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ZERO-FIELD μ^+SR STUDY OF THE COLOSSAL MAGNETORESISTANCE MATERIAL $La_{0.67}Ca_{0.33}MnO_3$

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Zero-field μ^+SR and resistivity experiments on $La_{0.67}Ca_{0.33}MnO_3$ powder show that the ferromagnetic transition temperature (T_C =274 K) and resistivity peak temperature coincide to within 1K, about 10 K higher than T_C determined from the bulk magnetization. The sublattice magnetization $\nu_\mu(T)$ is well described for $T \leq T_C$ by $(1-T/T_c)^\beta$, where $\beta = 0.345 \pm 0.015$. Unusual relaxational dynamics suggest a wide distribution of Mn-ion correlation times. These results are discussed in terms of the effects of polarons on the spin and charge dynamics.

1. Introduction

The basic behavior and structure of doped $La_{1-x}Ca_xMnO_3$ 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 $0.2 \leq x \leq 0.5$, as discussed below. Above T_C the system is insulating (i.e., the resistivity increases with decreasing temperature), but below T_C the system becomes metallic [2]. The present interest stems in part from the discovery [3,4] 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 tesla field. 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], in which the conductivity occurs via itinerant Mn d-electrons which hop most readily from Mn^{3+} to Mn^{4+} if the core d-spins ($S = 3/2$) are ferromagnetically aligned. This is due to the strong on-site Hund's rule coupling. However, recent theoretical calculations [6] have shown 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. It has therefore been suggested 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 [6,7].

2. Experiment

Time-differential μ^+SR experiments were carried out in $La_{1-x}Ca_xMnO_3$ with x = 0.33 using the surface muon M15 channel at TRIUMF in Vancouver, Canada. The sample was a pressed polycrystalline pellet possessing a maximum in the zero-field resistivity at $T_m = 272 \pm 1$ K, near the metal-insulator transition temperature denoted by the maximum in $d\rho/dT$ (265 ± 2 K). The sample temperature was controlled to within 1K between T = 10 - 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 (M/t^{β} vs. $B/t^{\beta\delta}$ where $t = |T - T_C|$) [8] of the magnetization M measured in applied fields up to 1.8T 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 would 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 μSR data are well described by a relaxation function given by:

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

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. We found no evidence for either multiple muon stopping sites or muon diffusion in the temperature range studied. Above T_C $A_1 = 0$, while below T_C A_1 increases, saturating at its maximum value of 2/3 for $T \leq 0.84\ T_C$.

3. Results and Discussion

Figure 1 shows the order parameter $\nu_\mu(T)$ plotted as a function of temperature. The solid line is a fit to 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 determined from μSR 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. As discussed below, we believe this arises from the microscopic physics inherent in this material. We note that $\beta^{-1}\, d\beta/dT_C$ is only 0.012 - 0.016 for $T/T_C = 0.90$ - 0.95 and $\delta T_C \cong 10$ K. Thus the error in β due to the possible spread in T_C is small ($\cong 0.02$ for β about 0.35).

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 [8], while a value of 0.50 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 to Fig. 1, where $\nu_\mu^3(T)$ is plotted as a function of temperature.

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 the distribution of demagnetization factors produced by varying grain shapes in a multi-domain sample, together with a system containing a random mix of Mn^{3+} ($S = 3/2$) and Mn^{4+} ($S = 2$) ions in a 2:1 ratio.

Figure 2 shows the dynamical relaxation rate Λ as a function of temperature. One observes a peak in Λ corresponding to the slowing down of the local field fluctuations for $T \geq T_C$. Below T_C Λ decreases because of the decreasing amplitude of the local-field fluctuations as the Mn spin system freezes. The dynamical fraction of the relaxation function (with amplitude A_2) changes from an exponential ($K = 1$) near 300K to a 'root-exponential' ($K = 1/2$) at $T \cong T_C$ (see inset to Fig. 2), 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 non-exponential forms.

