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Impurity-induced singlet breaking in $SrCu_2(BO_3)_2$

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We have performed muon spin relaxation (μSR) studies on single crystals of $SrCu_2(BO_3)_2$, a quasi-two-dimensional spin system with a spin-singlet ground state. We find evidence for two different muon sites which we associate with muons located adjacent to the two inequivalent O sites. One site, presumably located in the Cu-O-Cu superexchange path, exhibits a large increase in the frequency shift with decreasing temperature which is unaffected by the onset of the singlet ground state, indicating that the muon has perturbed the Cu-Cu interaction and created two quasifree spins. We have also performed μSR on single crystals of $SrMg_{0.05}Cu_{1.95}(BO_3)_2$, $Sr_{0.96}La_{0.04}Cu_2(BO_3)_2$, and $Sr_{0.95}Na_{0.05}Cu_2(BO_3)_2$. We have found that the frequency shifts of these doped samples are equivalent and contain three branches at low temperatures. Two of these branches map onto the branches observed in the pure sample, and so we attribute the third branch to a dopant effect. Specifically, this third branch represents the case when the muon resides at a site in the superexchange path where a local singlet cannot form due to doping. This leads to the conclusion that doping this system both in and out of the $CuBO_3$ planes prevents the formation of some singlets.

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I. INTRODUCTION

Low-dimensional spin systems with spin-singlet ground states have attracted considerable study over the past 15 years. These systems are interesting for a number of reasons, including possible relevance to high-temperature superconductivity and the existence of novel ground states. Most of the systems studied to date have been limited to quasi-one-dimension. These include spin ladder systems [e.g., $SrCu_2O_3$ (Ref. 1)], spin-Peierls systems [e.g., $CuGeO_3$ (Ref. 2)], and Haldane gap systems [e.g., Y_2BaNiO_5 (Ref. 3)]. These materials all have a spin gap in the energy spectrum, which is associated with the spin-singlet ground states. Theoretical studies of spin ladders[4] have predicted d-wave superconductivity at low concentrations of hole doping in these systems. In fact, the mixed ladder-chain system $Sr_{14-x}Ca_xCu_{24}O_{41}$ has been found to be a superconductor under pressure, specifically in the cases of $x=13.6$ (Ref. 5) and $x=11.5$ (Ref. 6) with the superconductivity thought to originate in the ladder layers. High-T_c cuprates have d-wave superconducting states and a partial spin (or pseudospin) gap, which provides further evidence for strong similiarities between doped ladders and doped CuO_2 planes and motivates study of the effects of perturbing spin gap systems.

Two-dimensional (2D) systems with spin-singlet ground states are comparatively rare and often involve lattices where the active spins have a small number of nearest neighbors. One example is CaV_4O_9,[7] where the depleted square lattice consists of plaquettes of four spins coupled to neighboring plaquettes through one vertex. $SrCu_2(BO_3)_2$ is another quasi-two-dimensional spin system with a spin-singlet ground state.[8] The unit cell is tetragonal and the structure is characterized by layers consisting of Cu^{2+}, O^{2-}, and B^{3+} running perpendicular to the c axis. These layers are separated from each other by planes composed of Sr^{2+} ions. All Cu^{2+} sites have localized spin $S=1/2$ moments and one nearest neighbor with which they form dimeric units, while each of these units is surrounded by four orthogonal dimers. This configuration of spins corresponds to the two-dimensional model that Shastry and Sutherland first introduced in 1981.[9] This model is topologically equivalent to a two-dimensional Heisenberg model with nearest-neighbor coupling J and next-nearest-neighbor coupling J'. With decreasing J'/J, a phase transition from a four-sublattice Néel state to a gapped spin-singlet state was shown to take place at a critical value of $J'/J\sim0.7$. The ratio of J'/J in $SrCu_2(BO_3)_2$ is about 0.68, a little bit smaller than the critical value.[10] High-resolution inelastic neutron measurements[11] have identified one-, two-, and three-triplet excitations. These measurements clearly show the appearance of the energy gap in the spectrum of excitations with decreasing temperature, and from them the energy gap is evaluated to be $\sim$34 K. The one- and two-triplet excitations both display a very large drop-off in inelastic intensity with increasing temperature. This temperature dependence is generally not seen in a system undergoing a phase transition, and no evidence of symmetry breaking has been associated with the appearance of the spin-singlet ground state. Another interesting feature of this system is the magnetization plateaus that are observed at 1/8, 1/4 (Ref. 8), and 1/3 (Ref. 12) of the saturation magnetization in high magnetic fields (>20 T). This is the first 2D system where these plateaus have been observed.

