

Zero-field ^{139}La nuclear magnetic resonance in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $0.125 \leq x \leq 0.5$

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The zero-field ^{139}La nuclear magnetic resonance (NMR) was studied in polycrystalline $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $0.125 \leq x \leq 0.5$ to investigate magnetic phases in ordered states. The main result of this work is that mixed states are found near any phase transition boundary induced by either temperature or hole doping. The analysis of the NMR signal intensity and resonance frequency provides the evidence for ferromagnetic clusters or magnetic polarons near the ferromagnetic transition temperature (T_C). The drastic change of the enhancement factor crossing the phase boundary at $x=0.2$ implies the existence of single domain ferromagnetic microregions imbedded in an antiferromagnetic host for $x < 0.2$. The comparison of NMR signal intensity with bulk magnetization shows that the macroscopic antiferromagnetic phase at $x=0.5$ is a mixed state of microscopic ferromagnetic and antiferromagnetic phases.

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I. INTRODUCTION

The perovskite oxides, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, have recently been the subject of intense study due to their ‘‘colossal magnetoresistance (CMR)’’ near the transition from a paramagnetic insulator to a ferromagnetic metal for $0.2 < x < 0.5$. The simultaneous occurrence of the paramagnetic to ferromagnetic, and insulator to metal transitions upon cooling has been qualitatively explained on the basis of Zener’s model of double exchange between Mn^{3+} and Mn^{4+} ions.¹ In this model, CMR is qualitatively understood to be due to the suppression of spin fluctuations by external magnetic field. The compound has several magnetic and electric phases depending on temperature and hole doping concentration.²⁻⁴ The ground state is an antiferromagnetic charge-ordered insulator in the high doping range of $0.5 < x < 0.8$, and at the phase boundary with $x=0.5$, undergoes first a ferromagnetic transition and then a simultaneous antiferromagnetic and charge ordering transition at a lower temperature. On the other hand, the magnetic phase for $x < 0.2$ and $x > 0.8$ is still controversial. Experimental results have been interpreted as supporting a weak ferromagnetism either resulting from canted antiferromagnetism or a mixed state of ferromagnetic and antiferromagnetic phases in these concentration ranges.⁴⁻⁷ The main purpose of this report is to study the magnetic phases of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ in its ordered states, especially near the ferromagnetic phase boundaries.

Nuclear magnetic resonance (NMR) can provide valuable informations on the microscopic magnetic properties in these oxides. The NMR spectrum of the magnetic ion, Mn, in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ was observed at 77 K in the frequency range of 250–450 MHz corresponding to a local field of 230–430 kG.⁶⁻¹⁰ The NMR spin echo spectrum of the non-magnetic ion, La, was observed in the frequency range of 11–26 MHz in $\text{La}_{0.9}\text{Na}_{0.1}\text{MnO}_3$.¹¹ In our work, the magnetic phases of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ were investigated covering a wide range of Ca concentration ($0.125 \leq x \leq 0.5$) by studying the zero field

^{139}La NMR spectrum as a function of temperature. One of the differences in the zero field NMR of magnetic and non-magnetic ions is that the latter is observed basically only in ferromagnetic states, which was essential to show the existence of mixed magnetic states in our experiments. The results of the analysis of the signal amplitude, resonance frequency, relaxation rates, and enhancement factor show that the magnetic phases in these manganites are inhomogeneous near the phase boundaries due to temperature and Ca concentration. In the vicinity of the paramagnetic to ferromagnetic transition temperature (T_C), a mixed state of these two phases was found, which could be magnetic polarons or ferromagnetic clusters in a paramagnetic host. In the concentration range of $0.125 < x < 0.2$, which is between a ferromagnetic phase ($x > 0.2$) and an antiferromagnetic phase ($x = 0$), a mixed state of these two phases were found instead of homogeneous canted antiferromagnetic phase predicted by previous theory¹² and experiments.^{5,6} A similar mixed state was observed at the phase boundary with $x=0.5$.

II. EXPERIMENTAL

Polycrystalline samples of manganese perovskites $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x=0.125, 0.15, 0.175, 0.2, 0.25, 0.3, 0.375, 0.4, \text{ and } 0.5$) were prepared through the conventional solid state reaction processing in air. The stoichiometry was verified by chemical analysis after various heat treatments. X-ray powder diffraction data were collected with a commercial diffractometer using $\text{Cu } K\alpha$ radiation from 4° to 140° in steps of 0.04° in 2θ . The temperature dependence of the magnetization was measured using a commercial SQUID magnetometer at 100 Oe and a custom made radio frequency (rf) magneto-susceptometer. Resistivity was measured using the standard four probe technique.

