Effects of Reduced Dimensionality on Spin Dynamics in the Layered Perovskite $La_{1.4}Sr_{1.6}Mn_2O_7$

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We report zero-field muon spin rotation data in single crystals of $La_{1.4}Sr_{1.6}Mn_2O_7$ for $T = 5-325$ K. The spin-lattice relaxation rate is spatially inhomogeneous below the 3D magnetic transition temperature T_C and anisotropic above T_C. We find evidence against 2D spin ordering or in-plane correlations above T_C. Additionally, the very slow spin fluctuations found below T_C in cubic (3D) perovskites like $(La, Ca)MnO_3$ or $(La, Sr)MnO_3$, and attributed to relatively small magnetoelastic polarons, are absent in $La_{1.4}Sr_{1.6}Mn_2O_7$. This suggests that the polaron size in the layered material is significantly larger than in the 3D perovskites. [S0031-9007(98)06898-7]

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The discovery of "colossal" negative magnetoresistance (CMR) in the cubic three-dimensional (3D) perovskite $(R, A)MnO_3$ manganites [1,2], where R is a trivalent rare earth and A is a divalent metal such as Ca, Sr, or Ba, has set off a vigorous experimental [3] and theoretical [4] effort to identify the microscopic mechanisms responsible for both the CMR and the ferromagnetic/metal-insulator (FM/MI) transition. These CMR effects involve strong couplings among spin, charge, and lattice degrees of freedom. An understanding of the competition between these couplings is important for a microscopic understanding of a broad range of transition metal oxides, such as high temperature superconductors (cuprates), ferroelectrics (titanates), and charge-ordering compounds (nickelates), as well as the CMR manganites.

In the 3D perovskite CMR materials transport measurements [5] give unequivocal evidence for small-polaron hopping above the 3D FM magnetic ordering temperature T_C, while neutron scattering [6] and XAFS [7] experiments show that small changes in the local structure persist below T_C. Muon spin relaxation (μSR) [8] and neutron scattering [9] measurements have further demonstrated that the FM transition in $(La, A)MnO_3$ is accompanied by very slow [8,9] spatially inhomogeneous [8] fluctuations which are not characteristic of more conventional ferromagnets. These unusual spin dynamics in the perovskites are likely due to the formation of *magnetoelastic* polarons, which consist of local lattice distortions surrounded by polarized spin clusters [4]. Characterization of magnetoelastic polarons is recognized to be a crucial step in the understanding of CMR phenomena.

Dimensionality has been shown to be an important consideration in the behavior of transition metal oxides. It is thus of great interest to compare similar measurements in $La_{2-2x}Sr_{1+2x}Mn_2O_7$, which consists of quasi-2D MnO_2 bilayers separated by an insulating $(La, Sr)_2O_2$ plane [10], to investigate the effects of dimensionality on polaron behavior. This Letter addresses the following key issues: (1) Does lower dimensionality in $La_{1.4}Sr_{1.6}Mn_2O_7$ cause 2D spin ordering and/or in-plane spin correlations above T_C, as suggested by the recent transport and magnetization data discussed below? (2) Are the slow inhomogeneous fluctuation rates observed in $(La, A)MnO_3$ perovskites also present in $La_{1.4}Sr_{1.6}Mn_2O_7$ under similar doping conditions? Our muon spin rotation (μSR) study gives negative answers to both questions. The absence of slow fluctuations below T_C can be explained if the magnetoelastic polarons in this layered (2D) material are significantly larger than in the 3D perovskites.

In $La_{1.4}Sr_{1.6}Mn_2O_7$ the anisotropic resistivity falls sharply below 90 K, which is a signature of a MI transition [11]. The low-field c-axis magnetization suggests two magnetic transitions, one near 80–90 K and a lower antiferromagnetic (AFM) transition below about 60 K. Furthermore, the low-field ab-plane magnetization rises with decreasing temperature below 300 K, with a plateau between 250 and 90 K [11]. This suggests [11] that the spin behavior in this system includes in-plane, short-range 2D FM correlations below about 300 K, a 3D FM transition near 90 K, and AFM along the c axis below 60 K. Recent neutron scattering data [12] give a somewhat more complicated picture, however, with AFM ab-plane ordering below about 90 K, which decreases in intensity and is accompanied by both FM- and AFM-type ordering along the c axis below about 60 K.

Zero-field μSR experiments on $La_{1.4}Sr_{1.6}Mn_2O_7$ were carried out using the M20 surface-muon channel at TRIUMF in a gas-flow cryostat between 2 and 325 K. Eight single crystals were synthesized at JRCAT and mounted in an array with their c axis aligned within a few

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degrees and parallel to the incoming muon momentum. Data were taken with the muon spin $\mathbf{S}_\mu$ parallel to the **a** and **c** crystallographic directions by rotating $\mathbf{S}_\mu$.

