^{139}La NMR Investigation of Quasistatic Orbital Ordering in $La_{1-x}Ca_xMnO_3$

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We report ^{139}La nuclear magnetic resonance in ferromagnetic and insulating (FMI) $La_{1-x}Ca_xMnO_3$, $0.10 \leq x \leq 0.20$, which at low temperatures shows the formation of Mn octants with enhanced Mn-O wave function overlapping and electron-spin alignment. The rapid increase of the relaxation rates and the "wipeout" of the ^{139}La NMR signal intensity on heating, imply a quasistatic character for the Mn octant cells in the FMI phase, which freeze below a transition temperature T_f.

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Doped lanthanum manganites with the general formula $La_{1-x}D_xMnO_3$ (D = Ca^{2+}, Sr^{2+}, Ba^{2+}, etc.) attain currently a lot of theoretical and experimental interest due to the close relation of their magnetic, transport, and structural properties. For hole doping $0.2 \leq x < 0.5$ these materials exhibit long-range ferromagnetic (FM) ordering accompanied by a huge reduction of the electrical resistivity below the Curie temperature T_c. The general framework to describe this behavior is the double exchange model (DE), according to which strong Hund's rule coupling enhances the hopping of e_g holes in successive Mn^{3+} and Mn^{4+} ions by establishing FM electron spin order. However, for $x < 0.2$ a FM and insulating (FMI) phase has been observed, which is in contrast with the DE model. Experiments in the low doping regime of $La_{1-x}Sr_xMnO_3$ (LSMO) have shown that such a FMI phase is associated with charge and orbital ordering (OO), and strong reduction of the cooperative Jahn-Teller lattice distortions [1–3], whereas the anisotropy in the orbital sector is considered to favor or disfavor the e_g hole mobility in an orbital orientation depended way. In the more complex case of $La_{1-x}Ca_xMnO_3$ (LCMO), experiments show that for low doping the formation of an orbitally disordered (OD) FMI phase is also possible [4,5]. Particularly, ^{55}Mn and ^{139}La NMR measurements on LCMO [5,6] have shown the presence of a transition line $T(x)$ deep into the FMI phase, which has been associated to OO effects. At the same time, electron and neutron scattering experiments on LCMO $x = 0.15$ revealed an unconventional layered OO, which is abruptly enhanced below 70 K [7]. In another neutron scattering study of LCMO, for doping $0.125 \leq x \leq 0.20$, a bell-shaped transition line $T_B(x)$ was observed at around 80 K, which defines a gradual "re-entrant" structural transition with strongly reduced orthorombicity [8]. Low-T OO effects in FMI LCMO were also confirmed by resistivity measurements under pressure [9]. It is thus evident by all experimental facts that at low temperatures an instability occurs in the orbital sector. However, in the case of LCMO it is still inconclusive whether the low-T orbital arrangement emerges from a normal phase transition, or is produced by a gradual freezing from the high-T orbital configuration [4,10].

In this Letter, we try to investigate the nature of this transition and its dependence on T and x, by applying ^{139}La NMR techniques on LCMO powder samples for $0.1 \leq x \leq 0.20$. Our measurements reveal that for temperatures lower than a characteristic temperature $T_f \equiv T_B$, Mn octant cells are formed with enhanced overlapping of the Mn-O wave functions or better Mn electron-spin alignment, in comparison to the high-T Mn octant cells. The strong enhancement of the ^{139}La $1/T_{1,2}$ relaxation rates and the rapid decrease of the NMR signal (wipeout effect), which follows the smearing of this feature on approaching T_f from below, is explained as showing the quasistatic character of the Mn octant cells in the FMI phase, and the onset of slow fluctuations in the spin and orbital sector by heating. We notice that the wipeout effect of NMR/NQR signals is produced by coupling of slow fluctuating degrees of freedom with the nuclear spin. In such a case, the relaxation rates $1/T_{1,2}$ become so fast that most of the signal relaxes before it can be observed [11]. Until now, wipeout effects have been observed in classical spin glass systems [12] and stripe-ordered cuprates [11,13,14], in the latter case due to the glassy nature of the charge striped phase. In the case of cuprates the wipeout effect is produced by slow fluctuations of the electric field gradient (EFG). However, as discussed below, in FMI CMR manganites the wipeout effect is produced by the slow fluctuations of the transferred hyperfine field B_{hf} at the position of the La nuclei.