The ^{139}La NMR spectra were obtained in the temperature range of 78 K to room temperature by the spin echo technique in zero external field. Since the spectra were very

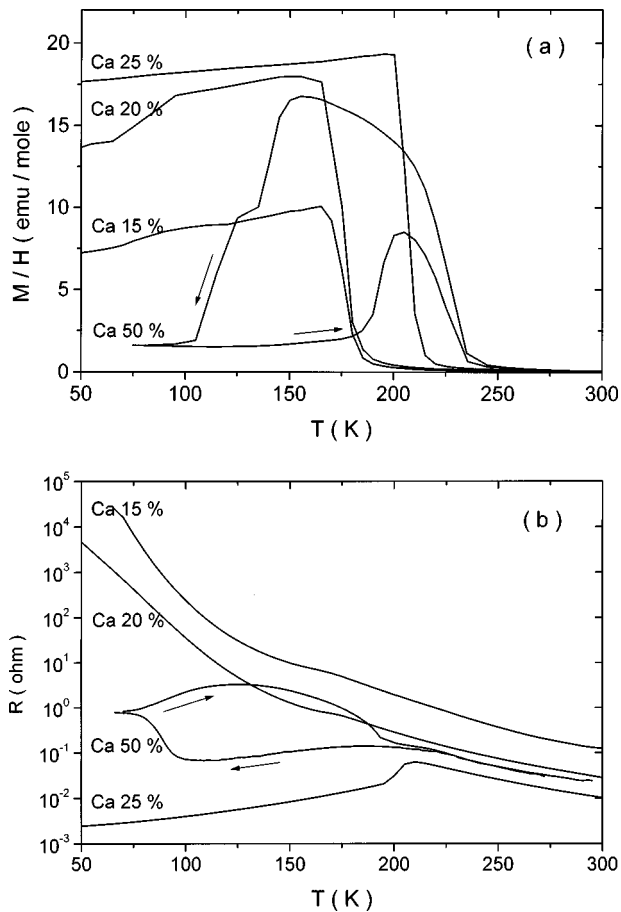


FIG. 1. (a) The temperature dependence of magnetization for $x=0.15, 0.2, 0.25,$ and 0.5 at 100 Oe. (b) The temperature dependence of resistance of the same samples. The arrows indicate the direction of temperature variation. Hysteresis was observed only for $x=0.5$.

broad (about 4 MHz), echo heights were measured as a function of frequency after a partial spectral excitation. A $90^\circ - 180^\circ$ pulse sequence was used for the echo generation and the width of the 90° pulse was $0.5\mu\text{s}$, corresponding to an excitation bandwidth of 2 MHz. The NMR spectra have been obtained by using a carefully tuned and matched coil for precise measurement of signal amplitude. The spin echo time was fixed at $20\mu\text{s}$, and the spin-spin relaxation was not single exponential.

III. RESULTS AND DISCUSSION

A. Magnetization and resistivity

Figure 1(a) shows the temperature dependent magnetization of some selected samples obtained by SQUID magnetometer at 100 Oe. Every sample undergoes a ferromagnetic transition, and the system at $x=0.5$ shows an additional antiferromagnetic transition below T_C . The ordered state of this system below the antiferromagnetic transition temperature (T_N) is not pure antiferromagnetic in the sense that the magnetization is nonzero. The amount of remnant magnetization at this concentration differs in each report.¹³⁻¹⁶ This is because the physical properties at this phase boundary concentration is very sensitive to the process of sample preparation, such as annealing condition or stoichiometry. A large

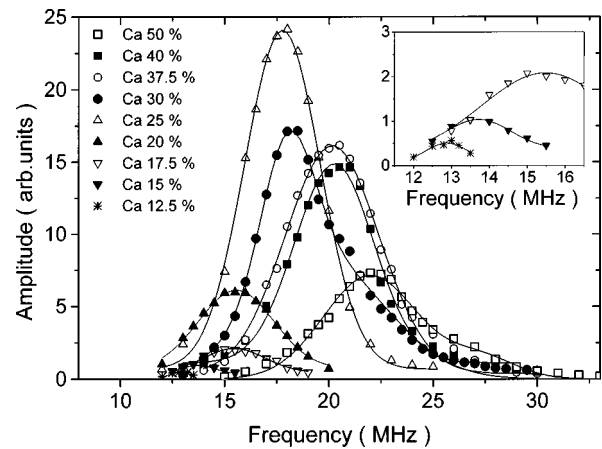


FIG. 2. The zero-field NMR spectra of ^{139}La obtained at 78 K for various Ca concentrations. The intensities are normalized with respect to the number of La ions.

hysteresis is observed upon cooling and warming at T_N , implying a strongly first order transition.