While superconductivity has been predicted and observed in some quasi-one-dimensional systems with a spin-singlet ground state, it has also been predicted in the doped Shastry-Sutherland model.[13–15] Liu *et al.* have recently investigated a series of polycrystalline $SrCu_2(BO_3)_2$ samples, with dopants added both in[16] and out[10] of the $CuBO_3$ planes. They found that the spin gap behavior was strongly affected by doping, but did not find any evidence for superconductivity. The resistivity of the pure sample at room temperature was found to be 41.73 M Ωm,[10] and the resistivity of all doped samples was found to be only one or two orders of magnitude smaller. This implies that all their samples were insulators and that the carriers introduced as a result of doping were not very mobile, at least at room temperature. However, the theoretical predictions discussed above help to emphasize the importance of better understanding Shastry-Sutherland systems such as $SrCu_2(BO_3)_2$ and their response to perturbations.

Muon spin relaxation (μSR) measurements of a spin-singlet state give a signal characteristic of a nonmagnetic state. Zero-field measurements[17] of the spin-Peierls system $CuGeO_3$ gave essentially a temperature-independent signal, with weak relaxation being ascribed to isolated defects associated with impurities. In the case of $SrCu_2(BO_3)_2$, Fukaya *et al.*[18] reported zero-field (ZF) and longitudinal-field (LF) μSR measurements of ceramic specimens. In contrast to their expectations of seeing no spin relaxation associated with this state, the authors reported the onset of a large, roughly constant relaxation for temperatures of 3 K and below. They attributed this relaxation to dilute defects or to μSR detecting weak intrinsic magnetism that other probes could not see. The authors also reported that dynamic fluctuations persisted in the system down to a base temperature (20 mK) and that these fluctuations likely have a quantum origin.

Lappas *et al.* also investigated ceramic samples of $SrCu_2(BO_3)_2$ using the μSR technique.[19] The authors reported the same anomalous relaxation in ZF as observed by Fukaya *et al.* using a different batch of samples. They attributed this relaxation to an unusual spin-freezing process. The authors went on to perform 0.6-T frequency shift measurements on their samples. They concluded that implanted muons may liberate spin density in the spin gap regime that spin freezes at very low temperatures.

II. EXPERIMENTAL DETAILS

We grew single crystals of $SrCu_2(BO_3)_2$, $SrMg_{0.05}Cu_{1.95}(BO_3)_2$, $Sr_{0.96}La_{0.04}Cu_2(BO_3)_2$, and $Sr_{0.95}Na_{0.05}Cu_2(BO_3)_2$ in floating zone image furnaces at Tokyo[20] and McMaster[21] Universities following slightly different procedures. Neutron-scattering measurements have been reported by Haravifard *et al.*[22] on the system $SrMg_{0.05}Cu_{1.95}(BO_3)_2$. Aside from the original crystal growth article,[21] this seems to be the only paper describing doped single crystals of this system as they have proven to be quite difficult to grow.

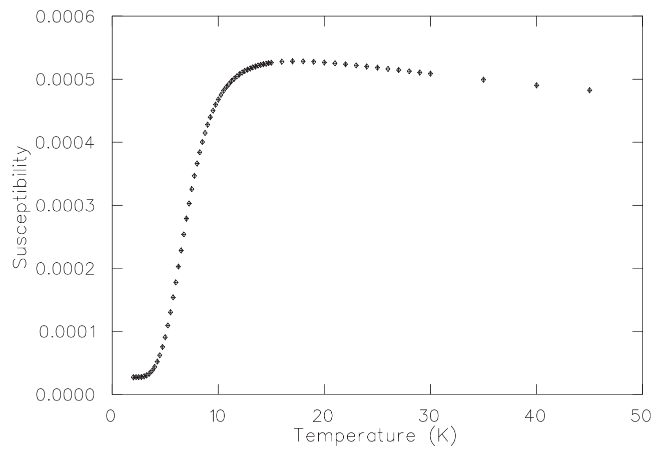

FIG. 1. dc volume susceptibility of single-crystal $SrCu_2(BO_3)_2$, measured in an applied magnetic field $H=5$ T$\parallel\hat{c}$.

