^{55}Mn NMR Investigation of Electronic Phase Separation in $La_{1-x}Ca_xMnO_3$ for $0.2 \leq x \leq 0.5$

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^{55}Mn NMR line shape measurements in $La_{1-x}Ca_xMnO_3$ for $0.20 \leq x \leq 0.50$ provide experimental evidence about the existence of two distinct regions in the T-x magnetic phase diagram, where the homogeneous ferromagnetic (FM) metallic state is separated into FM metallic and FM insulating regions. These results are in agreement with recent theoretical predictions, which reveal a novel electronic phase separation in two FM states, providing orbital ordering and Jahn-Teller phonons are taken into consideration.

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Manganese perovskites of the $La_{1-x}D_xMnO_3$ (D = Ca, Sr, Ba, or Pb) family are systems with remarkable structural, magnetic, and electronic properties. A variety of experiments revealed a very rich phase diagram with antiferromagnetic (AFM), ferromagnetic (FM), metallic, or charge ordered regions [1]. In most cases these phases are microscopically inhomogeneous, as implied by x-ray absorption [2] and neutron scattering [3,4] experiments, especially in regimes of relevance with the colossal magnetoresistance (CMR) effect. According to recent theoretical trends, such inhomogeneous phases may be attributed to novel electronic phase separation into FM insulating (FI) and FM metallic phases, mainly due to Jahn-Teller (JT) phonons [5] and anisotropy in the orbital space [5,6]. The presence of FI regions enhances resistivity of the system, whereas application of an external magnetic field is expected to reduce the insulating regions and consequently resistivity. This provides an appealing explanation of the CMR effect, which however has not yet been confirmed.

The present work is motivated to shed more light on the question of the inhomogeneity of the FM metallic phase of $La_{1-x}Ca_xMnO_3$ at a microscopic level, by using ^{55}Mn NMR in zero external magnetic field. We show experimentally for the first time that right below T_c, and for $0.20 \leq x \leq 0.5$, the FM metallic state is electronically phase separated into a mixture of FM metallic and FI regions, in agreement with the theoretical predictions [5]. By lowering temperature the FI regions decrease rapidly and subsequently disappear below a certain temperature, which depends on the doping concentration x. However, for $x \leq 0.25$, systems reenter into a mixed FM metallic-FI phase at low temperatures, whereas for $x \leq 0.15$ only the FI phase is detectable.

$La_{1-x}Ca_xMnO_3$ polycrystalline samples were prepared with the classical ceramic method by annealing the stoichiometric amounts of the corresponding oxides in air at 1300 to 1400 °C. All samples were then characterized structurally at room temperature with a D500 Siemens x-ray diffractometer, and magnetically with a SQUID magnetometer. The obtained crystallographic and magnetic data were found to be in accordance with literature. Figure 1 demonstrates magnetization measurements as a function of temperature for $La_{1-x}Ca_xMnO_3$, $x = 0.10$, 0.15, 0.25, 0.33, and 0.5 at a field of $H = 1000$ G. The M vs T curves in the doping range $0.10 \leq x \leq 0.33$ are those of typical FM transitions. The corresponding transition temperatures, defined as the inflection points of the M vs T curves, are $T_c(0.10) = 169$ K, $T_c(0.15) = 180$ K, $T_c(0.25) = 240$ K, and $T_c(0.33) = 265$ K, respectively. In the case of

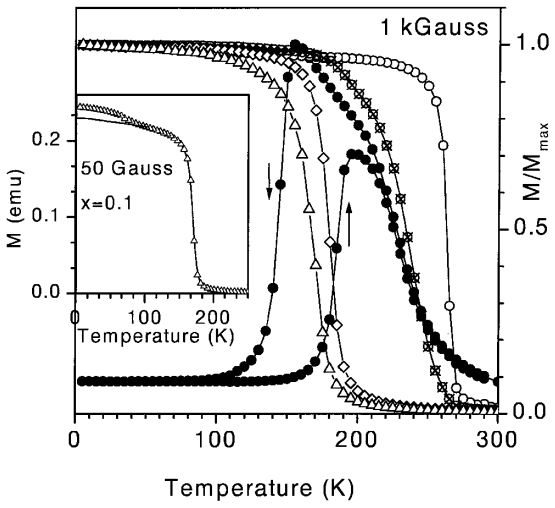

FIG. 1. Magnetization of $La_{1-x}Ca_xMnO_3$, for $x = 0.10$ (△), 0.15 (◇), 0.25 (⊗), 0.33 (∘), and 0.5 (•), as a function of temperature. The inset demonstrates M vs T data for $x = 0.10$ at a field of $H = 50$ G. An anomalous behavior at ≃70 K is clearly observed.

