Evidence of ultra-slow polaron dynamics in low-doped manganites from $^{139}\text{La}$ NMR-NQR and muon spin rotation

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We report a $^{139}\text{La}$ NMR investigation of low-doped insulating manganite samples (LaMnO$_3$+$\delta$ and La$_{1-x}$Ca$_x$MnO$_3$+$\delta$) as a function of temperature. A volume fraction with fast nuclear relaxations was revealed by the inhomogeneous loss of the NMR signal over a broad temperature interval. Comparison with $\mu$SR data demonstrates that the "wipe out" of the $^{139}\text{La}$ signal is mainly due to slowly fluctuating electric field gradients. This provides strong evidence for the slow diffusion of lattice excitations, identified with Jahn-Teller small polarons.

La NMR was performed in an applied field of 7 T, in a temperature range of 40-360 K. Spectra were recorded point by point with a standard 90°-τ-90° spin echo sequence on a phase coherent spectrometer. The pulse delay $\tau$ was kept as short as possible, limited by the dead time of the receiver following the transmission of a rf pulse (typically 10-14 $\mu$s). At all temperatures the spin-spin relaxation rates $T_2^{-1}$ were determined by varying $\tau$, and the echo amplitude decay was best fitted by two exponentials. The spin echo amplitudes were extrapolated back to $\tau = 0$, and divided by the NMR sensitivity $\propto \omega^2/k_B T$. With this correction, the integrated amplitudes of each spectrum is proportional to the number of nuclei giving rise to the signal. $\mu$SR spectra were recorded at ISIS, on either the MUSR or EMU instruments. The data shown here are part of an extensive $\mu$SR investigation of La manganites, reported elsewhere.

La NMR is sensitive both to the magnetic and to the electronic structure. Lanthanum nuclei ($\gamma/2\pi = 6.014$ MHz/T) are coupled to the neighboring Mn electronic spins by a transferred hyperfine interaction. The local field $B_i$, including the external field $\mu_0 H$, has the form

$$B_i \equiv \frac{\omega_L}{\gamma} = \frac{2\pi}{\gamma} g_B \sum_{j} C_j \langle S_j \rangle + \mu_0 H \quad (1)$$

The hyperfine coupling constant is estimated in all lanthanum manganites as $C \approx 0.1$ T/$\mu_B$ \cite{1, 2}. Owing to nearly cubic symmetry of the lanthanum site, the transferred hyperfine field on $^{139}\text{La}$ is approximately proportional to the ferromagnetic moment of the surrounding Mn octet. At $T \ll T_c$, the spontaneous field ranges from $\approx 3.5$ T ($\nu_L \approx 20$ MHz) in a fully ferromagnetic (F) environment \cite{3, 4}, down to a small but non zero value of $\approx 300$ mT in the pure antiferromagnetic (AF) structure of LaMnO$_3$ \cite{5}. Due to the distortion of the perovskite cell. In the paramagnetic (P) phase large frequency shifts proportional to the magnetic susceptibility are produced by hyperfine couplings in the presence of...
Note that in the present experiments we do not expect any critical divergence of the nuclear relaxations rates near the magnetic transition, since AF fluctuation modes yield negligible instantaneous fields at the La site, and F fluctuations are suppressed by the intense external field \[16\]. In addition, \(^{139}\)La \((I = 7/2)\) is coupled to the local electric field gradient (EFG) tensor \(V_{ij}\) through its electric quadrupole moment \(Q\). In the frame of reference of the EFG principal axes \((|V_{zz}| \ge |V_{yy}| \ge |V_{xx}|)\), the nuclear Hamiltonian accounting for both magnetic and electric interactions is written as \[17\]:

\[
H_n = \hbar \gamma B_l \cdot I + \frac{\hbar \nu_Q}{6} [3I_z^2 - I(I+1)] + \frac{1}{2} \eta (I_+^2 + I_-^2) \tag{2}
\]

Here \(\nu_Q = 3eQV_{zz}/[2\hbar(2I - 1)]\), and \(\eta = |V_{xx} - V_{yy}|/V_{zz}\) is the EFG asymmetry parameter. The quadrupole interaction resolves the Zeeman transitions, leading in a single crystal to angle-dependent multline spectra with quadrupolar satellites. In a polycrystalline sample the angular average of the satellite patterns gives rise to a characteristic powder spectrum.

