

Phase separation in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ observed by ^{55}Mn and ^{139}La NMR

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We studied zero-field ^{55}Mn and ^{139}La nuclear magnetic resonance (NMR) in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The ^{55}Mn and ^{139}La NMR intensities, resonance frequencies, and spin-spin relaxation times showed thermal hystereses upon cooling and warming. The analysis of the result shows that there are two distinct phase regions below T_C : a stable metallic ferromagnetic (FM) region and a region where metallic FM and insulating antiferromagnetic phases compete. The two metallic FM phases are distinguished by mobile e_g electron density. The e_g electron density of the stable FM phase is 0.5, but that of the FM phase in the competition region is lower than that. [S0163-1829(99)04945-0]

Perovskite manganites, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, have recently received much attention due to their unusually large magnetoresistance effect produced by interplay among spin, charge, and lattice. The end members of this series, LaMnO_3 and CaMnO_3 , are antiferromagnetic (AFM) insulators. Substitution of La in LaMnO_3 by divalent alkali metal leads to the injection of mobile holes into the valence band, which favors metallic ferromagnetic (FM) state via double exchange interaction.¹ Competition between AFM superexchange and FM double exchange interactions creates a rich variety of magnetic and electric phases depending on temperature and Ca concentration x . Upon cooling, $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ first experiences a metallic FM phase at $T_C \approx 230$ K and then an insulating AFM phase at $T_N \approx 150$ K.²⁻⁷ In 1955, Wollan and Koehler² observed two independent magnetic sublattices in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ at a low temperature by neutron powder diffraction. Goodenough⁸ discussed that this spin ordering is accompanied by charge ordering of Mn^{3+} and Mn^{4+} , which suppresses the FM coupling, allowing the system to enter an AFM phase.³ Recently, it was observed that FM and AFM phases coexist below T_N by means of ^{55}Mn and ^{139}La NMR.^{9,10} This phase separation was observed not only near $x=0.5$ but also near any phase boundaries of the metallic FM phase ($0.2 < x < 0.5$) induced by either temperature or hole doping.¹⁰ Theory also predicts separation of phases with different mobile e_g electron densities in several cases.¹¹ Long-range Coulomb interaction makes many small pieces of phase regions energetically more stable than a few big pieces. However, it is expected that the competing phases have similar electron density and macroscopic phase regions are created in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.

In this paper, we present a detailed investigation of the phase separation in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ by means of ^{55}Mn and ^{139}La NMR. It is found that there are two distinct phase regions below T_C : a stable metallic FM region and a region where metallic FM and insulating AFM phases compete. The e_g electron density of the FM phase in the competition region seems to be lower than that of the stable FM phase. NMR intensities, resonance frequencies, and spin-spin relaxations showed hystereses upon cooling and warming.

Polycrystalline $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ was prepared by the standard solid-state reaction method. X-ray powder diffraction

data showed that the lattice constants closely agree with published data.⁴ Temperature dependence of magnetization was measured using a commercial superconducting quantum interference device magnetometer at 100 Oe. ^{55}Mn and ^{139}La NMR spin echo spectra were measured as a function of frequency after partial spectral excitation in the temperature range of 78 K to room temperature in zero external field. A carefully tuned and matched coil was used for precise measurement of echo signal.

Figure 1 is magnetization obtained both upon cooling and warming $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The magnetization curve shows strong hysteresis. Upon cooling, the sample undergoes a FM transition at $T_C \approx 230$ K. The magnetization reaches its maximum at $T \approx 150$ K, and then drops down to a stable value at $T \approx 105$ K. The transition at $T_N \approx 150$ K is not a pure AFM transition in the sense that magnetization does not vanish but remains at about 10% of the maximum value. The amount of remnant magnetization at $x=0.5$ differs in each report,²⁻⁷ depending on the process of sample preparation.