$x = 0.5$ the system exhibits a strong hysterestic behavior, and undergoes two phase transitions, a paramagnetic (PM) to FM one at $T_c(0.5) = 220$ K and a FM-AFM one at $T_N(0.5) = 180$ K on cooling, in agreement with previous works [7].

In contrast to bulk experimental techniques which measure macroscopic properties, ^{55}Mn NMR in zero external magnetic field probes the local magnetic environment of the resonating Mn nuclei via the hyperfine field, $B_{hf} = A\langle S\rangle/\gamma\hbar$, where A is the hyperfine coupling constant and $\langle S\rangle$ the average Mn electronic spin. According to this formula ^{55}Mn NMR is possible to resolve the different Mn charge states, i.e., localized $Mn^{4+,3+}$ and intermediate FM metallic valence states. Previous works in manganese perovskites [8–10] have shown that at low temperatures NMR signals from Mn^{4+} and Mn^{3+} charge states have peaks at frequencies $\simeq$320–330 MHz [11] and $\simeq$400–420 MHz, respectively, whereas signals from FM metallic regions are located at intermediate frequencies, due to the fast electron transfer between Mn^{3+} and Mn^{4+} ions. By increasing temperature the signal frequency is expected to decrease, as the order parameter $\langle S\rangle \rightarrow 0$ on approaching T_c.

In the present experiments, ^{55}Mn NMR signals were obtained by using an untuned probe head and a 1 μsec$-\tau-1$ μsec spin-echo pulse sequence with $\tau = 3$ μsec. The used rf power level was very small, due to the strong rf enhancement created by the oscillating (at rf frequency) electron magnetic moments [12]. We stress that strong rf enhancement is typical of FM NMR and may be considered as evidence about the presence of FM domain walls. On the other hand, NMR signals from AFM regions have very low rf enhancement, hence strong rf power is needed in order to obtain the signal.

Figure 2 demonstrates zero external field ^{55}Mn NMR spectra of $La_{1-x}Ca_xMnO_3$ for $x = 0.10$, 0.15, 0.20, 0.25, 0.33, and 0.5 at $T = 3.2$ K. For the ferromagnetic insulators $x = 0.10$ and 0.15 (see phase diagram in Ref. [1]), spectra exhibit a strong FM Mn^{4+} peak at $\nu \simeq 330$ MHz, and a broad feature extending up to 430 MHz, which may be attributed to JT distorted Mn^{3+} sites [9]. The order of magnitude difference between the Mn^{4+} and Mn^{3+} signals is explainable if we take into consideration that the hyperfine field at Mn^{3+} sites has a strong anisotropic contribution from the spin-dipolar field of the $d_{x^2-y^2}$ orbital states [9]. Consequently, the Mn^{3+} NMR frequency depends on the local environment, thus spreading over a broad frequency range, and is practically smeared out. For $x = 0.33$ only the FM metallic signal is detectable [13], whereas the $x = 0.5$ sample exhibits a FM metallic signal at $\simeq$375 MHz, and an AFM Mn^{4+} signal with a low rf enhancement factor at $\simeq$310 MHz, in agreement with previous results [14]. For doping $0.15 < x < 0.33$ a mixed FM metallic-FI phase is clearly shown to be formed. Remarkably, the FI regions decrease and finally vanish upon heating at a temperature depending on x.

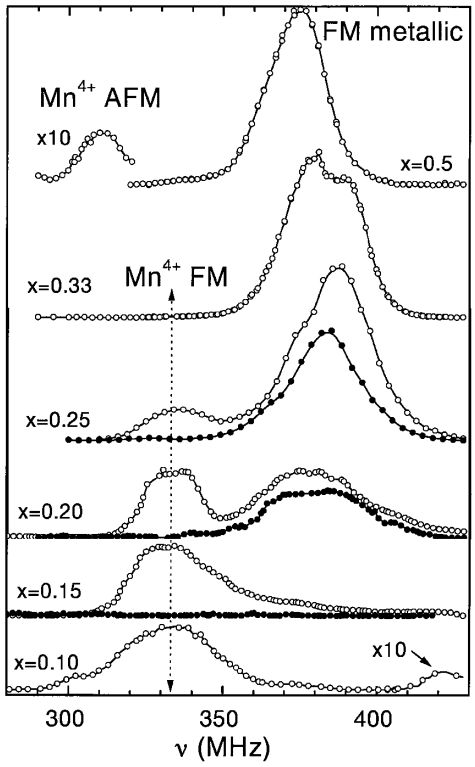

FIG. 2. ^{55}Mn NMR spectra of $La_{1-x}Ca_xMnO_3$ (∘) for $x = 0.10$, 0.15, 0.20, 0.25, 0.33, and 0.50 in a zero external magnetic field at $T = 3.2$ K. Filled circles (•) are spectra at 62 K ($x = 0.15$), 50 K ($x = 0.20$), and 20 K ($x = 0.25$).