In a ferromagnet such as $GdNi_5$, where the relaxation function remains exponential [9], the spin-lattice-relaxation rate $\Lambda \propto (\Delta\omega^2)\tau$, and the time-correlation function of the local fluctuating field can be characterized by a single correlation time τ. In the expression for Λ, $(\Delta\omega^2)$ is the coupling strength between the μ^+ and the Mn spins, which originates from dipolar and hyperfine interactions. 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 μSR studies of spin-glass alloys, where, for example, dilute concentrations of Fe or Mn (1 %) are dissolved in Au or Ag [10]. 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, the chemical inhomogeneity is not large, however, 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 non-exponential relaxation function

for 150 K < T ≤ 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 lead to ask whether the low temperature Λ is characteristic of two-magnon relaxation, as seen in μSR experiments on other ferromagnets, both ordered ($GdNi_5$ [9]) and disordered (PdMn [11]). For a 3D Heisenberg ferromagnet the μSR relaxation rate from a two-magnon process is given for dipolar coupling by [12]

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

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). We find that M(T) is well described by a $T^{3/2}$ 'Bloch law' [13] for T ≤ 80 K, and we derive D ≅ 155 meV Å^2 for this system. For comparison, pure Fe has D ≅ 280 meV Å^2 and $GdNi_5$ has D ≅ 5 meV Å^2. A value of 155 meV Å^2 gives $\Lambda_M \cong 10^{-5}$ - 10^{-6} μs^{-1}, which is 3 - 4 orders of magnitude smaller than the measured Λ for T ≤ 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 ≤ $T_C/3$. Thus, there exists an additional low-temperature relaxation mechanism which dominates in this system, and is not characteristic of typical ferromagnets like $GdNi_5$ or even random ferromagnets like PdMn.

4. Conclusions

To summarize, the static magnetic properties of $La_{0.67}Ca_{0.33}MnO_3$ behave as expected for a typical 3D ferromagnet [$\nu_\mu(T) \propto \nu_0^3(1 - T/T_C)$ and $\Delta M(T) \propto T^{3/2}$]. Despite these 'normalities', however, we find several novel distinguishing features in this system. First, the zero-field resistivity shows a peak at precisely the temperature T_m where the *local* spontaneous magnetization is projected to become non-zero, i.e., just at T_C, as determined by our microscopic magnetic probe. This is different than T_C determined from the scaling behavior of M, however. Second, the spin dynamics of $La_{0.67}Ca_{0.33}MnO_3$ are unusual, giving evidence for (1) a broad microscopic distribution of spin-spin correlation times, and (2) an additional, low-temperature dynamic relaxation mechanism not observed in more typical ferromagnets.

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 $\Delta_\rho \cong 10\Delta_S \cong 0.1$ eV, a characteristic signature of polaronic transport [14]. The nature of these polarons has yet to be determined, but theoretical models [6] suggest that they may be comprised of FM clusters (spin polarons), driven by the DE interaction, which are dressed by a local lattice or Jahn-Teller distortion (lattice polaron). The inhomogeneous relaxational dynamics suggest a kind of glassy state, perhaps consisting of polarons of varying size, or variable-size spin clusters. Furthermore, the fact that local static spin correlations are projected to set in slightly above the T_C determined from the scaling of the bulk magnetization M(B,T) and continue to grow below T_C (as shown by the gradual increase in the A_1 coefficient in Equation (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 approached T_C from below as a second-order phase transition, but is interupted by a weakly first-order transition to the paramagnetic state.

This leads to an important final point. The inhomogeneous dynamics observed in $La_{0.67}Ca_{0.33}MnO_3$ extend from near T_C to very low temperatures. If this is associated with polarons of any type, their signature exists far below the insulator-metal transition temperature, above which the transport data [14] clearly signify their presence. This persistence may be caused by the presence of lattice distortions which are coupled to the spin polarons, thus affecting both the polaron dynamics and the spin-lattice relaxation rates.