In zero-field NMR of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, Mn or La nuclear spins experience large local field originating from Mn 3d electron magnetic moments. The local field is represented as

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

where A and C are the on-site and transferred hyperfine coupling constants, respectively, μ is the on-site Mn magnetic moment, and n_j is the number of the j -site Mn moments, μ_j ,

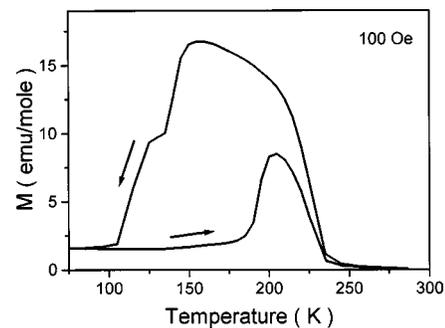


FIG. 1. The temperature dependence of the magnetization at 100 Oe.

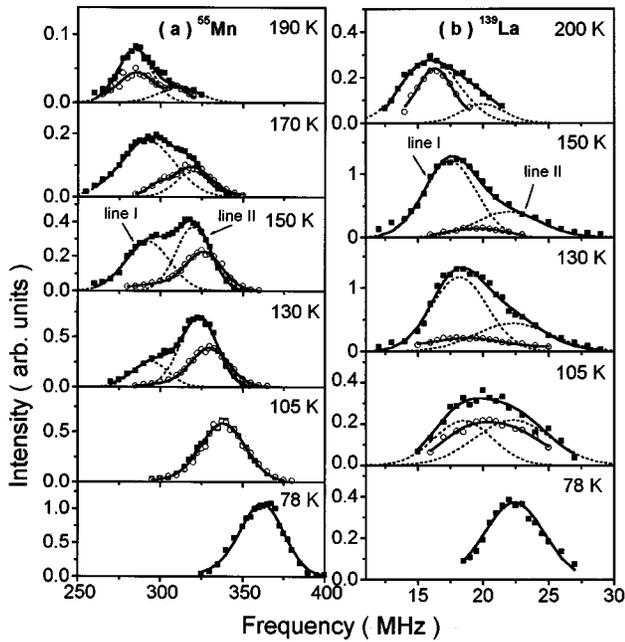


FIG. 2. The zero-field spectra of ^{55}Mn NMR (a) and the zero-field spectra of ^{139}La NMR (b), obtained upon cooling (solid square) and warming (open circle). Dashed lines represent the double Gaussian fit to the spectra.

neighboring the Mn or La ions. H_{d-d} is the dipolar field summed over all Mn magnetic moments. The on-site hyperfine field is dominant at Mn nuclei, while the transferred hyperfine field is dominant at La nuclei because La ions are nonmagnetic. Therefore, zero-field Mn NMR spectrum can be observed in any spin-ordered phases, while La NMR spectrum can be observed only in FM phase. The dipole field is canceled at a site of cubic symmetry, though a small dipole field was observed in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ by broken symmetry at low temperature.⁴

Figures 2(a) and 2(b) are the zero-field Mn and La NMR spectra obtained at various temperatures, respectively. Radio frequency (rf) fields required for the maximum echo signals of Mn and La NMR were orders of magnitude smaller than that of proton NMR, meaning that rf enhancement is very large.¹⁰ This rf enhancement is typical in FM NMR, and therefore the observed NMR signals come from the nuclear spins in FM phases. The Mn NMR signal coming from the nuclear spins in an AFM phase was observed only at very low temperature, below 5 K, in zero fields.⁹ Both the Mn and La NMR spectra show strong thermal hysteresis.