In the case of $x = 0.25$ the Mn^{4+} signal disappears at $T \approx 20$ K. For $20 \leq T \leq 160$ K only the FM metallic signal is observed, which by increasing temperature shifts gradually to lower frequencies. However, at $T = 160$ K an additional signal is formed, which grows rapidly on approaching T_c (Fig. 3). Insets in Fig. 3 show the results of a two-Gaussian line shape analysis. It is clearly seen that the frequency of the new-appearing low frequency signal, (i) decreases rapidly on approaching T_c, as expected for FM signals, and (ii) by decreasing temperature saturates at the Mn^{4+} frequency of $\simeq$330 MHz. Another important observation is the abrupt fall of the FM conductive signal intensity by heating, probably due to the significant decrease of the rf enhancement on approaching T_c. Apparently, for $T > 160$ K $Mn^{4+,3+}$ ionic states with FM spin order are formed, and by increasing temperature the system segregates gradually into FM conductive and FI regions. This interpretation is supported by the extended x-ray-absorption fine structure measurements of Ref. [2], which indicate the formation of very elongated MnO_6 octahedra in $La_{0.75}Ca_{0.25}MnO_3$ above 170 K, associated with the formation of small JT polarons with an average size of one hole per two Mn ions. A similar behavior is observed in both the $x = 0.33$ and $x = 0.5$ systems, as shown in Figs. 4a and 4b. In case of $x = 0.33$ the FI ^{55}Mn NMR signal appears above 200 K, whereas for $x = 0.5$ the FM insulating signal is detectable above 160 K only in the

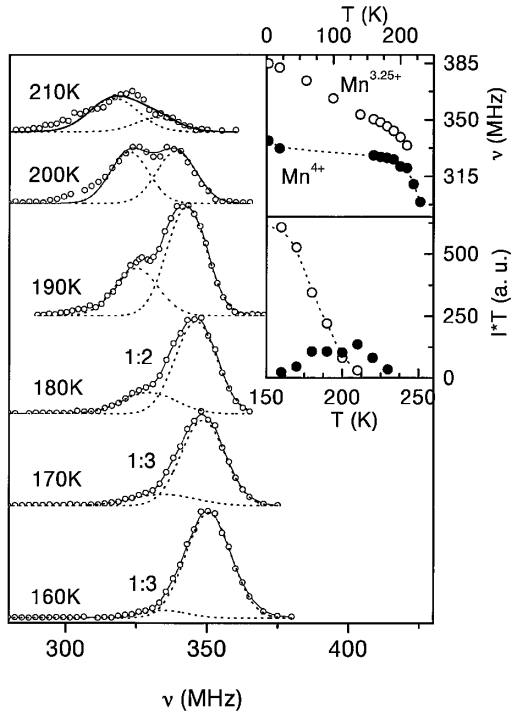

FIG. 3. ^{55}Mn NMR spectra of $La_{0.75}Ca_{0.25}MnO_3$ in a zero external magnetic field at various temperatures. The insets demonstrate signal frequencies vs T, and signal intensities corrected with the Boltzmann factor, IT vs T, obtained by a two-Gaussian line shape fit.

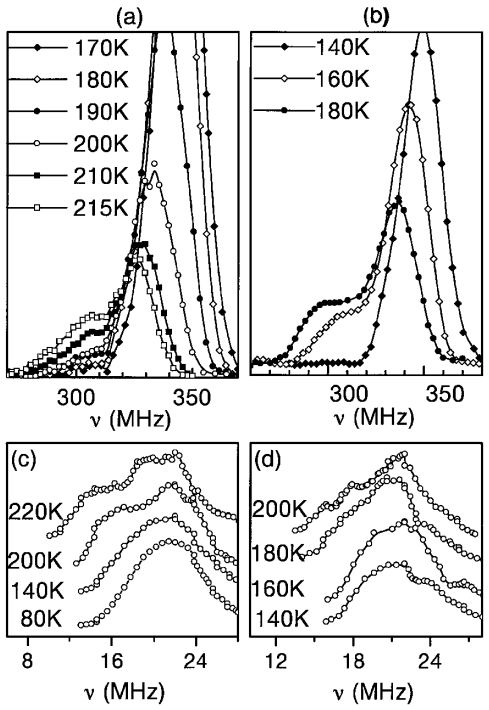

FIG. 4. ^{55}Mn NMR spectra of $La_{1-x}Ca_xMnO_3$ for $x = 0.33$ (a) and 0.5 (b) in a zero external magnetic field at various temperatures. In the same figure ^{139}La NMR spectra for $x = 0.33$ (c) and 0.5 (d) are also presented.

cooling route, due to the strong hysteresis of the FM phase [15]. Similarly with ^{55}Mn NMR, ^{139}La line shape vs T measurements for $x = 0.33$ and $x = 0.5$ (Figs. 4c and 4d, respectively) exhibit the formation of a low frequency tail right below T_c. Considering that the ^{139}La NMR frequency is inversely proportional to the average $\langle$Mn-O$\rangle$ bond length [10], this tail may be attributed to the formation of JT distorted Mn octants close to T_c.

