Crossover from Dilute to Majority Spin Freezing in Two Leg Ladder System $Sr(Cu, Zn)_2O_3$

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Muon spin relaxation has been measured in $Sr(Cu_{1-x}Zn_x)_2O_3$. The results for low Zn concentration $x \leq 0.6\%$ are consistent with freezing of dilute moments, with one Cu spin for each Zn, having $\sim 0.5\mu_B$ frozen moment. A sharp increase of the relaxation rate at $T \rightarrow 0$ occurred with increasing x around $x \simeq 0.8\%$, accompanied by a change of line shape to that expected in a concentrated magnetic environment. Analyses of the results for $x \geq 0.8\%$ suggest that the majority of Cu moments participate in spin freezing, yet with a significantly reduced and spatially inhomogeneous moment size having a 1D correlation length $\xi \sim 6$ lattice units, or a 2D correlation area involving ~ 19 Cu spins.

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Spin ladder systems provide a topical and new research subject for the physics of strongly correlated electron systems. Even-leg ladder systems exhibit spin gaps and spin singlet ground states, whereas odd-leg ladder systems are gapless [1,2]. Spin ladders interpolate between quasi-1-dimensional (1D) and 2D systems: two leg ladders in the former limit and square lattice Heisenberg systems in the latter. Superconductivity has been observed in the hole-doped ladder/chain hybrid compound $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ under externally applied pressure [3]. Extensive experimental and theoretical studies are underway to elucidate the evolution of the gapped ground state upon dilution of the magnetic site and/or charge doping.

$SrCu_2O_3$ is a spin-1/2 two leg ladder system which has been shown to have a spin gap and a nonmagnetic ground state [4–8]. This ground state is extremely sensitive to dilution: 1.0% (Cu, Zn) substitution leads to static spin ordering with a Néel temperature $T_N \sim 3$ K [9]. Theoretical works [10–13] predict that depletion of a spin-1/2 moment from an isolated ladder gives rise to a staggered spin polarization which has a maximum next to the depletion site and falls with increasing distance. This feature would lead to a spatially inhomogeneous magnitude of the ordered moment at $T \ll T_N$. Similar behavior in a spin Peierls system was predicted by Fukuyama *et al.* [14] and was observed in experiments on $CuGeO_3$ with a dilute amount of (Cu, Zn) or (Ge, Si) substitution [15].

It is not easy, however, to experimentally study static spin correlations of $Sr(Cu, Zn)_2O_3$. Neutron measurements for elastic magnetic scattering have not been successful because (1) a strong reduction of the ordered moment size occurs for low dimensional systems with $kT_N/J \ll 1$ [16], requiring a large sample volume; and (2) it is difficult to obtain single crystal samples. A nuclear quadrupole resonance study in $Sr(Cu, Zn)_2O_3$ by Óhsugi *et al.* [17] observed a line broadening due to correlated moments. However, not much information was extracted regarding spin correlations in the ground state, since (1) the measurements were limited to $T = 1.4$ K which is above T_N for dilute samples with $x \leq 0.5\%$, and (2) the observed signal reflected only $\sim 20\%$ of Cu moments, distant from depletion sites, with other Cu sites invisible due to an excessively large hyperfine broadening.

Muon spin relaxation (μSR) is a powerful tool for studying this problem, since one can detect static internal fields from an ordered moment with a wide range of magnitude (typically from $0.005\mu_B$–$5\mu_B$), and can study spatial correlations/randomness of frozen moments by analyzing the observed local field distribution. In this Letter, we report zero-field (ZF) and longitudinal-field (LF) μSR measurements in $Sr(Cu_{1-x}Zn_x)_2O_3$. Our results reveal spin freezing of dilute Cu moments adjacent to Zn for $x \leq 0.6\%$ with the development of magnetic order involving the majority of Cu moments for $x \geq 0.8\%$.