The dc susceptibility measurements of a McMaster crystal of $SrCu_2(BO_3)_2$ in a field of 5 T parallel to the c axis are shown in Fig. 1; the results for the Tokyo crystals are essentially identical. There is a sharp decrease in the susceptibility below 15 K which provides evidence for the spin-singlet ground state. A small upturn is seen in the susceptibility curve below 4 K, which likely arises due to magnetic impurities and/or defects of Cu^{2+} ions in $SrCu_2(BO_3)_2$. The susceptibility data below 7.5 K were fit to the following functional form:

$$\chi = C/T + Be^{-\Delta/T} + \chi_0. \tag{1}$$

The first Curie term is due to the contribution of magnetic impurities, the second term is to account for the spin gap, and the third temperature-independent term accounts for Van Vleck paramagnetism and core diamagnetism. The spin gap Δ was found to be ~20.2(7) K in our field of 5 T, which is in line with other reported estimates. If we ascribe the Curie term to free Cu spins, then this concentration would be only 0.12(4)%.

We performed 5-T transverse-field (TF) μSR measurements on pure and doped $SrCu_2(BO_3)_2$ samples to investigate the presumed nonmagnetic spin-singlet ground states in these systems. These measurements were conducted on the M15 surface muon channel at TRIUMF in Vancouver, Canada, using a helium gas flow cryostat in the temperature range 2 K$<T<$150 K. The samples were mounted in a low-background spectrometer with the c axis parallel to the incoming muon momentum (and the external field). In this high-field experiment, the measurements of the muon precession frequency signal in our samples and a reference material ($CaCO_3$) were taken simultaneously to allow for a precise determination of the frequency shift.

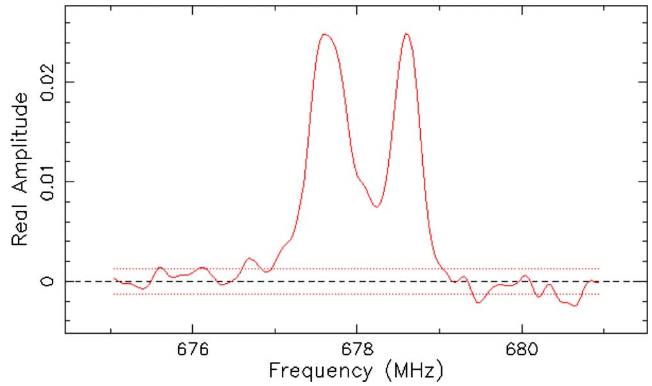

FIG. 2. (Color online) Fast Fourier transform of the muon precession signal for $SrCu_2(BO_3)_2$ measured in an applied magnetic field $H=5$ T$\|\hat{c}$ at 20 K. The two peaks correspond to two magnetically inequivalent muon sites.

In addition, we performed ZF-μSR and low TF-μSR measurements ($H<1$ T) on the pure sample. After observing the anomalous relaxation previously seen by Fukaya *et al.*[18] in the powder sample, we performed LF-μSR measurements on our single crystal to characterize the nature of this relaxation. For these low-temperature measurements (between 20 mK and 10 K), we used an Oxford Instruments dilution refrigerator on the M15 beamline. The sample was mounted on a silver sample holder, with the c axis parallel to the incoming muon beam, as in the case of the high-TF measurements.