Figure 1(b) shows the temperature dependent resistance of the same samples. The samples are insulating for $x \leq 0.2$, and metallic for $0.2 < x < 0.5$ at low temperature. Our sample with a nominal concentration of $x=0.2$ is a ferromagnetic insulator at low temperature in contrast to a previous report.² Chemical analysis showed that the exact Ca doping concentration of this sample is 0.194. A large hysteresis is also observed in resistance near T_N at $x=0.5$.

B. NMR results

The zero-field NMR spectra of ^{139}La measured at 78 K for $0.125 \leq x \leq 0.5$ is shown in Fig. 2. The signal intensity was normalized with respect to the number of La nuclei, and the dependences on the spin-spin relaxation time and frequency were carefully eliminated from the raw data. The La NMR spectra were observed in the frequency range of 12–33 MHz and the linewidths were 3–5 MHz. In the figure, two aspects are most noticeable. The signal intensity is high in the ferromagnetic metallic regime, that is, in the range of $0.2 < x < 0.5$, being maximum at $x=0.25$, and the peak resonance frequency increases monotonically with increasing x . Below, we first consider the resonance frequency.

Since La ions are nonmagnetic, the local field at the La site is mainly due to the electronic magnetic moments of Mn ions in the absence of an external field. The local field H_L at a La nucleus is the sum of the transferred hyperfine field, which is due to the overlap of Mn orbitals with the on-site s -wave functions, and the dipole field generated by Mn magnetic moments, which can be written as

$$H_L = C \sum_j n_j \mu_j + H_{d-d}, \quad (1)$$

where C is the hyperfine coupling constant and n_j is the number of the j -site Mn moments, μ_j , surrounding the La ion. H_{d-d} is the dipolar field summed over all Mn magnetic moments. The dipolar field is negligible and the main contribution comes from the transferred hyperfine field in manganese perovskites. The monotonically increasing local field with increasing x is somewhat unusual, because the average

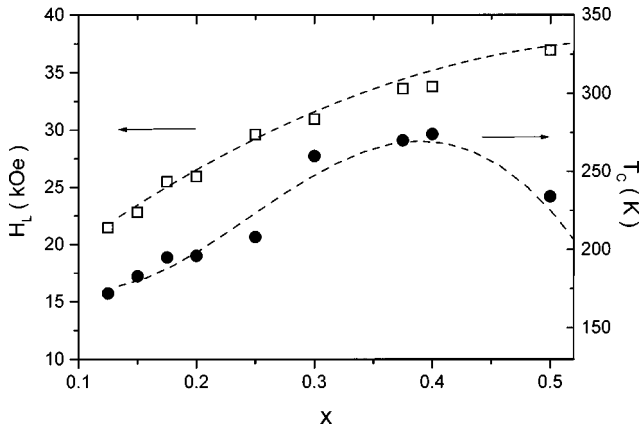


FIG. 3. The local field at La ions (open squares) and T_C (solid circles) obtained as a function of x at 78 K.

Mn magnetic moment decreases from $4\mu_B$ to $3\mu_B$ with x increasing from 0 to 1. If the coupling constant C is independent of x , the local field on a La nucleus should decrease with the decreasing average magnetic moment.

The local field at Mn nuclei was shown to increase in spite of the decreasing average magnetic moment with Ca concentration for $x < 0.3$ by Mn NMR.^{6,7} The shift of the Mn NMR spectrum to higher frequency with increasing x was attributed to an increasing transferred hyperfine field, because the mobility of Mn electrons increases with x at low doping concentration. There have been no report on the Mn NMR near Ca concentrations as high as 0.5. It is reported that the local field at La nuclei also increases with increasing hole doping at low hole concentrations in $\text{La}_{0.9}\text{Na}_{0.1}\text{MnO}_3$ and $\text{LaMnO}_{3+\delta}$.¹¹ In these studies it was argued that this local field increase at La ions was also due to the increased mobility of the spin-polarized carriers. Since the carrier mobility was proportional to the double exchange interaction, the local field at La nuclei was claimed to be proportional to T_C . However, we see that this argument is valid only for low hole concentrations in Fig. 3, where the local field is compared with T_C . The Curie temperature increases with increasing x from 0.125 to 0.4, and then decreases, whereas the local field monotonically increases with increasing x . Moreover, it is not quite clear how the mobility of carriers due to the double exchange interaction affects the overlap of Mn and La wave functions when those carriers move along Mn-O bonds.