Near $T_N \approx 150$ K, it is clearly noticed that the Mn NMR spectrum obtained on cooling is composed of two peaks. In the metallic FM state, e_g electrons hop fast between Mn^{3+} and Mn^{4+} ion sites. If the hopping time is shorter than the period of the Larmor precession, Mn nuclear spins experience an averaged local field of Mn^{3+} and Mn^{4+} electron magnetic moments. This leads to observation of a motion narrowed NMR spectrum of single peak, instead of double peaks coming separately from nuclear spins at Mn^{3+} and Mn^{4+} sites. The motion narrowed ^{55}Mn NMR spectrum has been observed in the whole metallic FM regime of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.2 < x < 0.5$). In an insulating FM state ($x < 0.2$), separate peaks of Mn^{3+} and Mn^{4+} are

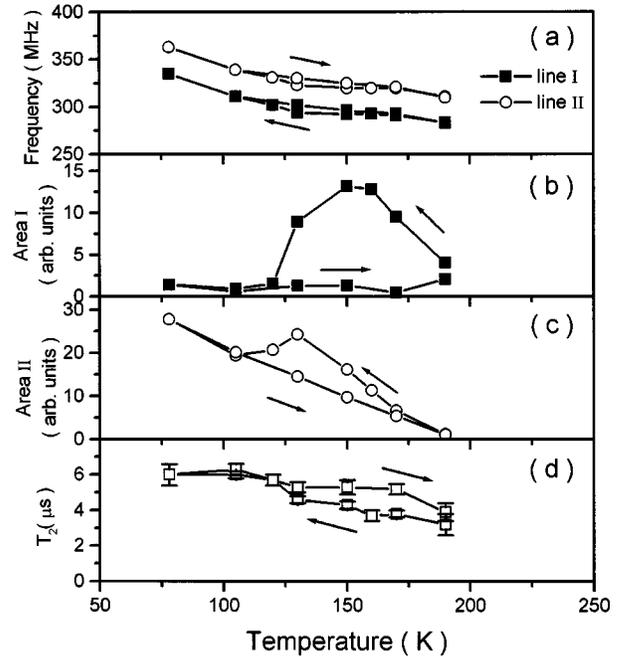


FIG. 3. The ^{55}Mn NMR frequency of line I (open circle) and line II (solid square) (a), the spectral area of line I (b), the spectral area of line II (c), and the spin-spin relaxation time (d) plotted as a function of temperature. The error range in (a), (b), and (c) is roughly the size of data points.

observed.^{12,13} The separate peaks shown in Fig. 2(a) are not due to freezing of mobile e_g electrons, however, because the relative frequency difference, $\Delta f/f_0$, is less than 10% while that of Mn^{3+} and Mn^{4+} peaks should be 33%. Therefore, the double peaks are interpreted to show the coexistence of two distinct metallic FM phase regions, as discussed in detail below.

Figure 3 shows the Mn NMR center frequencies and the spectral areas of the two lines obtained by the double Gaussian fit to the spectra in Fig. 2(a), together with the spin-spin relaxation time (T_2) as a function of temperature. Both of the center frequencies increase monotonously with decreasing temperature, and the frequency difference is about 28 MHz irrespective of temperature throughout the whole temperature range. The resonance frequencies remain finite when the spectral areas vanish as approaching T_C . This fact has been observed in several reports on perovskite manganites and interpreted to mean that the volume of the FM region vanishes at T_C rather than the magnetic moments, contrary to ordinary ferromagnets.^{10,14-16} In other words, a mixed state of FM and paramagnetic phases is observed near T_C , which includes the possibility of FM clusters or magnetic polarons.

In the spectral areas shown in Figs. 3(b) and 3(c), the Boltzmann factor was removed. The spectral area of line I shows strong thermal hysteresis compared to that of line II in the range of 105–190 K. The differences in the center frequency and spectral area imply that there are two distinct metallic FM regions. The NMR characteristics of line II indicate that the region from which this NMR line originates has the stable metallic FM phase found in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $0.2 < x < 0.5$. In this range of x , the spectral area was observed to increase with decreasing temperature as line II of

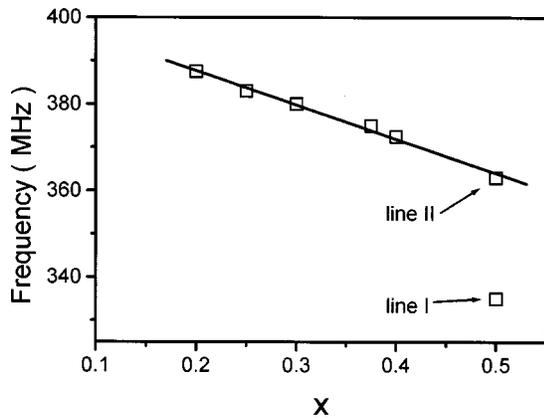


FIG. 4. The central frequency of ^{55}Mn NMR vs x at 78 K.