III. DISCUSSION AND ANALYSIS

Implanted positive muons reside at sites which are minima in the electrostatic potential. Generally, in oxides, muons are hydrogen bonded to O^{2-} ions, roughly 1 Å away.[23–25] Figure 2 shows a fast Fourier transform of the transverse-field muon precession signal measured in an applied magnetic field $H=5$ T$\|\hat{c}$ at $T=20$ K. Two peaks are clearly visible which correspond to two magnetically inequivalent muon sites in $SrCu_2(BO_3)_2$; we associate these with the two magnetically inequivalent oxygen sites in the system. From a simple electrostatic calculation treating all the ions as point charges and assuming a muon-oxygen distance of 1 Å, we have determined the most probable muon-stopping site associated with each O type. The results are shown in Fig. 3. To take these two sites into account, we tried to fit these 5-T TF data to the sum of two damped cosine functions. We considered the cases of both exponential and Gaussian relaxation, and since the latter yielded consistently higher χ^2 values, we adopted the former for all of our fits. Our exact fitting function is given by

$$A(t) = A_1 e^{-\lambda_1 t}\cos(\omega_1 t + \phi_1) + A_2 e^{-\lambda_2 t}\cos(\omega_2 t + \phi_2), \quad (2)$$

where ω_1 and ω_2 are the average muon precession frequencies, λ_1 and λ_2 are the muon relaxation rates for the two sites, and A_1 and A_2 are the initial asymmetries. The ratio of A_1 and A_2 was found to be $\sim 3:2$, with more muons stopping at the site out of the superexchange path. Barring an accidental degeneracy there should only be one true stable muon-stopping site in a material, so the second muon site we observe may be a metastable site that is long lived in the time range of our experiment.

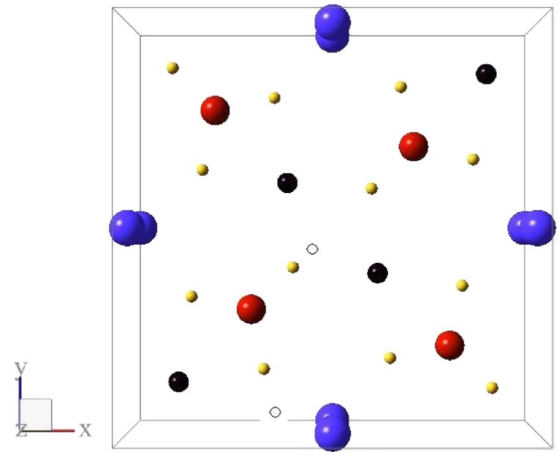

FIG. 3. (Color online) The bottom half of the unit cell of $SrCu_2(BO_3)_2$ viewed along $\hat{c}$. Listed in order of decreasing size, the ions correspond to Sr^{2+} (blue), B^{3+} (red), Cu^{2+} (black), and O^{2-} (yellow). The most probable muon-stopping sites 1 Å from each O type are indicated by open circles. These sites have fractional coordinates of (0.34, 0.04, 0.25) and (0.44, 0.44, 0.08). Symmetry-related equivalent sites (one per O) are not shown.

The frequency shift is the fractional difference between the applied field and the local field at the muon site, and it is proportional to the local spin susceptibility. We see that for one of the muon sites the frequency shift roughly follows a Curie-Weiss temperature dependence for $T>4$ K [represented by the crosses in Fig. 4(a)], with the precise value of

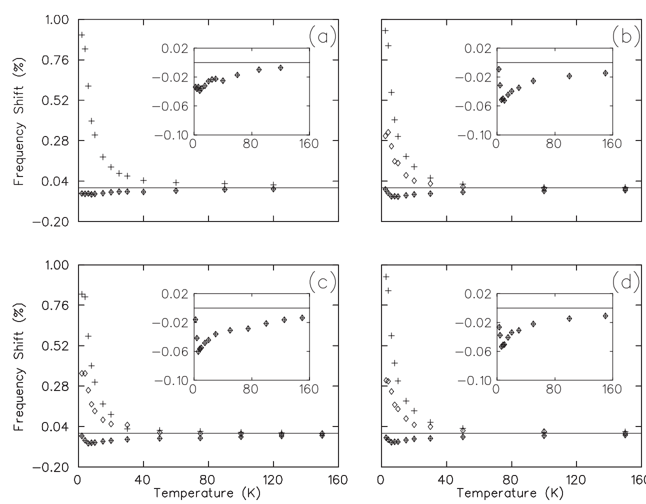

FIG. 4. Frequency shifts vs. temperature measured in an applied field of 5 T for (a) $SrCu_2(BO_3)_2$, (b) $Sr_{0.96}La_{0.04}Cu_2(BO_3)_2$, (c) $SrMg_{0.05}Cu_{1.95}(BO_3)_2$, and (d) $Sr_{0.95}Na_{0.05}Cu_2(BO_3)_2$. The insets show the temperature dependence of the frequency shift for the muon site outside of the superexchange path.