The spectra of stoichiometric LaMnO\(_3\) are plotted in broadened by magnetic interactions \[18\]. The best fit parameters for the EFG are \(\nu_Q = 3.8(1)\) MHz, \(\eta = 0.94(2)\) at all temperatures, in close agreement with data reported by Kumagai et. al. \[15\]. The paramagnetic shifts agree with magnetic susceptibility data, which follow a Curie-Weiss law for \(S = 2, g = 2\) moments, and the magnetic line broadening is negligibly small at \(T > T_N\). This indicates a highly homogeneous and accurate stoichiometry for this sample. The onset of an AF order is solely witnessed by a sizeable magnetic broadening below \(T_N = 139\) K. Figure 2 shows that the integrated spectral intensity, corrected for the NMR sensitivity, is constant within experimental accuracy, i.e. the signal originates from the whole sample volume at all temperatures.

Spectra from a subset of hole doped compounds are plotted in Fig. 1b-d. In the order phase they show magnetic shifts and line broadening increasing at increasing doping, in agreement with a ferromagnetic moment increasing with \(x\). The shifts at 70 K in LaMnO\(_{3.04}\), LaMnO\(_{3.06}\) (not shown, \(T_c = 125\) and 150 K) and La\(_{0.87}\)Ca\(_{0.13}\)MnO\(_{3.035}\) \((T_c = 170\) K) are 7, 12 and 15 MHz, respectively. A comparison with the spontaneous frequency of 20 MHz in the CMR ferromagnet La\(_{0.7}\)Ca\(_{0.3}\)-MnO\(_3\) indicates \(\approx 35\%, 60\%\) and 75% ferromagnetically polarized Mn octets in the three samples. Furthermore, a dependence of the EFG on composition was observed. In LaMnO\(_{3.02}\) and La\(_{0.95}\)Ca\(_{0.05}\)MnO\(_3\) (both \(T_N = 130\) K) the fit yields the same quadrupolar linewidth as in LaMnO\(_3\) within experimental accuracy. At doping concentrations \(0.06 < x \leq 0.1\), however, a progressively re-
duced EFG was detected, down to \( \nu_Q = 3.0 \text{ MHz, } \eta = 0.3 \) in \(
LaMnO_{3.05} \) \((T_c = 140 \text{ K})\), whereas no further EFG reduction was observed in the high temperature spectra at higher doping, up to \( x = 0.23 \) in the metallic \(
La_{0.8}\text{Ca}_{0.2}\text{MnO}_{3.015} \). The EFG reduction is probably due to a lower static distortion of the MnO\(_6\) octahedra in the doped compounds.

The most remarkable feature of the La spectra is however the strong reduction of the signal amplitude, which occurs over a wide temperature range in all the doped \textit{insulating} samples (Fig. 3). In \(
LaMnO_{3.04} \) \((T_c = 125 \text{ K})\) in particular, the signal was completely lost at \( 75 \text{ K} \leq T \leq 140 \text{ K} \). The temperature interval where the signal diminishes depends on composition. It is maximum in the least doped compounds \(
LaMnO_{3.02} \) and \(
La_{0.95}\text{Ca}_{0.05}\text{MnO}_3 \), where a missing fraction is already detected at \( T \gg T_c \), right below room temperature. At increasing doping the interval narrows, and its upper limit is lowered down to \( 140 \text{ K} \) in \(
La_{0.87}\text{Ca}_{0.13}\text{MnO}_{3.035} \), a temperature well below \( T_c \). The full signal amplitude is recovered in all samples only at \( T \leq 60 \text{ K} \).