$\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The center frequency provides a more quantitative support for this claim. Since the average Mn magnetic moment decreases from $4\mu_B$ to $3\mu_B$ with x increasing from 0 to 1, the local field at a Mn nucleus should decrease linearly with x in the metallic FM phase if the coupling constants A and C in Eq. (1) are independent of x . The plot in Fig. 4 shows that the Mn NMR frequency decreases linearly with x and the center frequency of line II locates on this line, while that of line I locates far below it. The graph strongly suggests that the density of e_g electrons in the region corresponding to line II is 0.5.

The electric and magnetic state of the region from which line I of the NMR signal comes can be inferred from the resemblance of the spectral area [Fig. 3(b)] and the magnetization curves (Fig. 1). The magnetization decays below T_N due to the suppression of the metallic FM ordering produced by the hopping of e_g electrons at higher temperature.⁸ When e_g electrons localize to form the AFM ordering below T_N , the motion narrowed NMR signal vanishes accordingly. Therefore, the close resemblance between these two curves indicates that the metallic FM and insulating AFM couplings are competing in the region producing line I. The local field in the metallic FM phase depends on the relative ratio of Mn^{3+} and Mn^{4+} ion numbers or, equivalently, e_g electron density. Therefore, the frequency difference of the two lines suggests that the e_g electron density of the metallic FM phase in the competing region is lower than that of the stable FM region. If the linear relation between the center frequency and x in Fig. 4 is extended to the competing region, the e_g electron density of the metallic FM phase of this region is about 0.1. Another possible reason for the frequency difference is different spin fluctuations, which would give different magnitude of $\langle S \rangle$. If the spin fluctuation is different in the two regions, the NMR relaxation times should show a difference. In the whole temperature range of experiment, however, the variation of the relaxation times with frequency was negligible. Therefore, different spin fluctuation characteristics in the two regions are not so likely.

Magnetization below T_C is mainly developed in the competition region, and the remnant magnetization at low temperature is mainly attributed to the stable region. Near T_N , three phases coexist; a stable metallic FM phase, an insulating AFM phase, and another metallic FM phase competing with the AFM phase. The coexistence of two magnetically

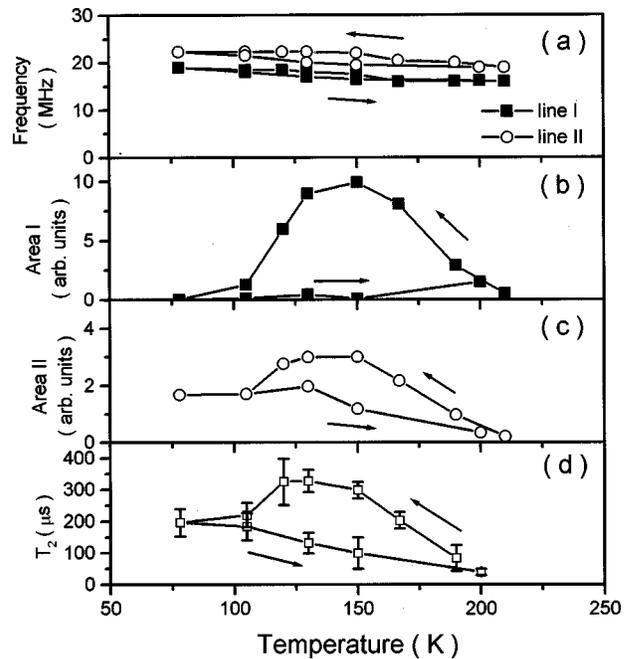


FIG. 5. The ^{139}La NMR frequency of line I (open circle) and line II (solid square) (a), the spectral area of line I (b), the spectral area of line II (c), and the spin-spin relaxation time (d) plotted as a function of temperature. The error range in (a), (b), and (c) is roughly the size of data points.