Polycrystalline samples of $Sr(Cu, Zn)_2O_3$ were prepared as described in Ref. [9]. μSR measurements were performed at TRIUMF with a ^{4}He gas-flow cryostat and dilution refrigerator, and time evolution of muon spins was evaluated using the conventional ZF/LF μSR technique [18,19]. μSR can easily distinguish between dilute and dense moment freezing, which has important implications for this system. Static, randomly ordered, dense (dilute) moments give rise to a Gaussian [18] (Lorentzian) [20] distribution of magnetic fields in the sample. These two distributions result in very different μSR signals. In almost every sample, dipolar fields from nearby nuclei produce small, random static fields at muon sites with a Gaussian distribution. If additional static moments appear due to spin freezing, then the resulting field distribution is the convolution of the distributions from the nuclei and the additional frozen spins. For dilute spin freezing, the Lorentzian distribution is convoluted with the background

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Gaussian distribution resulting in the following muon polarization function [21]:

$$P_{\mu}^{L\circ G}(t) = \frac{1}{3} + \frac{2}{3}[1 - at - (\Delta t)^2] \times \exp\left[-at - \frac{(\Delta t)^2}{2}\right], \quad (0.1)$$

where $\frac{\Delta}{\gamma_\mu}$ and $\frac{a}{\gamma_\mu}$ are the Gaussian and Lorentzian field widths, respectively, with the muon gyromagnetic ratio $\gamma_\mu = 13.54$ MHz/kG.

If, instead of dilute moment freezing, the majority of Cu moments freeze with some small moment of uniform amplitude, then the field distribution arising from the Cu moments should also be Gaussian. Convolution of a Gaussian with a Gaussian remains Gaussian, resulting in a $P_\mu(t)$ which is the classic Gaussian Kubo-Toyabe (GKT) function [identical to Eq. (0.1) with a set to zero].

ZF and LF μSR spectra for $x \leq 0.8\%$ are shown in Fig. 1. The spectra change (decouple) with an applied longitudinal field, demonstrating that the relaxation is predominantly due to static fields. A small relaxation in LF remains even at $T = 0.05$ K, however, implying the existence of some dynamic spin fluctuations. Dynamics, coexisting independently with static fields, would result in an overall relaxation. We fit LF spectra with a slowly decaying exponential function to estimate the dynamic contribution, and multiply that to static relaxation functions when fitting the ZF spectra. Dynamics account for $\sim\frac{1}{3}$ $(\leq\frac{1}{10})$ of the total relaxation in the $x = 0.3\%$ $(x \geq 0.6\%)$ sample.

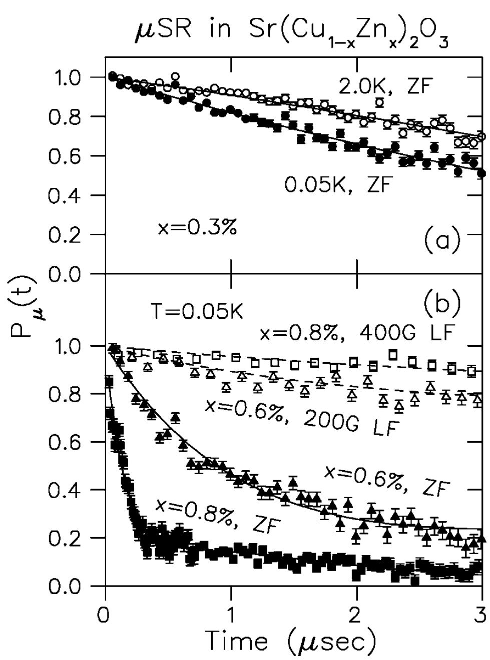

FIG. 1. (a) ZF μSR spectra of $Sr(Cu_{1-x}Zn_x)_2O_3$ with $x = 0.3\%$ at $T = 2.0$ K and $T = 0.05$ K. (b) ZF and LF μSR spectra with $x = 0.6\%$, 0.8% at $T = 0.05$ K. Solid lines on the data are fits using Eq. (0.1) as described in the text, and dashed lines are fits to exponentials.

Thus, we confine the following argument to static relaxation processes.

The spectra below T_N for $x = 0.3\%$ and 0.6% do not fit well to the GKT function, but do fit well to Eq. (0.1). This implies freezing of dilute moments in these low Zn concentration samples. Δ (for nuclear dipolar fields) is obtained from the results above T_N, and then fixed for all other temperatures while a is allowed to vary, reflecting the temperature dependence of the Lorentzian width.

The spectra from $x = 0.8\%$ do not fit as well to Eq. (0.1) as those for $x = 0.3\%$ and 0.6% samples, implying a change in the distribution of internal fields. For dilute frozen moments, $P_\mu(t)$ appears exponential at an early time [19]. The early time $P_\mu(t)$ for samples with $x \geq 1\%$ is closer to a Gaussian, suggesting freezing of moments dense in space. However, the spectra for $x \geq 1\%$ lack a key feature of the expected $P_\mu(t)$ arising from Gaussian fields, namely, a deep dip below $1/3$ of the initial polarization and then recovery to $1/3$.