Experiments were performed on polycrystalline samples prepared by annealing stoichiometric amounts of the corresponding oxides in air at 1300 to 1400 °C, for 4 days with intermediate grinding and reformation into pellets, and finally slowly cooled to room temperature by turning off the furnace. Special care was given to keep for all samples the preparation conditions the same, as in the low doping regime the magnetic and structural properties depend strongly on the preparation method [15]. 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. ^{139}La NMR spectra were acquired in zero external magnetic field by applying a two pulse spin-echo

technique, with pulse widths $t_{p1} = t_{p2} = 0.6$ μsec and recording the signal at equidistant irradiation frequencies, as in previous works [16–19]. For the T_1 and T_2 studies we have performed a saturation recovery (for T_1) and a spin-echo decay (for T_2) pulse sequences, whereas the signal intensity was measured at the peak of the signal. Because of the multiexponential nature of the saturation recovery curves, T_1 values in Fig. 4 are given as $1/e$ values, obtained by a stretched exponential fit.

Figure 1a shows ^{139}La NMR spectra at $T = 5$ K for $x = 0.1$, 0.125, 0.15, and 0.20. For reasons of comparison the spectrum for $x = 0.33$ is also presented (dotted line). In contrast to the symmetric signal for $x = 0.33$, the rest of the spectra exhibit a peak at ≈20 MHz and a strongly asymmetric line shape, which extends up to 35 MHz. The most profound effect is clearly observed for $x \leq 0.125$. By increasing hole doping the high frequency tail starts to smear out and for $x \geq 0.20$ a structureless almost symmetric line shape is formed. Figures 1b–1d exhibit spectra for $x = 0.1$, 0.125, and 0.175, respectively, as a function of temperature. By increasing temperature spectra loose significantly in intensity, whereas the high frequency tail decreases much faster and disappears at $T \approx 80$ K. This is clearly seen in the inset of Fig. 1c, which shows the ratio of the intensity of the high frequency tail to the intensity of the main peak for $x = 0.125$, after decomposing the signal in two Gaussians.

The origin of the ^{139}La NMR line shapes in Fig. 1 is explainable, if we consider that in case of the spinless La ion ($S = 0$) the line shapes reflect mainly the transferred hyperfine field $B_{hf} = (1/\gamma\hbar)A\langle S\rangle$ at the position of the La nuclei (A is the hyperfine coupling constant, and $\langle S\rangle$ the average electronic spin of the eight surrounding Mn ions). The quadrupolar interaction (^{139}La $I = 7/2$) does not seem to contribute to the high frequency tail as (i) satellite transitions would produce a symmetric NMR signal broadening around the central line, and (ii) for LCMO $\nu_Q \leq 4$ MHz [20], so the second order quadrupolar shift from a distribution of quadrupolar frequencies would not be larger than ≈1 MHz [21]. Since in lanthanum manganites B_{hf}(La) arises indirectly from overlapping between the Mn $|3d\rangle$ and the oxygen $|2p\rangle$ wave functions, in conjunction with σ bonding of the oxygen with the $|sp^3\rangle$ hybrid states of the La^{3+} ion [16,17], the ^{139}La NMR signal reflects (i) the parallel alignment of the t_{2g} electron spins, and (ii) possible deformations of the Mn-O-Mn bonding, which alter the hyperfine coupling constant A. It may thus be inferred that the appearance of the high frequency tail shows the formation of Mn octant cells with enhanced Mn-O wave function overlapping and better Mn electron-spin alignment in the low-T FMI regime of the x-T phase diagram.

The smearing of the high frequency tail on heating is accompanied by a remarkable decrease of the ^{139}La NMR signal intensity. About 90% of the FMI signal is lost in the temperature interval 5–80 K for the systems $x = 0.175$ and 0.15, whereas for $x = 0.10$ the NMR signal disappears at ≈100 K, as shown in Fig. 2. For $x \geq 0.15$, the

