.

The temperature dependence of the \(^{139}\text{La} \) NMR signal intensity of sample 2 shown in Fig. 5 supports the simultaneous generation of conduction paths and domain walls. The signal intensity of homogeneous ferromagnets such as LCMO for \( 0 < x < 0.5 \) well follow Curie’s \( T^{-1} \) law except in the narrow region near \( T_C \) [1]. However, the signal intensity of sample 2 decreases much faster than \( T^{-1} \), and almost disappears near 140 K where the metallic behavior fades out (Fig. 4). This means that the total volume of domain walls decreases as temperature increases and the ferromagnetic and metallic conduction paths vanish near 140 K. As approaching this temperature from below, ferromagnetic clusters are disconnected and therefore conduction paths are broken continuously.

While the magnetoresistance (MR) curve of stoichiometric perovskite manganite crystals show only one peak near \( T_C \), that of sample 2 shows one more peak near 140 K as seen in Fig. 4. The MR peak near 170 K is an ordinary CMR peak due to the suppression of spin fluctuation by external field, while the peak near 140 K is undoubtedly related with PS. It is worthwhile to note that the MR near the temperature where the percolative PS is induced is as large as that near the phase transition temperature. External field helps connecting clusters somehow.

We now discuss the second difference of the spectra of sample 1 and 2, the difference in resonance frequency and linewidth. The local field \( H_L \) at the position of a non-magnetic \(^{3+}\text{La} \) ion can be described as

\[
H_L = A \sum_j n_j \mu_j + H_{d-d},
\]

where \( A \) is the transferred hyperfine coupling constant and \( n_j \) is the number of the j-site Mn moments \( \mu_j \), sur-
rounding the La ion. \( H_{d-d} \) is the dipolar field summed over all Mn magnetic moments. In perovskite manganites, the dipolar field is negligible and the main contribution to \( H_L \) comes from the transferred hyperfine field. The transferred hyperfine field is thought to be produced by the \( \pi \) type overlapping between the Mn \( t_{2g} \) electron wave function and the oxygen \( |2p_{\pi}\rangle \) wave function, and the \( \sigma \) bonding of the oxygen with the \( |sp^3\rangle \) hybrid states of the La\(^{3+}\) ion [13]. That is, an indirect transferred hyperfine field of the Fermi contact type is mediated by oxygens. Therefore, the constant \( A \) is a function of the distance between oxygens and a La\(^{3+}\) ion, and the number of the oxygens surrounding the La\(^{3+}\) ion. \( n_j \) and \( \mu_j \) are almost same in two samples. The distance between oxygens and a La\(^{3+}\) ion is not an important factor making the difference of the NMR peak frequencies because the peak frequency of sample 2 is higher than that of sample 1 even though the lattice constants of sample 2 are slightly larger than those of sample 1 [13]. Therefore, the difference of peak frequencies should be attributed to the difference of the number of oxygens surrounding a La\(^{3+}\) ion. That is to say, the peak frequency of sample 2 is increased due to the excess interstitial oxygens. There is a report that LaMnO\(_{3+\delta}\) with excess oxygens is characterized by cation vacancy in La and Mn sites rather than by interstitial anions [15]. In this case, however, the lattice parameters decrease as \( \delta \) increases contrary to our case [10]. Moreover, the NMR spectrum of LaMnO\(_{3+\delta}\) having cation vacancy is well fitted by a single gaussian curve while our sample 2 is not as discussed below.

The La NMR spectrum of sample 2 is asymmetric and broader than that of sample 1 in the high frequency side. Since \( \delta \) is less than 0.02, homogeneous distribution of oxygens cannot enhance the signal in the high frequency side as much as the spectrum in Fig. 2. Therefore, oxygens aggregate to make local ferromagnetic orderings in consistence with Nagaev’s claim that oxygens have a tendency to concentrate. One of the reasons why conduction paths are continuously disconnected as approaching 140 K could be the distribution of excess oxygens becoming more and more uniform as temperature increases.

Contrary to La nuclei, the local field at Mn nuclei is negligibly influenced by the local distribution of oxygens because the hyperfine field of the direct Fermi contact type generated by it’s own 3d electrons is much stronger. Therefore, the gaussian shape of the Mn NMR spectrum does not change by the presence of excess oxygens as shown in the inset of Fig. 2. The \( ^{55}\text{Mn} \) NMR spectra are motionally narrowed by the fast hopping of \( e_g \) electrons between Mn\(^{3+}\) and Mn\(^{4+}\) ion sites [7,15]. Only the Mn nuclei in ferromagnetic regions with the delocalized \( e_g \) electrons contribute to the \( ^{55}\text{Mn} \) NMR signal. The local field at Mn nuclei is proportional to the number of average delocalized \( e_g \) electrons. The peak frequency shift by excess oxygens is not less than 10 Mhz. If the distribution of holes is uniform, such a shift corresponds to \( \delta \sim 0.075 \), while \( \delta \) of sample 2 is less than 0.02. This means that the holes are concentrated in ferromagnetic regions. The results of La and Mn NMR imply the concentrated oxygens and holes in ferromagnetic regions, respectively. This support the fact that the PS in low doped LCMO is the electroneutral type. Moreover, considering the easy formation of conduction paths by the aggregation of excess oxygens less than 0.7 %, the size of ferromagnetic clusters are not so small as predicted by the charge segregation type PS.

In conclusion, the excess oxygens have a tendency to aggregate and change surroundings into ferromagnetic phase. These local ferromagnetic regions connect ferromagnetic clusters previously existed in stoichiometric samples, which are suspected to be also generated by inhomogeneous distribution of oxygens. This connection produces percolative conduction paths on which domain walls are formed. The observed PS is rather a electroneutral type than a charge segregation type. As temperature increases, the MR peak was observed at the temperature where the percolative PS disappears in addition to the ordinary peak near the phase transition temperature.

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FIG. 1. The temperature dependence of magnetization at 1 Tesla.

FIG. 2. The zero field $^{139}$La NMR spectra obtained at 78 K. The frequency and the spin-spin relaxation time dependences of signal intensity were removed. Inset: the zero field $^{55}$Mn NMR spectra obtained at 78 K. The intensity of sample 1 is about forty time amplified.

FIG. 3. The rf-power dependence(a) and external magnetic field dependence(b) of $^{139}$La NMR signal intensity obtained at 78 K.

FIG. 4. The temperature dependence of resistivity and magnetoresistance (MR). The MR value is defined as $(\rho(0) - \rho(9 \text{koe}))/\rho(0)$.

FIG. 5. The temperature dependence of the $^{139}$La NMR intensity of sample 2. The signal dependence on the spin-spin relaxation time and frequency were carefully eliminated from the raw data. The solid line represents a $T^{-1}$ curve.