In an empirical attempt to reproduce the observed line shape by some analytic function, we considered an exponential *distribution* of fields:

$$\rho^{\exp}(H_i) = \frac{\gamma_\mu}{2a} e^{-|\frac{\gamma_\mu H_i}{a}|}, \qquad i = x, y, z \quad (0.2)$$

resulting in the muon polarization function [21]:

$$P_\mu^{\exp}(t) = \frac{1}{3} + \frac{2}{3}\left\{\frac{1 - (at)^2}{(1 + (at)^2)^2}\right\}. \quad (0.3)$$

This relaxation function has Gaussian early time behavior, but much less dip below $1/3$ than the GKT function.

In Fig. 2 we show ZF μSR spectra from the $x = 2\%$ sample at $T = 2.5$ K, along with a fit to Eq. (0.3) (after taking into account dynamic effects and the nuclear dipolar background). This new function does fit the data fairly well for $x \geq 1\%$, which suggests that, at the least, it can be used as a good parametrization of the field width a.

Figure 3 shows the temperature dependence of the static relaxation rate a and corresponding field width for all samples. For $x = 0.8\%$, we include results from fits using both functions, Eqs. (0.1) and (0.3), for Lorentzian and exponential field distributions. These fits yield very similar field widths and χ^2. The results of $a(T)$ in Fig. 3 for all samples have been fit to a phenomenological function $a(T) = a_0[1 - (\frac{T}{T_N})^n]^m$ for $T < T_N$ with $n = 2.1$ and $m = 0.8$.

Figures 4(a) and 4(b) show the resulting $a_0 = a(T \to 0)$ and T_N as a function of Zn concentration x. The relaxation rate a_0 exhibits a rapid, nonlinear increase with x up to $\sim$0.8%. For $0.8\% < x < 2\%$, a_0 continues to increase, but perhaps linearly, and there is a saturation in the field width for $x > 2\%$. The values of a_0 for $x \leq 0.6\%$ are consistent with a picture of a single Cu moment adjacent to the depletion Zn site which acquires an ordered moment of $\sim 0.5\mu_B$ and freezes with a random direction like a dilute alloy spin glass [19], while the majority of

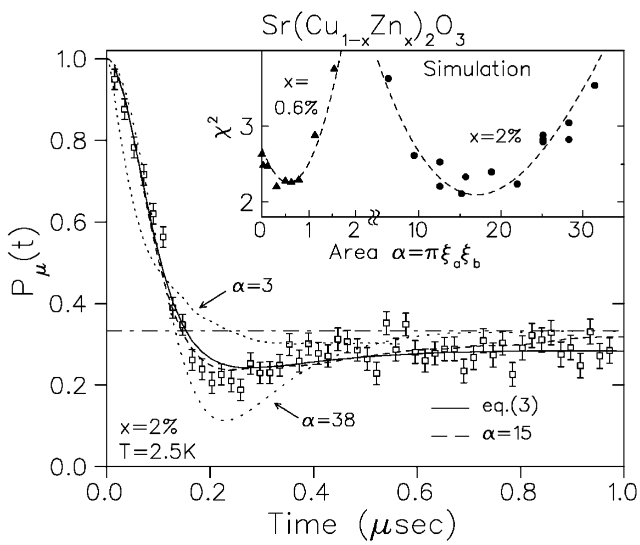

FIG. 2. $P_\mu(t)$ for $x = 2\%$ at $T = 2.5$ K. The solid line is the fit using Eq. (0.3). Simulated spectra are shown for the correlated area $\pi\xi_a\xi_b \equiv \alpha = 3$, 15, and 38, with maximum moment size $M_0 = 0.87$, 0.20, and $0.13\mu_B$, respectively. The inset shows χ^2 between simulation and observed spectra vs α for $x = 0.6\%$ and $x = 2\%$ samples.

Cu moments remain in a nonmagnetic singlet state. The jump of a_0 near $x \sim 0.8\%$, together with the qualitative change of the line shape, indicates that static order develops among the majority of Cu spins for $x \geq 0.8\%$. Unlike a_0, T_N does not show a dramatic change near $x = 0.8\%$, consistent with previously reported results [9].