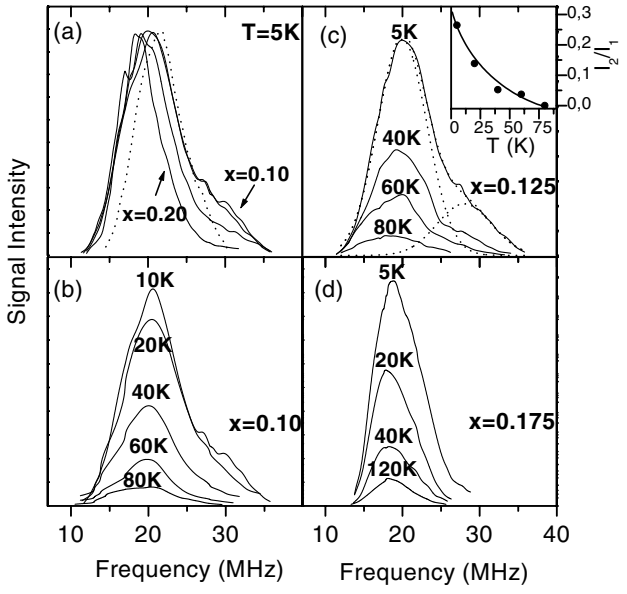

FIG. 1. (a) ^{139}La NMR line shapes for $x = 0.10$, 0.125, 0.15, and 0.20. The dotted line is the line shape for $x = 0.33$. (b)-(d) ^{139}La NMR line shapes for $x = 0.10$, 0.125, and 0.175 as a function of temperature, after considering the Boltzmann temperature correction. The inset in (c) shows the ratio of the intensity of the high frequency tail I_2 to the intensity of the main peak I_1 for $x = 0.125$, after decomposing the signal in two Gaussians.

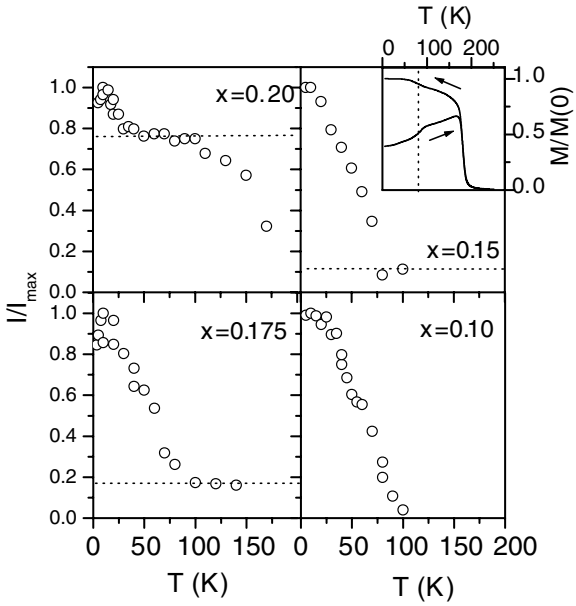

FIG. 2. ^{139}La NMR signal intensity I vs T as given by the spectral intensity over frequency at various dopings, after considering the T_2 and the Boltzmann temperature corrections. The dashed lines show the percentage of the FMC signal component. The inset in the upper right panel shows the magnetization vs T for the $x = 0.15$ sample in an external field of 50 G.

remaining high temperature signal belongs solely to the minority ferromagnetic and conductive (FMC) phase, as recently shown by ^{55}Mn NMR line shape [5] and ^{139}La rf enhancement [6] experiments. At the same time we have found that for all samples with $x < 0.20$, magnetization vs T measurements in a low external magnetic field exhibit a sudden slope change at 80 K in both the zero field cooling (ZFC) and field cooling (FC) branches, in agreement with previous works [5,6,10]. This effect is demonstrated in the inset of Fig. 2 for the $x = 0.15$ sample. In close relevance are neutron scattering experiments, which show an anomalous increase of some magnetic Bragg peaks below that temperature, which depends strongly on the cooling rate [8]. This might indicate a kind of freezing mechanism on cooling at $T_f \approx 80$ K [8,10], related with the formation of a low-T polaronic (i.e., orbital) short range ordered state as discussed in Ref. [4]. The nice correlation in the temperature variation of the wipeout effect with the neutron [7,8] and magnetization data [5,6,10] implies that the wipeout effect is associated with low frequency dynamics of Mn octant cells, i.e., with slow fluctuations in the spin and orbital sector.