A simple explanation for the local field increase at La ions is the change in lattice constants with x . The transferred hyperfine field at La nuclei comes from the overlap of the Mn d -orbitals with the on-site s -orbital, which is sensitive to the Mn-La distance.¹⁷ The average lattice constants of our manganese samples decrease monotonically with x and the value at $x=0.5$ is about 2.3 % smaller than that at $x=0.125$. Therefore, the increased overlap of the Mn and La orbitals owing to the decreased average lattice constant will increase the local field on La nuclei.

The top panel of Fig. 4 shows the integrated NMR signal intensity per La ion, measured at 78 K, for various Ca concentrations. The intensity is almost constant in the ferromagnetic metallic state, but decreases at the phase boundaries. Note that the NMR intensity drops drastically as the concentration crosses the ferromagnetic metal-insulator phase

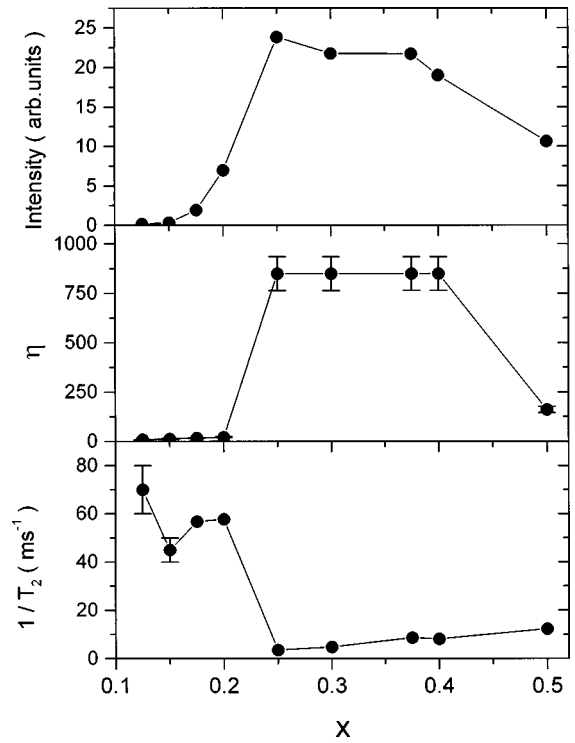


FIG. 4. The integrated NMR signal intensity (top), average rf enhancement factor (middle), and initial spin-spin relaxation rate ($1/T_2$) (bottom) vs x .

boundary at $x=0.2$, while the bulk magnetization changes slowly as seen in Fig. 1(a). The NMR signal intensity of a ferromagnet in zero field is proportional to $\eta V H_L / T$, where V is the volume of a sample and η is the enhancement factor. In ferromagnetic NMR, generally both the signal and rf input is enhanced due to the accompanying oscillation of electronic magnetic moments. The enhancement factor is usually $10-10^2$ in domains and 10^2-10^4 in domain walls.¹⁹ The rapid drop of signal intensity in the ferromagnetic insulating phase should result from the rapid drop of the enhancement factor, volume of ferromagnetic phase, or the local field. The local field does not change drastically upon crossing the phase boundary at $x=0.2$, as seen in Fig. 3. If the volume of the ferromagnetic phase decreases, it is reflected in the bulk magnetization which is proportional to the volume integrated magnetic moment. Figure 1(a) shows this is not the case. Therefore, the rapid decay of the NMR signal intensity is due to the rapid decay of the enhancement factor.

The experimental result of the enhancement effect measurement (middle panel of Fig. 4) provides evidence for this argument. To measure the enhancement factor, we compared the input rf power, which generates the maximum La NMR echo signal for a $90^\circ-180^\circ$ pulse sequence, with that of proton NMR. The measured enhancement factor is the volume weighted average of the enhancement factors in domain walls and within domains. The average enhancement factor is 850 for $0.25 \leq x \leq 0.4$, which is a bit smaller than previous results ($\eta > 1000$),^{7,13} and drops to 10–20 for $x \leq 0.2$. The rf enhancement factor was nearly independent of temperature and frequency over the whole spectral range.