To obtain more quantitative information concerning the distribution of moments near a dilution site, we simulated μSR results assuming maximum moment size M_0 next

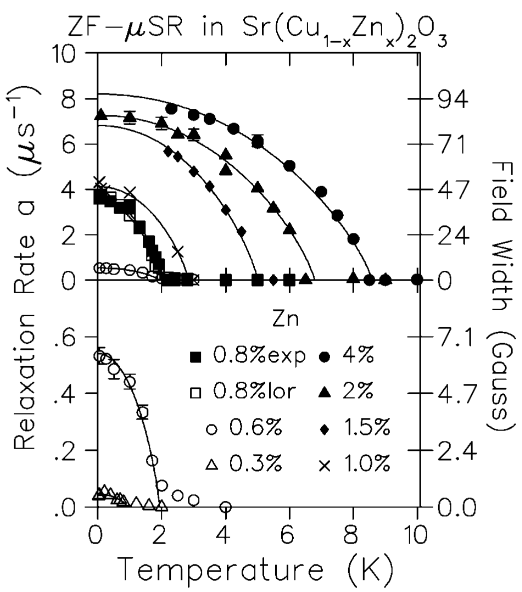

FIG. 3. Lorentzian ($x \leq 0.8\%$) or exponential ($x \geq 0.8\%$) field width as a function of temperature. Solid lines are fits to the function described in text.

to the dilution site, and an exponential decrease of the staggered frozen moment size, as

$$M(i,j) = (-1)^{i+j} M_0 \exp\left\{-\sqrt{\left(\frac{x_i}{d_a\xi_a}\right)^2 + \left(\frac{y_j}{d_b\xi_b}\right)^2}\right\},$$

where ξ_a, ξ_b denote the correlation length parallel and perpendicular (in plane), respectively, to the ladder, and d_a, d_b are the Cu-Cu leg and rung spacing, respectively ($d_a \approx d_b$).

We assume antiferromagnetic correlations within a cluster and a random direction for the overall spin axis of the cluster. This assumed moment distribution is elliptical, and ξ_b was kept smaller than ξ_a. $\xi_b = 1$ represents the case with a correlation almost entirely along a ladder. We consider in the simulation both 1D and 2D cases for the following reasons. First, ladders are assumed to be isolated from one another due to a frustrated interladder interaction. This frustration is somewhat resolved if there is an inhomogeneous moment distribution on a neighboring ladder.

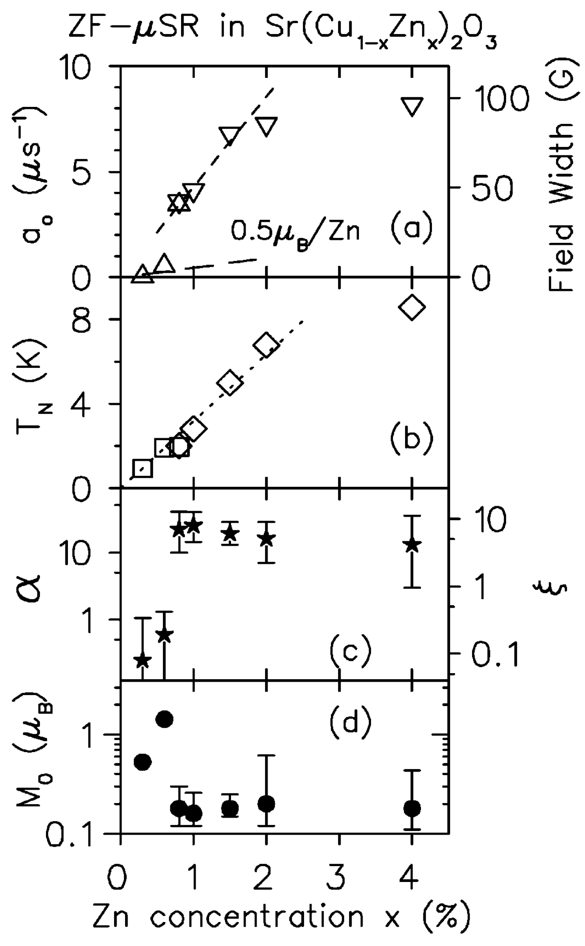

FIG. 4. (a) $T \to 0$ K relaxation rate a_0 vs Zn concentration x. The long-dashed line is the simulation result for $0.5\mu_B$ moment for each Zn with $\xi = 0$. (b) T_N vs x. The triangles and squares (upside-down triangles and diamonds) represent fits assuming a Lorentzian (exponential) distribution of fields. (c) Simulation results for the correlation area $\alpha = \pi\xi_a\xi_b$, and (d) the size of the maximum moment M_0 near the Zn site.

