Ferromagnetic Ordering and Unusual Magnetic Ion Dynamics in $La_{0.67}Ca_{0.33}MnO_3$

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Zero-field muon spin relaxation and resistivity experiments on $La_{0.67}Ca_{0.33}MnO_3$ powder show that the sublattice magnetization $\nu_\mu(T)$ is well described for $T \leq T_c$ by $(1 - T/T_c)^\beta$, where $\beta = 0.345 \pm 0.015$, characteristic of a second-order phase transition for a 3D spin system, and the ferromagnetic transition temperature ($T_c = 274$ K) and resistivity peak temperature coincide to within 1 K. Below T_C ν_μ and the zero-field resistivity ρ are correlated, with $\nu_\mu \propto -\ln\rho$. Unusual relaxational dynamics suggest spatially inhomogeneous Mn-ion correlation times. These results are discussed in terms of the possible effects of polarons on the spin and charge dynamics. [S0031-9007(96)00958-1]

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The basic behavior and structure of doped $LaMnO_3$ was established many years ago [1]. $LaMnO_3$ is an insulating antiferromagnet (AFM) with a perovskite structure. As Ca^{2+} is substituted for La^{3+}, charge conservation requires Mn^{3+} conversion to Mn^{4+}, resulting in FM correlations for $0.2 \leq x \leq 0.5$. Above T_C the system is insulating (i.e., the resistivity increases with decreasing temperature), but below T_C the system becomes metallic [2]. There is growing evidence that polaron formation in these materials plays an important role in the charge and heat transport. For example, a comparison of the activation energies obtained for the resistivity Δ_ρ and thermopower Δ_S for $T \geq T_C$ in $La_{1-x}Ca_xMnO_3$ gives $\Delta_\rho \approx 10\Delta_S \approx 0.1$ eV, a characteristic signature of polaronic transport [3]. The precise nature of these polarons has yet to be determined. Present interest therefore stems from the interplay of magnetism and electronic transport in these materials, as evidenced by the discovery [4] that $La_{1-x}Ca_xMnO_3$ and similar systems doped with Sr and Ba possess a very large negative magnetoresistance ΔR near T_C, where $\Delta R/R(0) \approx -95\%$ for 5 T field.

Theoretically, our current understanding of these manganites is far from complete. In the past, the transition from an insulating paramagnet to a metallic ferromagnet has been interpreted in terms of a double-exchange (DE) mechanism [5]. Recent dynamical mean-field calculations of the magnetoresistance near and above T_C in $(La,Sr)MnO_3$ agree with this DE model [6]. However, other authors claim that the DE model alone greatly overestimates the magnitude of both the conductivity and T_C, and underestimates the large $\Delta R/R(0)$ values [7]. They suggest that the electronic transport near and above T_C must involve charge, lattice, and spin degrees of freedom, perhaps coupled in a spin-lattice polaron [7,8]. Finally, a recent examination of DE with greater than one itinerant electron finds that the ground state contains only *local, short-range* ferromagnetic correlations, i.e., no long-range ferromagnetic order [9].

Many recent experiments in these materials have focused on electrical transport, structural properties, bulk magnetization, and specific heat [10]. In this Letter we present zero-field positive muon spin relaxation (μ^+SR) studies which (1) probe the microscopic development of the magnetic order parameter and (2) find evidence for a broad distribution of anomalously long and spatially inhomogeneous Mn-ion correlation times near and below T_C. These relaxation data, and the unusual scaling of the order parameter with the resistivity, are features which any models of the ferromagnetic state in these maganites must incorporate.