The observed μSR zero-field relaxation function $G_z(t)$ is well described by the formula

$$G_z(t) = A_1 e^{-(t/T_1)^K} + A_2 e^{-t/T_2} \cos(\omega_\mu t + \phi_\mu). \quad (1)$$

The first term describes dynamic relaxation due to temporal fluctuations of the local field; the second term describes static relaxation due to a Lorentzian distribution of Larmor precession frequencies and vanishes for $T > T_C$. Here $1/T_1$ and $1/T_2$ are the dynamic (spin-lattice) and static relaxation rates, respectively, and $\omega_\mu = \gamma_\mu B$ is the muon precession frequency in the average static internal field **B**. The amplitudes of the two terms are given by $A_1 = \cos^2\theta$ and $A_2 = \sin^2\theta$, where θ is the angle between $\mathbf{S}_\mu$ and **B**. In a system possessing a unique local-field correlation time τ one expects [13] exponential relaxation ($K = 1$) if τ is much less than the measurement time scale (here a few muon lifetimes or 10 μs). Values of the exponent $K < 1$ therefore give an empirical "stretched exponential" fit in the presence of an *inhomogeneous* distribution of relatively fast dynamic relaxation rates.

Figure 1 shows $1/T_1$ in zero applied field. From our measurements we denote T_C as the temperature where $1/T_1$ peaks; thus $T_C \simeq 77$–81 K. For both muon spin directions the relaxation rate decreases smoothly and gradually with increasing temperature above 110 K. At all temperatures $\geq T_C$, the relaxation rate $(1/T_1)_a$ for $\mathbf{S}_\mu \| \mathbf{a}$ exceeds the rate $(1/T_1)_c$ for $\mathbf{S}_\mu \| \mathbf{c}$ by a factor of about 2.5. The inset of Fig. 1 shows $\omega_\mu(T)/2\pi$ versus T for $\mathbf{S}_\mu \| \mathbf{a}$. The temperature dependence of the "order parameter" is not smooth, probably because of the competing magnetic ground states mentioned above.

Figure 2 shows the temperature dependence of the exponent K. At high temperatures $K \simeq 1$, falling to <0.5 below 70 K. The observed stretched-exponential behavior ($K < 1$) indicates that a distribution of T_1 values sets in near or slightly above T_C.

Figure 3 shows the temperature dependence of the amplitude A_1 of the "dynamic" term in Eq. (1). Below about 80 K A_1 falls as the onset of spontaneous magnetic order creates a nonzero precession amplitude A_2. For $\mathbf{S}_\mu \| \mathbf{c}$ A_1 reaches a minimum near 70 K and then recovers nearly its full amplitude below 50 K, whereas for $\mathbf{S}_\mu \| \mathbf{a}$ A_1 continues to decrease down to 2 K. Therefore, **B** rotates below about 80 K, making an angle of about 45° with the c axis ($A_1 \simeq A_2 \simeq 1/2$) near 75 K and returning to an angle of 20°–30° at the lowest temperatures.

The muon position can be inferred from the magnetic structure and the magnitude and direction of **B** at low temperatures. We have considered two structures: alternating FM bilayers aligned along the c axis [11] (structure #1), and the more complicated FM/AFM structure mentioned above [12] (structure #2). μSR experiments in a variety of oxides [14] have shown that the muon forms