Since the enhancement effect is orders of magnitude larger in domain walls than in domains, the average enhancement factor in multidomain ferromagnets decreases as do-

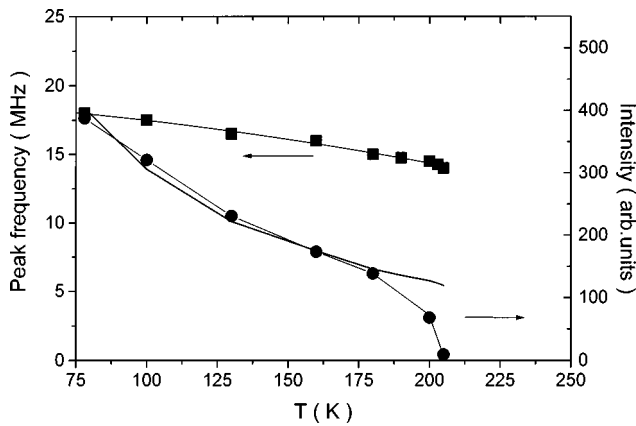


FIG. 5. The integrated NMR signal intensity (solid circle), the intensity predicted when the volume of the ferromagnetic region is constant (solid line), and the peak NMR frequency (solid square) at $x=0.25$.

main walls disappear with increasing external field. In addition, the NMR intensity in multi-domain ferromagnets also decreases as domain walls disappear with increasing external field. These decreases of the enhancement factor and the NMR intensity with field were observed for $x>0.2$, but not for $x\leq 0.2$. This observation, and the orders of magnitude smaller η for $x<0.2$, imply that there are no domain walls for $x<0.2$. This means that the ferromagnetic regions in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ are too small to have multi-domains in this concentration range. Microscopic ferromagnetic regions are imbedded in some other magnetic phase. The magnetic phase of the end members of these manganites are antiferromagnetic, and experiments provide evidences for an antiferromagnetic phase for $0<x<0.2$. Therefore, the most probable state for $x<0.2$ is isolated single domain ferromagnetic micro-regions imbedded in an antiferromagnetic host. The bulk magnetization in Fig. 1(a) implies that the number and/or size of ferromagnetic regions decreases with decreasing x .

The sudden increase of the initial spin-spin relaxation rate ($1/T_2$) shown in the bottom panel of Fig. 4 also supports this picture. The spin-spin relaxation for $0.2<x<0.5$ can be attributed to the usual relaxation mechanisms in ferromagnets, such as the dipole-dipole and Suhl-Nakamura interactions, but they cannot explain an order of magnitude larger relaxation rate in compounds for $x<0.2$. The elevated spin-spin relaxation rate is believed to be due to the spin fluctuations in the mixed state of ferromagnetic and antiferromagnetic phases, as near T_C where a paramagnetic phase is mixed with a ferromagnetic phase (discussed later). The spin glass behavior observed in magnetization at low hole doping¹⁸ also suggests that the magnetic phase in this concentration range is not an ordinary homogeneous ferromagnet. The smooth change of the local field excludes the possibility of canted antiferromagnetism over the whole experimental range of concentration.

The NMR intensity at $x=0.5$, where the phase is not purely antiferromagnetic at low temperature, is much larger than expected by bulk magnetization contrary to the low doping case. The magnetization at $x=0.5$ is an order of magnitude smaller than that at 0.25 at 78 K [as seen in Fig. 1(a)]. Nevertheless, the NMR intensity at $x=0.5$ is about a half

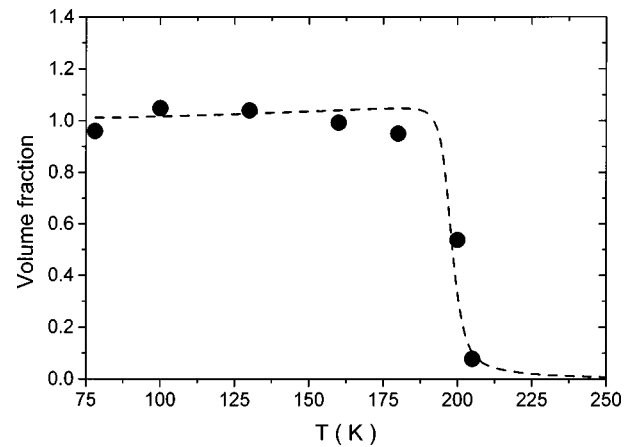


FIG. 6. The volume fraction change of the ferromagnetic region as a function of temperature at $x=0.25$. The dashed line is the normalized magnetic susceptibility.