The origin of the wipeout from inhomogeneous relaxation is clearly demonstrated in Fig. 3, which shows ^{139}La NMR spin-echo decay curves for LCMO, $x = 0.125$, and 0.175 at characteristic temperatures. In both systems and at low temperatures, the spin-echo decay shapes are nicely fitted with the convolution of a Gaussian [$I = I_0 \exp(-(\tau/T_{2G})^2)$] and a Lorentzian [$I = I_0 \exp(-2\tau/T_{2L})$]. The Gaussian spin-echo decay in exchange-coupled systems is a manifestation of the presence of indirect nuclear spin-spin coupling between neighboring nuclear spins [22]. By increasing temperature, the Gaussian shape disappears rapidly, and spin echoes decay faster, attaining a stretched exponential shape for $T \geq 20$ K [$I = I_0 \exp(-(2\tau/T_{2L})^{\alpha})$], with $0 \leq \alpha \leq 1$. This is evidence for a broad distribution of T_2 values above 20 K. At the same time the signal intensity decreases rapidly and most of the signal becomes invisible. We notice that the high-T slow decaying signal component for $x = 0.175$ belongs to the FMC minority phase, whereas the small fast relaxing signal component above 80 K corresponds to the mostly "invisible" majority FMI phase component. Remarkably, a decomposition in two relaxation times shows that T_2 for the FMI signal component does not change significantly above 80 K. This indicates that $T_f \approx 80$ K defines rather a freezing temperature, than a normal phase transition. In the latter case a critical enhancement of the relaxation rates is expected from both sides of the transition temperature. In a similar way, $1/T_1$ shows a rapid increase for all $x \leq 0.175$ on approaching T_f from below, as shown in Fig. 4, whereas a slight downturn may be anticipated for $T \geq 80$ K (inset of Fig. 4). It may thus be argued that both $1/T_1$ and $1/T_2$ reveal an inhomogeneous freezing of the hyperfine field B_{hf} at the site of the La nuclei, which possibly matches the MHz region at ≈80 K.

The influence of a broad distribution of "freezing" correlation times τ_c on the relaxation rates $1/T_{1,2}$ may be followed by considering a stretched exponential autocorrelation function for the hyperfine field $\langle B_{hf}(t)B_{hf}(0)\rangle = \langle B_{hf}^2\rangle \exp[-(t/\tau_c)^{\alpha}]$. The relaxation rate $1/T_1$ from such

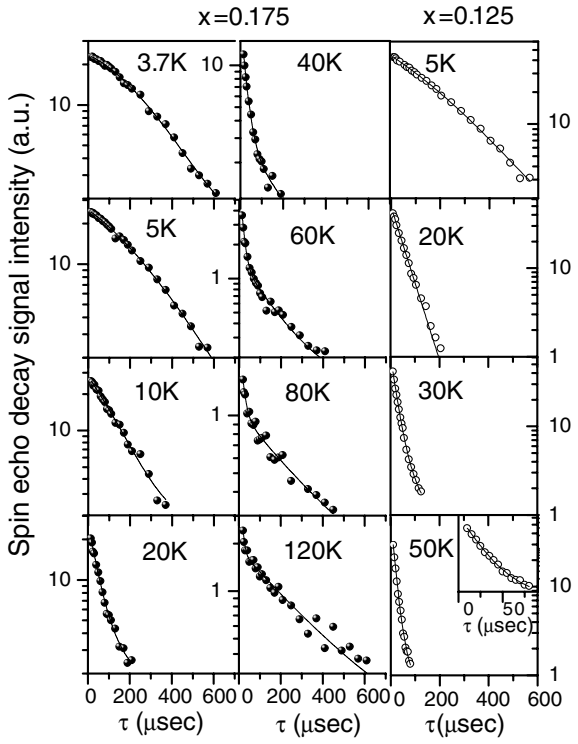

FIG. 3. ^{139}La NMR spin-echo decays as a function of the separation time τ between the two pulses at various temperatures, for $x = 0.125$ and 0.175.