Above \( T = 250 \text{ K} \) the ratio of the La and muon relaxation rates is \( T_{2(La)}^{-1}/\lambda_\mu = 1/5 \), which indicates that \( T_{2M}^{-1} \) is at most \( 1/5 \) of the muon rate. This empirical upper limit implies that \( T_{2M}^{-1}/\lambda_\mu \geq 5/10 \mu\text{s} \) also close to \( T_c \) where the La signal vanishes. If the La relaxation were dominated by the magnetic channel it would be safely within the time window of NMR, contrary to the experimental evidence. Note that relaxation rates scale as \( \lambda_\mu \geq 5 \nu_\mu \), which indicates that \( \lambda_\mu \geq 5 \nu_\mu \).

A similar loss of the Cu NQR signal intensity has been recently reported for the cuprate series \(
La_{2-x-y}\text{R}_x\text{Sr}_y\text{CuO}_4 \) \((R = \text{ rare earth})\), which exhibit stripe instability, and, close to the concentration \( x = 1/8 \), the localization...
of static incommensurate charge-ordered stripes below a transition temperature $T_{\text{charge}}$. The wipe out of the Cu signal was ascribed to the glassy slowing down of the stripes, which are dynamic above $T_{\text{charge}}$. In the case of cuprates, however, it is still debated whether the diverging nuclear relaxations mainly involve spin or charge degrees of freedom.

In lightly doped manganites no long range superstructure has ever been detected above $T_c$. Here, the wipe out of the La signal must arise from the diffusion of short range charge excitations coupled to lattice distortions. A fine dispersion of these centers is actually indicated by the residual NMR signal, which also relaxes very fast and with several time constants, like in the case of a distribution of distances between the diffusing local distortion and the La nuclei. Like in cuprates, however, the diffusion slows down continuously without any critical behavior as temperature is lowered, as in a glass transition. A relaxation model adapted from Curro et al. fits our $^{139}$La amplitude data (Fig. 2): we assume i) an instantaneous quadrupolar frequency $\Delta \omega_Q$ fluctuating with a lorentzian spectrum and a correlation time $\tau_c = \tau_{\text{rec}} \exp(E_a/k_B T)$, ii) an inhomogeneous $T_2^{-1} = \Delta \omega^2 \tau_c$ arising from a distribution of either the activation energy $E_a$ or $\Delta \omega_Q$, and iii) the recovery of the signal in the static limit whereby $\tau_c$ is longer than the duration $\Delta t$ of the whole pulse sequence ($\Delta t \approx 30 \mu s$). The narrowing of the wipe out temperature interval at increasing doping corresponds to the decrease of $T_a/k_B$ from 750(50) K in LaMnO$_{3.02}$ down to 350(50) K in La$_{0.87}$Ca$_{0.13}$MnO$_{3.035}$. Assuming also for convenience EFG fluctuations of comparable amplitude to the static EFG (i.e., $\Delta \omega_Q/2\pi \approx 1$ MHz), the following threshold for the occurrence of the wipe out can be established: $\tau_c \geq 10^{-9}$ s. We stress that direct determination of collective dynamics on this time scale is only accessible to slow microscopic probes like NMR-NQR and $\mu$SR.

It is remarkable that the wipe out occurs throughout the whole low doping insulating region of the phase diagram, whereas it is absent in both the undoped and the metallic phases. This peculiar fact, namely the occurrence of this phenomenon under the combination of charge carriers and a macroscopic insulating behavior, strongly suggests that the diffusing centers are JT small polarons. The recovery of the full signal amplitude at approximately the same temperature $T_{\text{rec}} \approx 60$ K in all the samples denotes the freezing of the polarons, which appear static to NMR at $T < T_{\text{rec}}$. It is worth noting that, in the same composition range investigated here,Millis recently reported private communications by S.W. Cheong on a charge ordered (CO) phase at low temperature. The flat phase boundary of the CO region with $T_{\text{CO}}(x) \approx 60$-70 K is in good agreement with our nearly $x$-independent $T_{\text{rec}}$. We therefore associate the polaron freezing with the onset of a CO state. If the identification holds, the CO transition may be viewed as the transition from a polaron liquid to a polaron crystal.

In conclusion, comparison of $^{139}$La NMR and $\mu$SR data from low doped manganites demonstrates the slow diffusion of charge-lattice excitations, which we identify with small JT polarons.

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