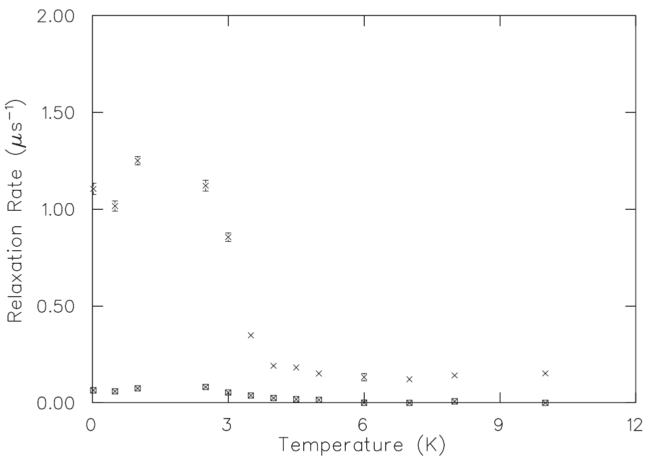

FIG. 5. Exponential relaxation rates vs temperature for zero applied field in $SrCu_2(BO_3)_2$.

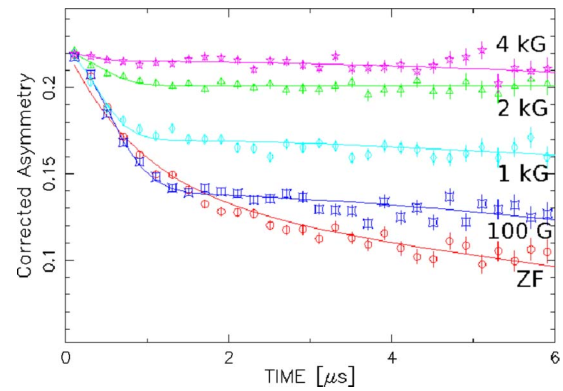

FIG. 6. (Color online) LF-μSR line shapes for selected applied fields at 20 mK. There is significant relaxation even in the case of 2 kG. The lines are a guide for the eye.

the Curie constant depending on the temperature range being fit. This is in contrast to ^{11}B NMR frequency shift measurements.[26] In that case, the authors applied a field of 7 T perpendicular to the $[1\,{-1}\,0]$ direction and observed a decrease in the frequency shift below the onset of the singlet ground state. The lack of a similar decrease in our μ^+ frequency shift for this site indicates the presence of a larger local field than expected in the singlet ground-state regime. If we associate this muon site with the oxygen site in the Cu-O-Cu superexchange path, then a possible explanation for this is that the muon perturbs the system and essentially removes the interaction between the two neighboring Cu spins. Since this perturbation affects the Cu spin dynamics even before the singlet state is the only existing state, we begin to see an increase in the frequency shift for this site well before the singlet ground-state sets in. We do not observe a decrease in the shift after entering the singlet ground-state regime because the lack of a nearest-neighbor Cu-Cu interaction means a local singlet can no longer form. Instead, we now have two quasifree spins in close proximity to the muon site.

The shift at the other muon site is considerably smaller and negative [see inset of Fig. 4(a)]. In this case, the frequency shift follows the temperature dependence of the bulk susceptibility reasonably well, indicating the lack of any strong muon perturbation. For this reason, this site likely corresponds to the O^{2-} ion out of the Cu-O-Cu superexchange path.