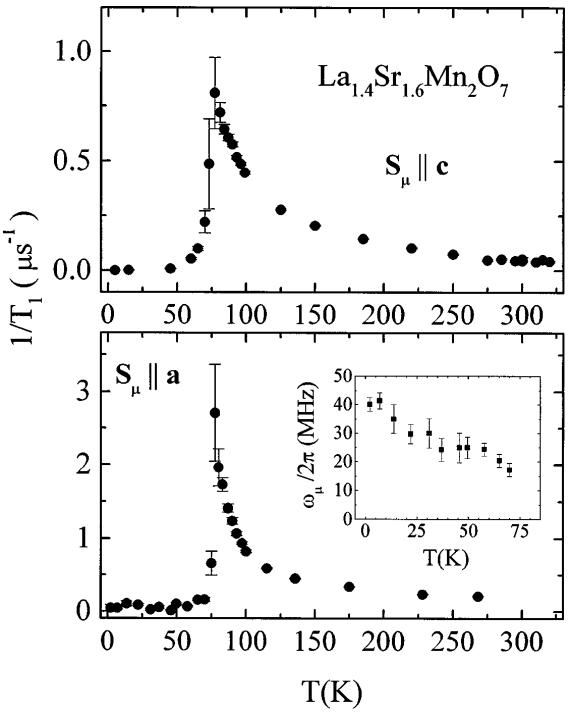

FIG. 1. Temperature dependence of the spin lattice relaxation rate $1/T_1$ in $La_{1.4}Sr_{1.6}Mn_2O_7$. Top: $(1/T_1)_c$ ($\mathbf{S}_\mu \| \mathbf{c}$). Bottom: $(1/T_1)_a$ ($\mathbf{S}_\mu \| \mathbf{a}$). Inset: Temperature dependence of the muon frequency $\omega_\mu/2\pi$ below T_C, determined from fits to time-differential μSR relaxation data.

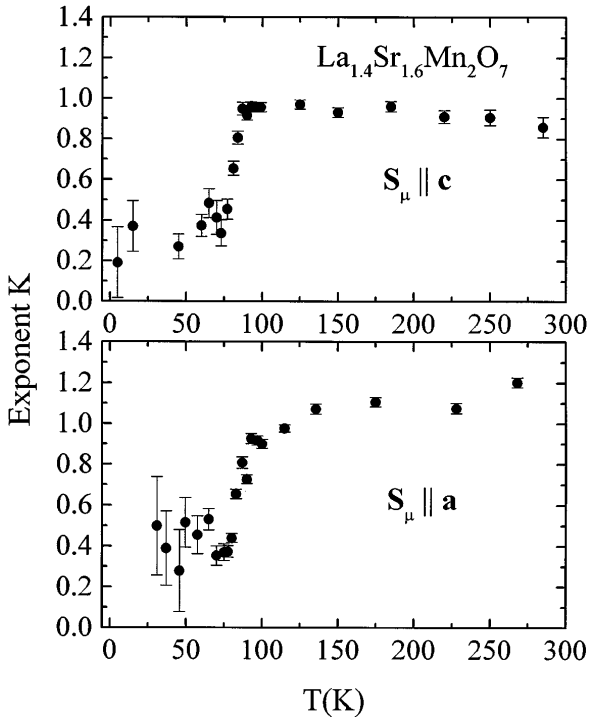

FIG. 2. Temperature dependence of the exponent K of the stretched-exponential dynamic relaxation function [first term of Eq. (1)] in $La_{1.4}Sr_{1.6}Mn_2O_7$. Top: $\mathbf{S}_\mu \| \mathbf{c}$. Bottom: $\mathbf{S}_\mu \| \mathbf{a}$. (Data are not plotted at the lowest temperatures for $\mathbf{S}_\mu \| \mathbf{a}$, because K cannot be determined accurately when the fluctuating amplitude and the relaxation rate are small.)

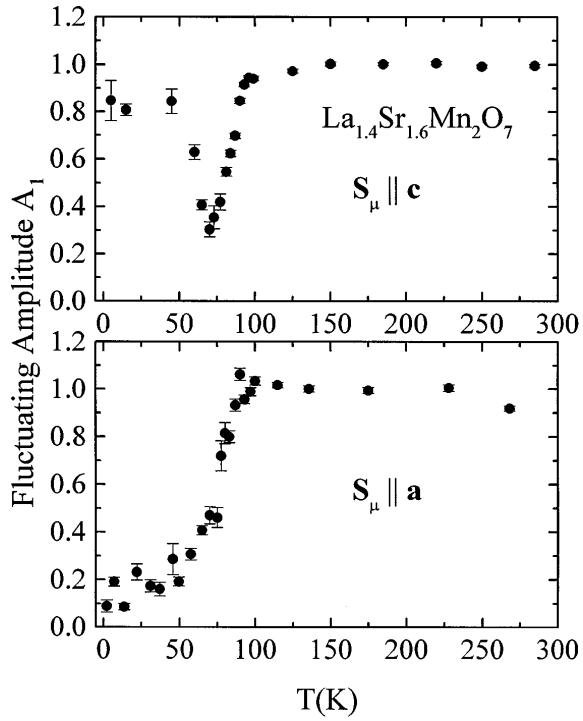

FIG. 3. Temperature dependence of the amplitude A_1 of the "dynamic" term of Eq. (1) in $La_{1.4}Sr_{1.6}Mn_2O_7$. Top: $\mathbf{S}_\mu \| \mathbf{c}$. Bottom: $\mathbf{S}_\mu \| \mathbf{a}$.