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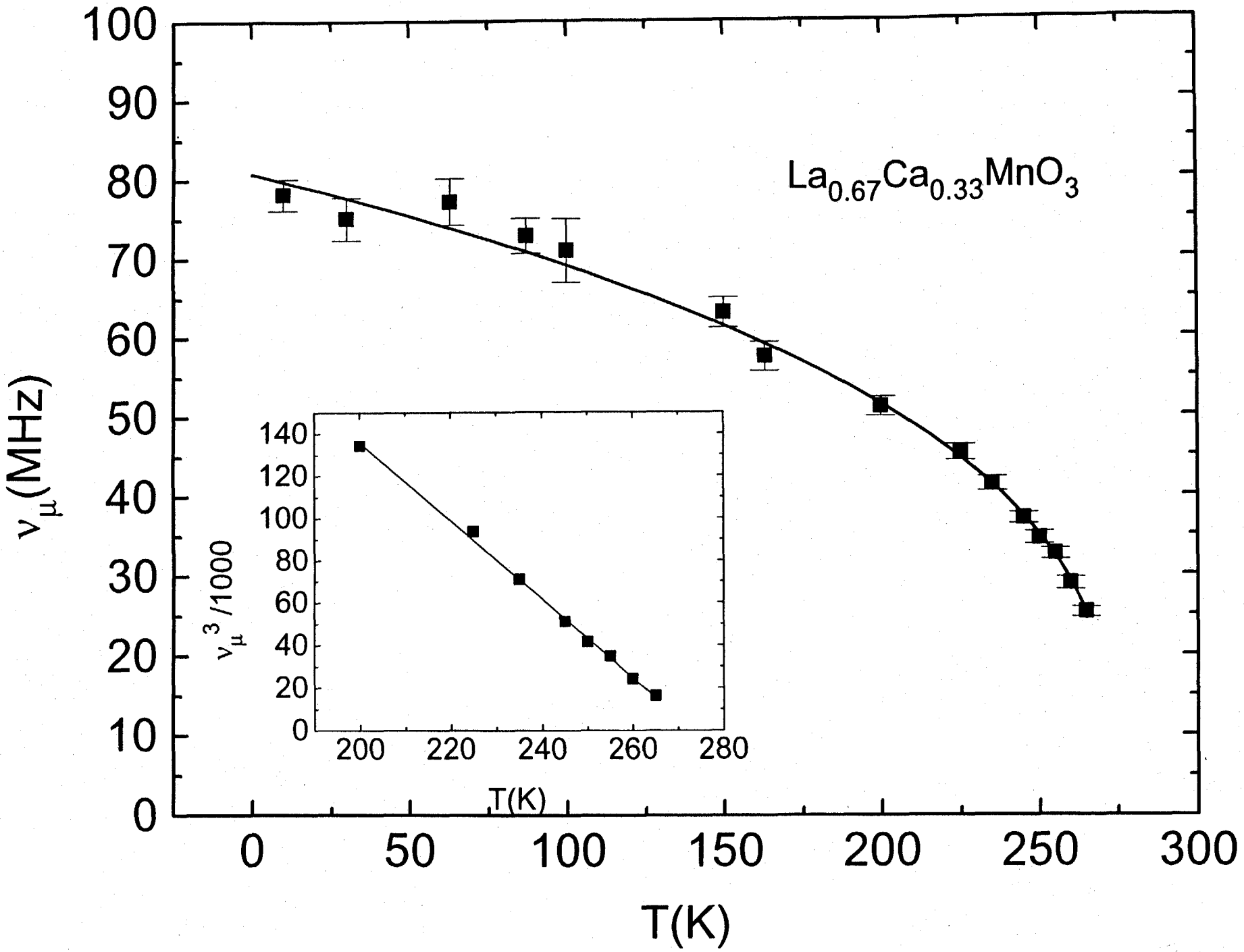
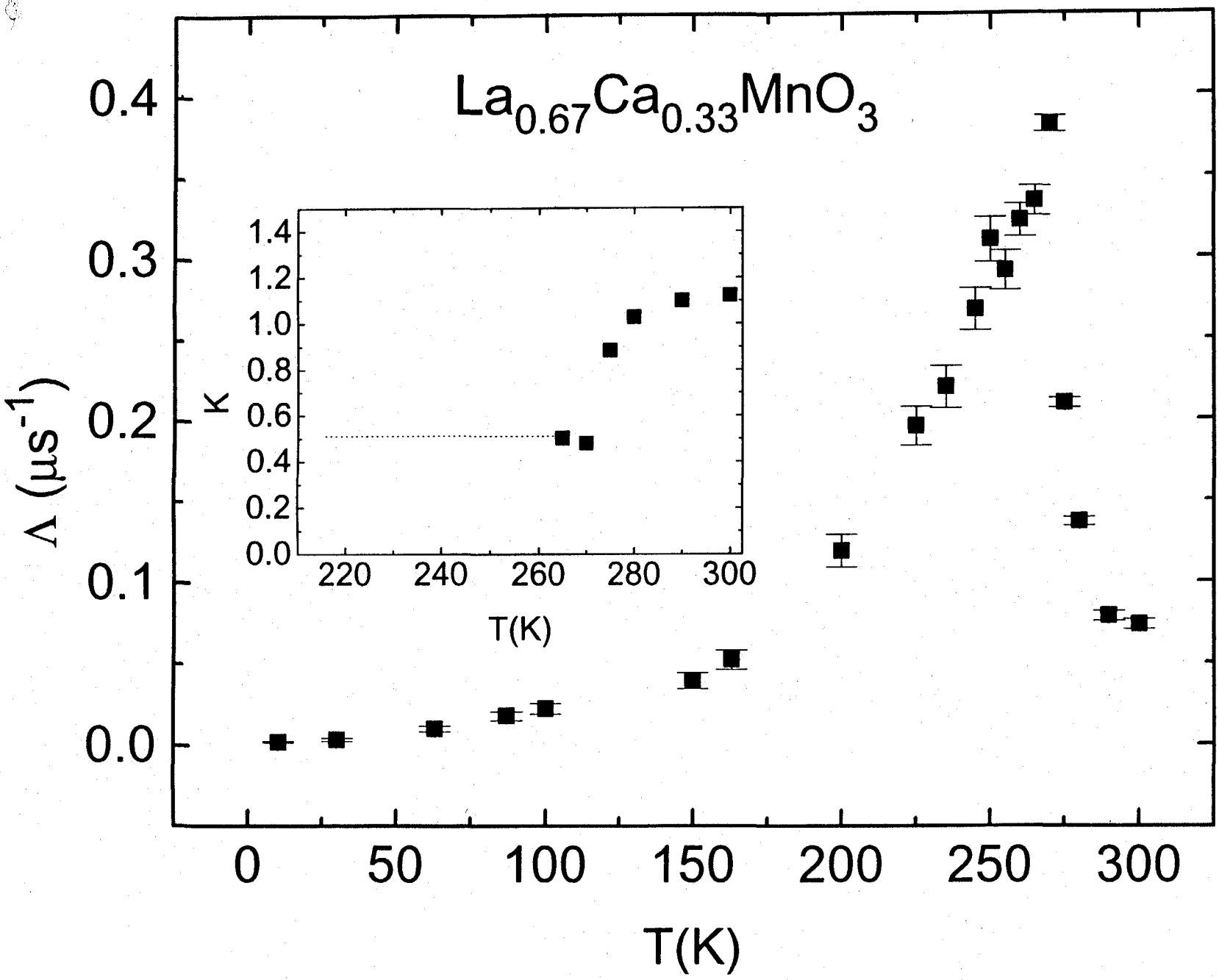
Figure Captions

Figure 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) $\approx 1/3$.

Figure 2. Temperature dependence of the μSR 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.


$La_{0.67}Ca_{0.33}MnO_3$
ν_μ(MHz)
T(K)
ν_μ^3/1000
T(K)


La0.67Ca0.33MnO3
Λ (μs-1)
T(K)
0.0
0.1
0.2
0.3
0.4
0
50
100
150
200
250
300
K
T(K)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
220
240
260
280
300

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