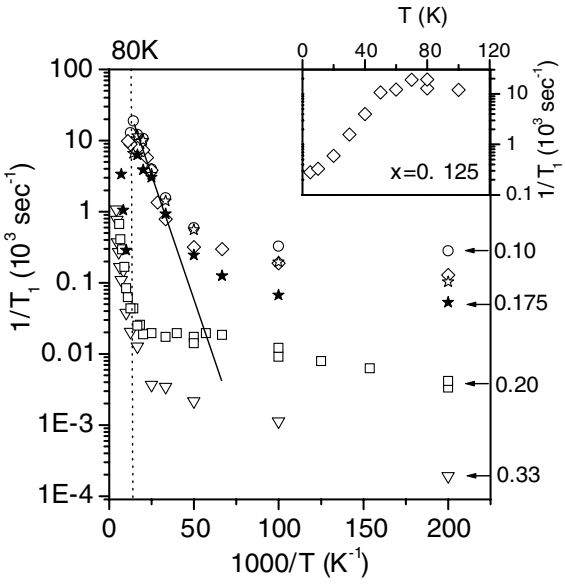

FIG. 4. ^{139}La NMR $1/T_1$ as a function of T for $x = 0.1$, 0.125, 0.15, 0.175, 0.20, and 0.33. The inset exhibits $1/T_1$ vs T for $x = 0.125$.

a distribution is given by $1/T_1 \propto J(\omega) = \langle B_{hf}^2 \rangle \int_0^\infty \times \exp[-(t/\tau_c)^\alpha] \exp(-i\omega t)\, dt$. In the fast motion regime $\omega\tau_c \ll 1$ this relation gives $1/T_1 \propto \langle B_{hf}^2 \rangle \Gamma(\frac{1+\alpha}{\alpha})\tau_c$, whereas in the "slow motion" regime $\omega\tau_c \gg 1$, $1/T_1 \propto 2\alpha/(\omega^{1+\alpha}\tau_c^\alpha) \int_0^\infty x^{-n} \sin x\, dx$, $x = \omega t$. In case of gradual freezing, as spectral fluctuations slow down and cross the Larmor frequency, $J(\omega)$ passes from the fast to the slow motion regime, and $1/T_1$ becomes maximum at a temperature defined as the freezing temperature T_f. In the framework of this model and by considering an activation law $\tau_c = \tau_0 \exp(E_\alpha/kT)$ below 80 K, an average activation energy $E_\alpha \approx 7$ meV may be calculated (solid line in Fig. 4). A similar behavior is expected for $1/T_2$, as T_1 and T_2 are of the same order of magnitude for FMI signals.

Finally, we would like to comment on the $1/T_1$ vs T curves for the systems which exhibit a mixed FMI-FMC phase. It is clearly observed that in respect to $1/T_1$, the system $x = 0.175$ is a boundary case. There are two regimes with different $1/T_1$ temperature dependence; one in the pure FMI phase for $x < 0.15$, and the other in the pure FMC phase for $x > 0.25$. For doping $0.15 \leq x \leq 0.20$, where the mixed FMI/FMC is observed at low temperatures, $1/T_1$ exhibits a weighted T dependence from both the FMI and FMC signal components. At high temperatures, where the wipeout of the FMI signal unravels the NMR signal from the minority FMC phase, $1/T_1$ follows relatively well the curve for $x = 0.33$.

Summarizing the above results we may say that at low temperatures, ^{139}La NMR signals of FMI LCMO systems show an asymmetric line shape with a tail in the high frequency direction. This feature may be assigned to the formation of Mn octant cells with enhanced Mn-O wave function overlapping and Mn electron-spin alignment. It also appears that this arrangement of Mn ions has an inhomogeneous quasistatic character as indicated by the ^{139}La NMR relaxation experiments. By increasing temperature the tail of the NMR signal smears out, whereas the wipeout of the overall signal indicates the gradual onset of very slow fluctuations of the B_{hf}(La). The quantitative explanation for the wipeout effect is that by increasing temperature, a T-dependent fraction of the La nuclear spins experiences slow fluctuations of B_{hf}, which shorten the relaxation times so much that they become invisible. Besides, the detection of slow fluctuations above T_f implies that correlated Mn octant cells are involved almost at all temperatures below T_c. This observation is in agreement with recent diffuse neutron scattering experiments, which indicate a polaron glass for LCMO, e.g., for $x = 0.20$ [4]. It is also possible that above T_f the system comprises slowly fluctuating ordered clusters with a random orientation of the order parameter as recently proposed by Burgy *et al.* [23].

Note added.—On submission of this manuscript, we became aware of a ^{139}La NMR work on FMI LCMO in a high external magnetic field, by Allodi *et al.* [24]. In that paper the authors show the wipeout effect from room temperature down to 50 K. Our La relaxation data correlate also excellently with recent muon relaxation data of ferromagnetic insulating LCMO, $x = 0.18$ [25].

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