a covalent bond with an oxygen atom such that the μ^+-oxygen distance is 1.0 ± 0.1 Å. There are three inequivalent oxygen sites: O(1) at $(0,0,0)$, O(2) at $(0,0,0.2)$, and O(3) at $(0,1/2,0.4)$, [15]. Taking the average Mn moment to be about $3.7\mu_B$ (30% Mn^{4+}) we find two possible sites, one close to O(2) and a second close to O(3), with dipolar fields $B_{\rm dip}$ near the experimental value $B = (840 \pm 40)\ G/\mu_B$ obtained from $\omega_\mu/2\pi$ measured at 2 K (inset of Fig. 1). The site near O(2) yields $B_{\rm dip} = 700{-}900\ {\rm G}/\mu_B$ for both magnetic structures, but only structure #2 yields the correct field direction. The site near O(3) is consistent with structure #2, with $B_{\rm dip} = 600{-}800\ {\rm G}/\mu_B$; structure #1 produces fields $4{-}5\ {\rm kOe}/\mu_B$ near O(3) and is therefore ruled out by the data. The O(2) position yields the measured anisotropy in $1/T_1$ discussed below, and is also in good agreement with the assigned muon site in La_2CuO_4 [16] which has a structure similar to that of $(La,Sr)_3Mn_2O_7$. The low-temperature field can be explained by $B_{\rm dip}$ alone; no transferred hyperfine field is required.

A tendency for magnetic order is observable as a slowing of the mean spin correlation time τ. μSR experiments are sensitive to this in two ways. First, ordering will produce a static field **B** that results in muon precession or a reduced dynamic amplitude (if the precession frequency is too high or the static linewidth too broad for the precession itself to be observed). This is also true for short-range ordering or glassy spin freezing, because the muon is a local probe. In the region between 150 and 325 K we observe only a single, full-amplitude exponential relaxation function. Second, slowing of τ would result in an appreciable anomaly in the temperature dependence of $1/T_1$, as seen near 80 K; no such anomaly is observed between 250 and 325 K (Fig. 1). These two results set an upper limit of $0.001\mu_B$ on any static field component arising from Mn spin ordering between 100–325 K.

Even if there is no magnetic order above ~90 K, correlated in-plane spin fluctuations might arise in this temperature range from the 2D nature of the system. We therefore consider the anisotropy of the muon relaxation rate noted above. Because the system is axially symmetric, the relaxation rates are given by

$$(1/T_1)_a \propto \sum_{\mathbf{q}} [\delta B_a(\mathbf{q})]^2 \tau_a(\mathbf{q}) + [\delta B_c(\mathbf{q})]^2 \tau_c(\mathbf{q}) \quad (2a)$$

and

$$(1/T_1)_c \propto 2 \sum_{\mathbf{q}} [\delta B_a(\mathbf{q})]^2 \tau_a(\mathbf{q}), \quad (2b)$$

where $\delta B_\alpha(\mathbf{q})$ are the fluctuating local-field-component amplitudes in the ab plane ($\alpha = a$) and along the c axis ($\alpha = c$), $\mathbf{q}$ is the momentum of the associated excitation, and $\tau_\alpha(\mathbf{q})$ are the corresponding correlation times.

The relation $[\delta B_\alpha(\mathbf{q})]^2 \propto T[B_\alpha(\mathbf{q})]^2 \chi_\alpha(\mathbf{q})$, where $\chi_\alpha(\mathbf{q})$ is the static susceptibility for field in the α direction [17], together with Eq. (2) and the experimental anisotropy $(1/T_1)_a \simeq 2.5(1/T_1)_c$, imply that $\sum_{\mathbf{q}} [B_c(\mathbf{q})]^2 \chi_c(\mathbf{q}) \tau_c(\mathbf{q}) \simeq 4 \sum_{\mathbf{q}} [B_a(\mathbf{q})]^2 \chi_a(\mathbf{q}) \tau_a(\mathbf{q})$. The calculated dipole fields for the candidate muon sites show that $(B_{\rm dip})_c < (B_{\rm dip})_a$ for a simple model of spins fluctuating only in the ab plane. Then one needs $\sum_{\mathbf{q}} \chi_c(\mathbf{q}) \tau_c(\mathbf{q}) > 4 \sum_{\mathbf{q}} \chi_a(\mathbf{q}) \tau_a(\mathbf{q})$ to account for the experimental results. This is very unlikely if $\sum_{\mathbf{q}} \chi_c(\mathbf{q}) < \sum_{\mathbf{q}} \chi_a(\mathbf{q})$ (recall that $\chi_c(0) \ll \chi_a(0)$ [11]), because large susceptibilities are generally associated with "soft" fluctuations (long τ's).