Time-differential μ^+SR experiments were carried out using the surface muon M15 channel at TRIUMF in Vancouver, Canada. The sample was a pressed pellet of polycrystalline $La_{1-x}Ca_xMnO_3$, $x = 0.33$, possessing a maximum in the zero-field resistivity at $T_m = 272 \pm 1$ K. This is near the metal-insulator transition temperature, which is usually taken to be the maximum in $d\rho/dT$ (265 ± 2 K). The sample temperature was controlled to within 1 K between $T = 10$ and 300 K using a helium-flow cryostat. Sample quality was investigated using electron microprobe analysis to search for possible atomic clustering; no such evidence was found at the level of 5%. Furthermore, scaling plots of the magnetization M (M/t^β vs $H/t^{\beta\delta}$, where $t = |T - T_C|$) [11]

measured in applied fields up to 1.8 T yield a well-defined T_C (262 ± 3 K) for $\beta = 0.35$ and $\delta = 4.8$. This value corresponds closely to the temperature where $d\rho/dT$ has its maximum. Collectively, these macroscopic data indicate that the system is a well-behaved ferromagnet with a range of T_C's from sample inhomogeneity of at most a few kelvin.

The zero-field μ^+SR data are well described by a relaxation function given by

$$G(t) = A_1 \exp[-\lambda t]\cos[2\pi\nu_\mu(T)t + \phi] + A_2 \exp[-(\Lambda t)^K], \quad (1)$$

where $A_1 + A_2 = 1$. Here $\nu_\mu(T)$ is the muon precession frequency, proportional to the sublattice magnetization below T_C, λ is the inhomogeneous linewidth, and Λ is the dynamic spin-lattice-relaxation rate for a stretched-exponential relaxation function. Unlike previous μ^+SR studies on orthoferrites [12], which showed multiple muon frequencies (from different stopping sites) and peaks in $\Lambda(T)$ which were uncorrelated with the materials' magnetic transition temperatures (signifying μ^+ diffusion), we found no evidence for either multiple stopping sites or muon diffusion in $La_{0.67}Ca_{0.33}MnO_3$ in the temperature range studied. The latter is probably due to disorder-induced localization. The muon site has not been determined yet, though it likely lies near an oxygen atom, as found in other oxides [12,13]. Above T_C $A_1 = 0$, while below T_C A_1 increases, saturating at its maximum value of $2/3$ for $T \leq 0.84T_C$. This low-temperature amplitude behavior ($A_1 \approx 2/3$ and $A_2 \approx 1/3$) is expected [14] for a multidomain sample in zero applied field, where the local magnetization averaged over domains points along the muon spin direction with probability $1/3$.

Figure 1 shows the order parameter $\nu_\mu(T)$ plotted as a function of temperature. The solid line is a fit by the function $\nu_\mu(T) = \nu_0(1 - T/T_C)^\beta$; we find that $\beta = 0.345 \pm 0.015$ and $T_C = 274.3 \pm 1.4$ K. Thus T_C as determined from μ^+SR as the onset of microscopic spin ordering is slightly larger than determined from the M scaling, but agrees within error with the resistivity maximum T_m.

The functional form for $\nu_\mu(T)$, usually applicable only to the asymptotic critical regime $(1 - T/T_C) < 10^{-2}$ around a second-order phase transition, gives a reasonable description of the magnetic order parameter over the entire temperature range measured. [At low temperatures this may be due to the relatively larger errors in $\nu_\mu(T)$.] Theoretical values of the critical exponent for 3D Heisenberg, XY, and Ising systems are 0.38, 0.33, and 0.31, respectively [11], while a value of $1/2$ corresponds to a mean-field transition. The measured value of β is thus close to the theoretical critical value expected for a 3D spin system, as shown in the inset of Fig. 1, where $\nu_\mu^3(T)$ is plotted as a function of temperature. We note that $\frac{1}{\beta} d\beta/dT_C$ is only 0.012–0.016 for $T/T_C =$ 0.90–0.95 and $\delta T_C \approx 10$ K. Thus the error in β due to the possible spread in T_C is small.