Figure 5 exhibits the T-x magnetic phase diagram for $0.1 \leq x \leq 0.5$ according to the magnetization (∘) and NMR results (⊗), (•). The vertical phase boundary lines are defined from Ref. [1]. The FM phase regime consists of three distinct regions: a low temperature homogeneous FM metallic one, and two regions, where a mixed FM metallic-FI phase is observed. The physical origin of the mixed-phase regions may be qualitatively understood, by exploiting the relation of FM coupling with orbital ordering (OO) and JT distortions. At low temperatures JT distortions reduce drastically in the FM phase and can be neglected [16]. A theoretical analysis based on the t-J model [6], where orbital degrees of freedom have been treated under strong electron correlation, revealed the formation of a low temperature FI phase with AFM-type OO, which is gradually suppressed by increasing x. It is observed that the T_{OO} line, i.e., the OO phase boundary proposed by this model [6], fits remarkably well with the low temperature NMR data (•), as shown in Fig. 5. In order to ensure that this is not a coincidence and the disappearance of the Mn^{4+} NMR signal signifies an important change of the magnetic structure, M vs T measurements were performed for the $x = 0.1$ sample at $H = 50$ G (inset of Fig. 1), i.e., very close to the experimental conditions of zero external field NMR. The anomalous increase of M at around 70 K (i.e., at exactly the same temperature, where the Mn^{4+} NMR signal disappears) is in excellent agreement with that shown in the theoretically predicted M vs T curve in Ref. [6], if OO effects are considered below 70 K. Apparently, the difficulty to detect NMR signals

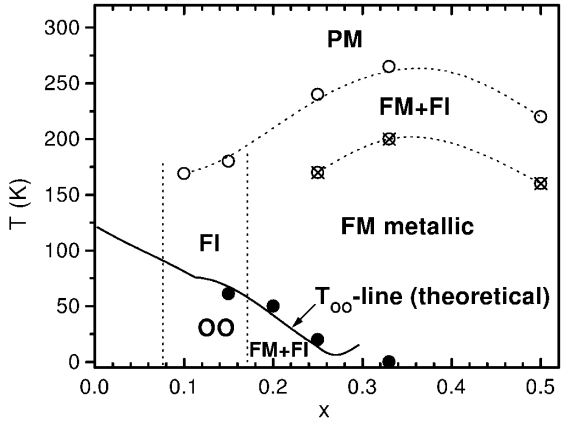

FIG. 5. The phase diagram T-x for $0.15 \leq x \leq 0.5$ according to the magnetic (∘), and NMR (⊗), (•) measurements. The theoretical T_{OO} line from Ref. [6] is also schematically shown.

for $T > T_{OO}$ and $x \leq 0.15$ is due to the strong reduction of the rf enhancement in this regime of the phase diagram.

A more elaborate investigation [17] with the previous model [6] has revealed the formation of a mixed state almost in the whole T-x region below T_{OO}. This suggests that for $0.20 \leq x \leq 0.33$ the low temperature FM phase segregates in two FM states differing in the OO. By increasing temperature the T_{OO} line is crossed, and the uniform orbitally disorder FM metallic state is established. On the other hand, close to T_c the rapid increase of JT distortions [2,16] favors once more charge localization thus giving rise to the high temperature mixed FM metallic-FI phase observed with NMR. This result is in agreement with the predictions of the 2-orbital Kondo model with classical JT phonons [5], which shows that in the low doping regime, and by increasing coupling with JT phonons, the homogeneous FM metallic state may become unstable against the formation of a mixed FM state with orbitally disordered and orbitally AFM regions.

In conclusion, by using NMR techniques we provide for the first time experimental evidence about the existence of phase separation in two different FM phases, as recently predicted by theory. The excellent agreement of the low temperature NMR results with theoretical models including orbital degrees of freedom implies that most probably OO is responsible for the low temperature mixed phase. Accordingly, JT distortions seem to be responsible for the high temperature mixed phase detected with NMR. The latter may play a key role in the appearance of colossal magnetoresistance in manganese perovskites. It is probable that close to T_c, by applying an external magnetic field the number and size of FI regions reduce drastically, thus enhancing conductivity. Work on this subject is in progress.

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