Second, it is difficult to understand how the samples with very dilute Zn concentration can exhibit spin freezing in a purely 1D case. Introducing the second dimension reduces the effective average Zn-Zn spacing.

We assume dipolar coupling to the muon. Muon sites were obtained by assuming a 1 Å μ-O bond length, and then finding the electrostatic minima on that sphere. Three equivalent sites were found (two on the chain O and one on the rung O), and simulation results for the three sites were averaged before being compared to the observed spectra. We found that $P_\mu^{\rm sim}(t)$ was not sensitive to the anisotropy ξ_a/ξ_b, but rather to the total "area" of moments created by each dilution site. We define the correlation area $\alpha \equiv \pi \xi_a \xi_b$, within which the moment size is larger than $M_0 e^{-1}$. If we assume $\xi_b = 1$, the correlation along the ladder $\xi = \frac{\alpha}{\pi}$. Within this simplified model, the functional form of $P_\mu^{\rm sim}(t)$ is determined predominantly by the correlation area α and the concentration x. M_0, the maximum moment size, provides an overall scaling in time.

Simulated μSR data for $x = 2\%$ and $\alpha = 3$, 15, and 38 are shown in Fig. 2. M_0 are chosen which minimize χ^2 between the simulation and observed spectra. The analytic (solid line) and simulation spectra almost overlap each other for $\alpha = 15$. This figure demonstrates (1) a line shape very close to that for an exponential field distribution can actually be expected for the spatial variation of ordered moments assumed in the present simulation; and (2) one can clearly distinguish different sizes of the correlation area by comparing the simulation and the data. In the inset, we also show χ^2 as a function of α for $x = 0.6\%$ and 2%. The scatter in χ^2 arises from different choices of ξ_a and ξ_b which result in the same or similar α. The scatter is small compared to the effect of changing α, and so we cannot resolve an anisotropy.

The set of α and M_0 was obtained by minimizing χ^2 between simulated and real data. Figures 4(c) and 4(d) show such results for $x \leq 4\%$. ξ (α) is very small for $x = 0.3\%$ and 0.6%, consistent with our earlier conclusion of freezing of dilute moments. ξ (α) jumps to about 7 (22) for $x = 0.8\%$, and decreases weakly with x at $x \geq 0.8\%$, suggesting a sudden increase of the Cu spin population participating in static spin freezing. The moment size M_0 decreases to about $\sim 0.2\mu_B$ for $x \geq 0.8\%$: those majority Cu moments freeze with a significantly reduced moment size, presumably due to quantum fluctuations, reminiscent of the case observed in low dimensional Heisenberg spin chains with reduced kT_N/J [16]. Our results of $\xi \sim 6$ ($\alpha \sim 19$) for $x \geq 0.8\%$ represent the first experimental estimate available at $T \ll T_N$. The order of magnitude is comparable to the correlation length estimated from the NMR line shape well above T_N [17].

For $x < 0.8\%$, we find a qualitatively different spin correlation with $\xi \rightarrow 0$–1. In this very dilute region, NMR results [17,22] of the Knight shift have been interpreted to indicate a very long correlation length $\xi \geq 20$ at $T \gg T_N$. It is not clear how such a long correlation length can be reconciled with the much shorter ξ in theoretical calculations [12] as well as with our results at $T \ll T_N$. In the inelastic neutron scattering study at $T = 10$ K by Azuma *et al.* [8], a clear peak indicating the persistence of the spin gap has been found for $x = 0.3\%$. This feature is consistent with our results, which indicate that the majority of Cu moments are still in the singlet state in the dilute region.

The observed change at $x_c \sim 0.8\%$ may be related to a percolation phenomenon. If we consider decay of the static moment size to e^{-2} of the largest Cu moment near Zn, the effective size of the correlated area becomes 4α, and the product $x_c \times 4\alpha$ becomes of order unity. For $x \geq x_c$, our results support the Fukuyama picture, and participation of the majority of Cu moments in spin freezing. The results at $x \leq x_c$ suggest a freezing of almost isolated Cu spins. The mechanism for this behavior and the reason for a smooth change of T_N near x_c are to be clarified by further studies.

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