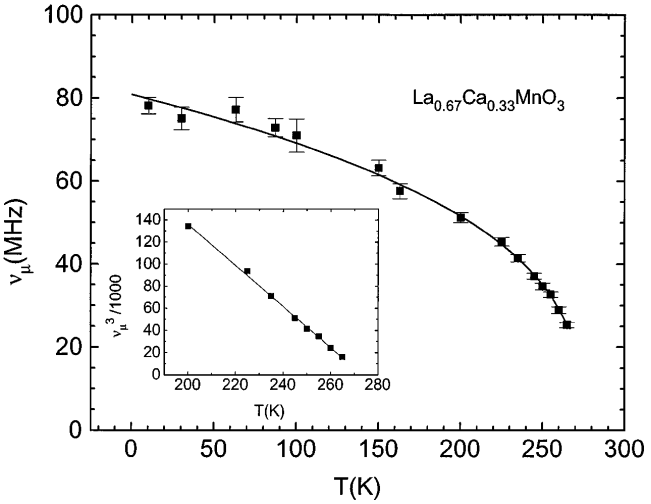

FIG. 1. Temperature dependence of the zero-field muon precession frequency $\nu_\mu(T)$, proportional to the sublattice magnetization. The inset shows that $\nu_\mu^3(T)$ is approximately linear in temperature, giving a value of β (see text) $\cong 1/3$.

The inhomogeneous linewidth λ in zero field (not shown) has about the same temperature dependence below T_C as $\nu_\mu(T)$, with $\lambda/(2\pi\nu) \approx 1/3$ at $T = 10$ K. This represents a distribution of local fields which is roughly consistent with (1) the calculated distribution of demagnetization factors produced by varying grain shapes in a multidomain sample, and (2) the calculated distribution of dipole fields arising from a random mix of Mn^{3+} ($S = 2$) and Mn^{4+} ($S = 3/2$) ions in a 2:1 ratio.

Earlier studies of 1000 Å thick films of the $x = 0.30$ material [15] found an interesting correlation between the magnetization M and the resistivity ρ below T_C in applied fields ≥1 T. This relation, $\rho(H,T) = \rho_0 \exp[-M(H,T)/M_0$, is not understood theoretically, but is indicative of how the evolving magnetic order affects the dc conductivity below T_C. It is therefore of interest to see if the exponential relation between ρ and M found at high fields still holds in zero field. Figure 2 shows that indeed $\nu_\mu(T) \propto M \propto \ln(1/\rho)$. This is important because, unlike the uniform magnetization M, μ^+SR measures the *local* spin polarization in *zero* applied field, rather than a uniform average in an orienting field.

Figure 3 shows the dynamical relaxation rate Λ as a function of temperature. One observes a peak in Λ corresponding to the critical slowing down of the local field fluctuations for $T \geq T_C$. The dynamical fraction of the relaxation function (with amplitude A_2) changes from an exponential ($K = 1$) near 300 K to a "root exponential" ($K = 1/2$) at $T \approx T_C$ (see inset in Fig. 3), and is well described using $K = 1/2$ for 150 K $< T < T_C$. Below about 150 K the relaxation rate is too small to distinguish unambiguously between the exponential and nonexponential forms. Most ferromagnetic materials stud-

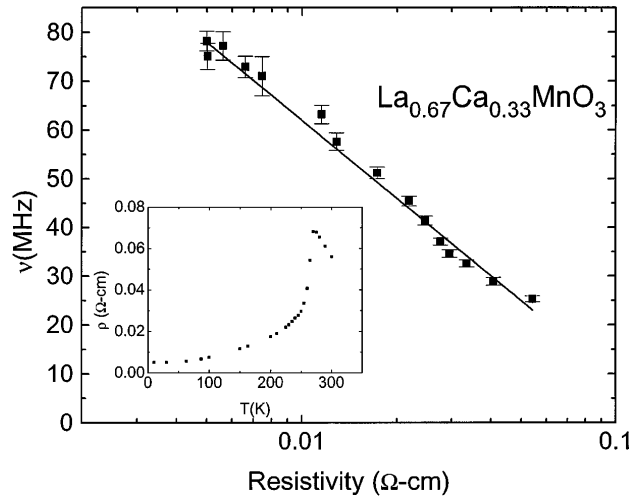

FIG. 2. Temperature dependence of $\nu_\mu(T)$ vs resistivity on a log scale. The solid line is a least squares fit showing $\nu_\mu(T) \propto -\ln[\rho(T)]$. The inset shows resistivity vs temperature.