that at $x=0.25$ (top panel of Fig. 4). The signal amplitude at $x=0.5$ is even bigger than those for $x<0.2$ while the magnetization is smaller. The hyperfine field in a cubic structure should be cancelled out for antiferromagnetic ordering, and therefore the zero field NMR signal cannot be detected at the same frequency, even though the antiferromagnetic ordering is imperfect. This means that non-negligible amounts of a ferromagnetic phase is mixed with the antiferromagnetic phase at $x=0.5$. This is not due to chemical inhomogeneity of our sample. The magnetic ordering below $x=0.5$ is known as the B-type ferromagnet, and that at $x=0.5$ is known as the charge ordered CE-type.⁴ The small residual magnetization and NMR signal could be attributed to B-type ferromagnetic impurity regions in an antiferromagnetic host. However, x-ray diffraction data has shown a single perovskite structure for our sample of $x=0.5$, and the error range is too small to explain the large NMR signal and residual magnetization.

Papavassiliou *et al.*¹³ suggested that the hyperfine field is not symmetrically transferred from the Mn octant due to broken cubic symmetry, or the Jahn-Teller distortion of the oxygen octahedra. However, this broken symmetry does not appear to be significant enough to explain the similarity of the local field in the antiferromagnetic phase with that in the ferromagnetic phase. Another possibility is the freezing of the spin-polarized carriers at Mn ions around La ions with charge ordering, which occurs simultaneously with antiferromagnetic ordering. Since the valence of La ions is +1 larger than that of Ca ions, it is feasible that charge carriers have the tendency of freezing at Mn ions around La ions rather than Ca ions at the charge ordering phase transition. Then the spin-polarized carriers transferred to La nuclei can generate a large local field though the bulk magnetization is small. So far there is no direct experimental evidence for the charge freezing near La ions.

Figure 5 shows the integrated NMR intensity and the peak resonance frequency vs temperature for $x=0.25$. The most peculiar feature of this graph is that the resonance frequency does not vanish when the NMR signal does at T_C . In all samples with $0.2<x<0.5$, the NMR signal disappeared at T_C , but the resonance frequency remained at about 65% of its maximum value in the zero temperature limit. Similar

results have been obtained by other workers.^{9–11,13} The NMR resonance frequency is proportional to H_L , while the signal amplitude is proportional to $H_L V$. Therefore, the resonance frequency vanishes with the signal amplitude on the disappearance of magnetic moments at T_C in ordinary ferromagnets. The finite resonance frequency with vanishing signal amplitude at T_C in our case means, therefore, that the volume of the ferromagnetic region vanishes at T_C , rather than the magnetic moments.

The intensity estimated from the local field data assuming a fixed volume of the ferromagnetic phase is drawn together in Fig. 5. The measured intensity deviates downward from the estimated intensity approaching T_C , reflecting the volume decrease of the ferromagnetic phase. The volume fraction of the ferromagnetic phase can be obtained as the ratio of the measured intensity to the estimated intensity. In Fig. 6, this volume fraction is compared with the normalized magnetic susceptibility. The close similarity of these two graphs implies that the bulk magnetization also vanishes approaching T_C , not due to the loss of the magnetic moment but due to the loss of the volume of the ferromagnetic phase. This is interpreted as the existence of ferromagnetic clusters or magnetic polarons near T_C . The total volume of these ferromag-

netic clusters or the number and/or the size of magnetic polarons decreases approaching T_C from below. Kasuya reported that the magnetization within each magnetic polaron was roughly saturated even at T_C ,²⁰ consistent with our result. This interpretation is also consistent with the result of neutron scattering in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$,²¹ which shows that the phase preferred at low temperature was an ordered ferromagnet with finite magnetization and well-defined spin waves, while at high temperature, a paramagnet where electrons diffuse on a short length scale. As temperature is increased toward T_C , the ratio of the paramagnetic phase to the ferromagnetic phase increases. A study of electron paramagnetic resonance in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (Ref. 13) showed that the paramagnetic phase exists even at $T \sim 160$ K, which is far below T_C .

In conclusion, we have found mixed states in every phase boundary of ferromagnetic $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. Near the phase boundaries at $x = 0.2$ and 0.5 , a mixed state of ferromagnetic and antiferromagnetic phases is found. Near T_C , a mixed state of ferromagnetic and paramagnetic phases is found, which includes the possibility of ferromagnetic clusters or magnetic polarons.

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