very similar, but electronically inequivalent, phases was also found in EuB_6 by the observation of double peaks in ^{153}Eu NMR spectrum.¹⁷

La NMR spectrum in Fig. 2(b) also shows a double peak feature near T_N although it is not so distinct as in the Mn NMR spectrum. Papavassiliou *et al.* also observed La spectra of the double Gaussian shape,¹⁴ and claimed that the signals at 19 MHz and 22.5 MHz were attributed to FM and AFM phases, respectively. The frequency difference of the two lines was explained by the dipole field. However, the difference of the local fields of the two lines is about 5.5 kG, while the dipole field on La nuclei was reported to be about 0.7 kG in LaMnO_3 .¹⁸ Considering the fact that the relative La NMR frequency difference of the two lines is of the same order with that of Mn, it might be more reasonable to attribute the frequency difference of two lines in the La spectra not to the dipole field, but to the difference of the average Mn magnetic moment as in the ^{55}Mn spectra. In fact, most features of the La NMR spectrum in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ are interpreted consistently with those of Mn NMR spectrum, as we can guess from the resemblance of Fig. 3 and Fig. 5.

In Fig. 5, the zero-field La NMR frequencies, the spectral areas of the two lines, and the La spin-spin relaxation time (T_2) are plotted. As in the case of the Mn spectra, the center frequencies and spectral areas were obtained by the double Gaussian fit to the spectra in Fig. 2(b), and the nuclear Boltzmann factor was corrected in the spectral areas. La NMR frequencies also showed weak hysteresis as Mn, and increased monotonously with decreasing temperature, while the magnetization decays fast below T_N . This is another evidence that La NMR signals come from FM regions. The resonance frequency of line I was lower than that of line II as Mn, and the frequency difference of the two lines was about

3.5 MHz throughout the whole temperature range. The frequency of line II coincides with those observed in homogeneous ferromagnets, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.2 < x < 0.5$).¹⁰ From the comparison of the frequencies and spectral areas of the La and Mn NMR spectra, it is quite clear that lines I and II of the La spectra comes from the regions that produce lines I and II of the Mn spectra, respectively.

The spectral areas of La NMR show similar behaviors with those of Mn NMR qualitatively; large hysteresis in line I and nonvanishing amplitude of line II at low temperature. Line I comes from the region where the metallic FM and insulating AFM couplings compete and the decay of the spectral area of line I below T_N is attributed to the change of spin order from FM to AFM phases accompanied by charge ordering, whereas the phase of the region producing line II remains a relatively stable metallic FM state throughout the whole temperature range. One of the interesting features of the La spectra is that the total spectral area resembles the magnetization curve contrary to the Mn spectra. The sum of the two spectral areas was maximum at 150 K upon cooling, and it was about 10 times bigger than that upon warming. This ratio matches that of the magnetization. This means that

the signal enhancement factor is independent of temperature, and the spectral areas are proportional to the volumes of the corresponding FM regions.

Both the spin-spin relaxation times of Mn and La NMR showed hysteresis though that of La NMR is stronger. These hysteresees mainly reflect the hysteresis of the FM volume fraction in the competing region, since the hysteresis of the stable FM volume fraction is much weaker. In a recent report, however, Allodi *et al.* mentioned that the local field and relaxation time did not show thermal hysteresis.⁹ In our opinion, the main reason for this discrepancy is difference in sample characteristics. The ratio of the maximal magnetization to the remnant magnetization at low temperature is much smaller in their sample than ours. The FM phase in the competing region mainly contributes to the maximal magnetization, while the stable FM phase contributes to the remnant magnetization as mentioned above. Therefore, a small ratio of these magnetizations means that the volume ratio of the FM phase in the competing region to the stable FM phase is small, and the hysteresees of relaxation times are weak.

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