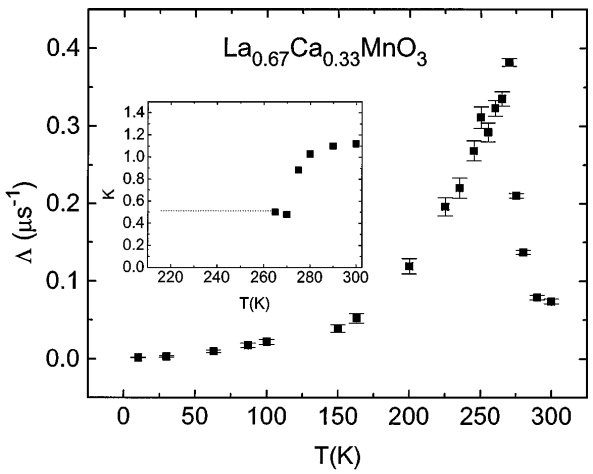

FIG. 3. Temperature dependence of the μ^+SR stretched exponential relaxation rate Λ, with the inset showing the exponent K vs temperature [see Eq. (1)]. Below $T = T_C, K = 1/2$ was used to fit the data.

ied by μ^+SR show an exponential relaxation function with a rate which approaches divergence at T_C. This is seen, for example, in the Heisenberg ferromagnet $GdNi_5$, where $T_C = 31.5$ K [16]. Furthermore, in $GdNi_5$ both the magnitude of the relaxation rate and its temperature dependence $[T^2 \ln(T)]$ at low temperatures ($T \ll T_C$) are consistent with that expected [17] for a two-magnon scattering process. Similar behavior has also been observed in the random ferromagnet Pd-2.0 at.% Mn alloy, with $T_C = 5.8$ K [18].

In a ferromagnet such as $GdNi_5$, where the relaxation function remains exponential, the spin-lattice-relaxation rate $\Lambda \propto (\Delta\omega^2)\tau$, where $\Delta\omega^2$ is the coupling strength between the μ^+ and the Mn spins, which originates from dipolar and hyperfine interactions. The time-correlation function of the local fluctuating field $\delta\vec{H}(t)$ can be characterized by a single correlation time τ, i.e., $\langle \delta\vec{H}(0) \cdot \delta\vec{H}(t)\rangle \propto \exp(-t/\tau)$. Significant deviations from an exponential relaxation function usually signify either a broad distribution of correlation times or a broad distribution of coupling strengths. This may be from either "intrinsic" or "extrinsic" sources. Intrinsically, this situation has been observed in μ^+SR studies of spin-glass alloys, where, for example, dilute concentrations of Fe or Mn ($\sim$1%) are dissolved in Au or Ag [19] or in oxide spin glasses such as $Fe_{1.75}Ti_{1.25}O_5$ [20]. In these cases, the variations in $\Delta\omega^2$ and τ arise because of the random positions of the dilute magnetic ions relative to the μ^+ and the $1/r^3$ dependence of the dipolar coupling. Alternatively, a distribution of measured correlation times near T_C could arise from extrinsic sample inhomogeneity, for example, if there were a broad distribution of transition temperatures produced by an inhomogeneous chemical composition. As mentioned above, however, the chemical inhomogeneity is not large, and furthermore T_C is a slowly varying function of hole doping near 33% Ca [2]. Also, the scaling behavior of M indicates a macroscopic spread in T_C of only a few kelvin, as noted above. We therefore conclude that the observation of a nonexponential relaxation function for 150 K $< T \leq T_C$ suggests that the spin dynamics are "glassy," i.e., cannot be characterized by a single correlation time τ.

The development of the magnetic order parameter $\nu_\mu(t)$ appears to be quite "normal" for a 3D spin system. One is therefore led to ask whether the low temperature Λ is characteristic of two-magnon relaxation, as seen in μ^+SR experiments on other ferromagnets, both ordered (e.g., $GdNi_5$) and disordered (e.g., *Pd*Mn). For a 3D Heisenberg ferromagnet the μ^+SR relaxation rate from a two-magnon process is given for dipolar coupling by [17]

$$\Lambda_M = [9\gamma_\mu^2\gamma_e^2 G(k_B T)^2/16(\pi D)^3] \times \ln(k_B T/\hbar\omega_A), \quad (2)$$