The relaxation data therefore require significant c-axis spin fluctuations, in contradiction to the hypothesis of dominant in-plane fluctuations. Furthermore, if the muon resides near the apical O(2) site, then the calculated dipole fields account for essentially all of the anisotropy in $1/T_1$, implying isotropic spin fluctuations. Thus, from the absence of any signature of spin ordering, and from the inferred out-of-plane spin fluctuations above T_C, we find no evidence in the μSR results for 2D spin freezing or predominant ab-plane spin correlations between 90 and 300 K.

We turn to the spin-lattice relaxation data for $T \leq T_C$, noting that previous μSR experiments in $La_{0.67}Ca_{0.33}MnO_3$ [8] found a significant spatially inhomogeneous μSR rate ($K < 1$) below $T_C = 274$ K. In conventional ferromagnets muon spin relaxation below T_C occurs via a two-magnon process, with $1/T_1$ inversely proportional to the cube of the spin-wave stiffness D [18]. Thus, no significant muon relaxation would have been expected below T_C in $La_{0.67}Ca_{0.33}MnO_3$ because of the relatively large value $D \approx 155\ {\rm meV\,Å}^2$ [8], contrary to

observation. The slow and inhomogeneous spin dynamics observed in $La_{0.67}Ca_{0.33}MnO_3$ can be interpreted [19] as the signature of small magnetoelastic polarons that are localized near Ca atoms above T_C, and which retain some identity in the form of more extended but still relatively small FM clusters below T_C. Slow inhomogeneous spin fluctuations occur as the charges move (or tunnel) various distances between clusters, overturning spins in the process. These fluctuations have also been observed in quasielastic neutron scattering [9] as a "central peak" near zero energy transfer in both the 30% Ca- and Sr-doped perovskite materials.

$La_{1.4}Sr_{1.6}Mn_2O_7$ has the same nominal Mn^{4+}/Mn^{3+} ratio (about 30%) as the perovskite $La_{0.67}Ca_{0.33}MnO_3$, but *the magnitudes of the relaxation rates below T_C are strikingly different.* In the layered material the spin lattice relaxation rates drops abruptly to nearly zero within a few degrees below T_C; there is no indication of the very slow dynamics observed in the 3D perovskites. Although this result might suggest the absence of magnetoelastic polarons, such an explanation is inconsistent with the distribution of T_1 values ($K < 1$) and also with two other recent results: the observation of a polaronlike peak around 0.4 eV in the optical conductivity spectrum in $La_{1.2}Sr_{1.8}Mn_2O_7$ at low temperatures [20], and neutron pair-distribution-function evidence [21] for local structural distortions in $La_{1.4}Sr_{1.6}Mn_2O_7$ similar to those in the 3D perovskites [22].

Instead, we argue for a much larger polaron size in $La_{1.4}Sr_{1.6}Mn_2O_7$ than in the 3D perovskites. Above T_C the size of the double-exchange/Jahn-Teller-induced magnetoelastic polarons in these materials results from a balance between the kinetic energy of the Mn d-electrons and the entropic pressure from the unaligned spins outside the polaron boundary. From very general arguments one expects larger magnetoelastic polarons in the 2D layered system than in the 3D perovskites [23]. Also, the lower T_C in the layered material ($T_C \simeq 80$ K), compared to the perovskites, is more likely to result from the former's reduced dimensionality than from a reduced exchange coupling J. Once the two-layer system undergoes 3D magnetic order, the spins are likely to behave like those in the higher T_C 3D perovskite materials with a similar J. Thus, one would expect to find spin fluctuations at 70 K in $La_{1.4}Sr_{1.6}Mn_2O_7$ similar to those at 70 K (i.e., well below T_C) in the perovskite materials, where the large conductivity of the Mn t_{2g} electrons leads to very large regions of polarized spins via the double-exchange mechanism [4]. Large magnetoelastic polarons would be unlikely to undergo the slow motion or tunneling observed near T_C in the perovskites. The only remaining excitations would be spin waves, and these would have a characteristic stiffness too large to relax the muon spin. Thus the observed behavior of $1/T_1$ would be explained.

In conclusion, we find no evidence for 2D spin ordering or predominant ab-plane spin correlations in $La_{1.4}Sr_{1.6}Mn_2O_7$ above the 3D ordering transition. $La_{1.4}Sr_{1.6}Mn_2O_7$ also lacks the low-energy spin fluctuations below T_C found in the perovskites and attributed to the existence of small magnetoelastic polarons. This suggests that the polaron size in $La_{1.4}Sr_{1.6}Mn_2O_7$ is considerably larger than in the 3D perovskites, due to the reduced dimensionality of the 2-layer material.

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