where γ_μ and γ_e are the muon and electron gyromagnetic ratios, D is the spin-wave stiffness constant, and ω_A is the anisotropy energy. The quantity G depends on the muon location and lattice geometry. A similar relation for hyperfine coupling gives the same order of magnitude for Λ_M. To estimate Λ_M we obtain D from the low-temperature magnetization data $M(T)$. For a 3D Heisenberg system $M(T)/M_0 = 1 - b(T/T_C)^{3/2}$ and $D = a^2 k_B T_C (0.06/SQb)^{2/3}$ [21]. Here S is the average Mn spin, a is the lattice constant, and $Q = 1$ for the perovskite structure. We find that $M(T)$ is well described by this $T^{3/2}$ "Bloch law" for $T \leq 80$ K, and we derive $D \approx 155$ meV Å^2 for this system. For comparison, pure Fe has $D \approx 280$ meV Å^2 and $GdNi_5$ has $D \approx 5$ meV Å^2. A value of 155 meV Å^2 gives $\Lambda_M \approx 10^{-5} - 10^{-6}$ μs^{-1}, which is 3–4 orders of magnitude smaller than the measured Λ for $T \leq 100$ K, with any reasonable choice of ω_A and G in Eq. (2). Linear spin-wave theory, upon which this simple analysis is based, often holds for $T \lesssim$

$T_C/3$. Thus, there exists an additional low-temperature relaxation mechanism which dominates in this system, and is not characteristic of typical ferromagnets such as $GdNi_5$, or even random ferromagnets such as *Pd*Mn. This points to anomalously slow spin fluctuations, as discussed below.

To summarize, the static magnetic properties of $La_{0.67}Ca_{0.33}MnO_3$ behave as expected for a typical 3D ferromagnet [$\nu_\mu(T)^3 \propto \nu_0^3(1 - T/T_C)$ and $\Delta M(T) \propto T^{3/2}$]. Despite these "normalities," however, we find several novel distinguishing features in this system. First, the spin dynamics of $La_{0.67}Ca_{0.33}MnO_3$ are unusual, giving evidence for a broad microscopic distribution of very slow spin-spin correlation times. These slow fluctuations produce additional low-temperature relaxation not observed in more typical ferromagnets, where spin wave excitations dominate. Second, below T_C the resistivity falls off exponentially with the growth of the spontaneous FM order parameter in our powder samples. This behavior is apparently quite general, because it was also observed [15] in thin-film samples under applied fields of several tesla where the domain structure was saturated.

The inhomogeneous relaxational dynamics suggest a kind of glassy state, where the fast-relaxing and slow-relaxing regions retain their identity for a time $>\Lambda^{-1}$. The fact that the local static spin correlations are projected to set in slightly above the T_C determined from the scaling of the bulk magnetization $M(H, T)$ and continue to grow below T_C [as shown by the gradual increase in the A_1 coefficient in Eq. (1)] indicates that the microscopic spin freezing percolates over an extended temperature range, again suggesting a kind of unconventional glassy state. (Alternatively, it may be that the system approaches T_c from below as a second-order phase transition, but is interrupted by a weakly first-order transition to the paramagnetic state.) One possible scenario is that the small polarons indicated above T_C by transport measurements [3] grow larger below T_C, retaining some identity to temperatures significantly below the onset of magnetic order. This could yield variable-size spin clusters below T_C, which may undergo diffusive relaxation. In this connection, recent neutron experiments [22] on (La,Ca)MnO_3 show the growth of an anomalous quasielastic scattering peak below T_C, with a width which is consistent with the fluctuation rates observed in our μSR studies ($\approx 10^{11}$ s^{-1}). These different kinds of experiments could be observing the same spin dynamics; however, because μSR probes in real space (and neutrons in momentum space) we are able to demonstrate the spatial inhomogeneity present in the spin fluctuations. Although our results may be interpreted in terms of polaronic degrees of freedom, we wish to emphasize that they are more general; i.e., it may be that the ground state of these ferromagnets is simply not homogeneous, as suggested by recent theoretical calculations for the many-body DE model mentioned above [9]. This needs further theoretical understanding.

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