Motivated by the discovery of the two muon sites in $SrCu_2(BO_3)_2$, we fit the ZF-μSR data to the sum of two terms, each taken to be the product of an exponential and a static Gaussian Kubo-Toyabe relaxation function. The Gaussian Kubo-Toyabe part represents relaxation due to nuclear moments that are oriented randomly in ZF. This is generally a temperature-independent contribution to the relaxation and this was assumed in this case by fixing the Gaussian Kubo-Toyabe relaxation rates. The ratio of the asymmetries of the two sites was fixed to the value obtained when fitting the high-TF data. Figure 5 shows that the exponential relaxation of one site is roughly independent of temperature for $T > 4$ K, then rises sharply at 4 K, and saturates for temperatures of 3 K and below. The other site has a very small, almost temperature-independent relaxation. The large increase and saturation of the exponential relaxation for the one muon site at low temperatures may imply slowing down or freezing of the spins liberated by the muon perturbation effect as previously suggested by Lappas *et al.*[19]

To see if this was a suitable description, it was necessary to examine LF-μSR data taken below the saturation temperature, specifically at 20 mK in this case (Fig. 6). Values of $\sim$1 G and 13 G were estimated for the local fields at the two muon sites from the ZF time spectrum at $T=20$ mK using the relation $B \sim \lambda/\gamma_\mu$ ($\gamma_\mu = 135.5 \times 2\pi$ MHz/T) with λ representing the muon relaxation rate as before. Assuming these local fields are static, a comparable LF (up to one order of magnitude larger) should be enough to completely decouple them. However, we are still seeing significant relaxation even in the case of LF=2 kG. This implies that the spins are dynamic in the low-temperature regime and their behavior cannot be described by spin freezing. These spin fluctuations are fast for $T > 4$ K and then slow down substantially below $T \sim 4$ K. The saturation of the relaxation at the low temperatures suggests that these fluctuations are not thermal but instead have a quantum origin. This is in agreement with what Fukaya *et al.* reported on in the case of ceramic samples.[18] If the LF spectra are examined closely at early times, it becomes clear that they have a distinct Gaussian nature. In general, dynamic spin fluctuations cannot be described by a Gaussian line shape. This appears to be one of the rare cases of undecouplable Gaussian behavior in μSR studies, which is still poorly understood. Such behavior has been previously observed in frustrated and/or low-dimensional systems.[27,28]

Figure 7 shows a fast Fourier transform (FFT) of the transverse-field muon precession signal measured in an applied magnetic field $H = 5$ T$\parallel \hat{c}$ at $T = 20$ K for $SrMg_{0.05}Cu_{1.95}(BO_3)_2$. Similar FFTs were obtained for the La- and Na-doped samples. There are clearly three frequency peaks in this case as opposed to the two that were seen in the FFT of the pure sample. For this reason, the data were fit to the same functional form as given by Eq. (2), but three exponentially damped cosine terms were included instead of

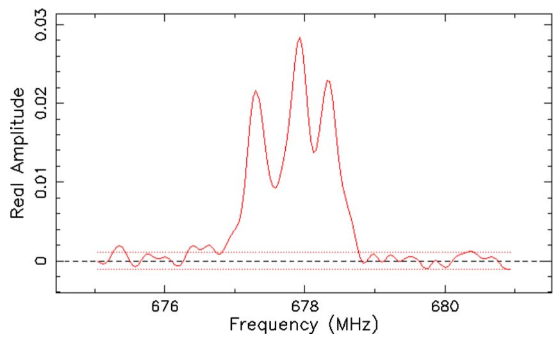

FIG. 7. (Color online) Fast Fourier transform of the precession signal for $SrMg_{0.05}Cu_{1.95}(BO_3)_2$ measured in an applied magnetic field $H=5$ T$\|\hat{c}$ at 20 K. There are now three peaks instead of two; the third peak is due to the Mg^{2+} ions.

two. The frequency shifts calculated from these fits are given in Figs. 4(b)–4(d); the shifts for all three doped samples examined appear to be essentially equivalent. The upper and lower branches are remarkably similar to the two branches in the pure case, but the middle branch is new and so it seems is associated with the dopants.

In one situation, we are substituting nonmagnetic Mg in for the Cu sites. This should prevent some singlets from forming, as not all Cu spins have a nearest-neighbor Cu any longer. In the other two cases, we are substituting La or Na for the Sr sites. These are both forms of charge doping, with each La introducing one electron into our system and each Na introducing one hole. Each electron or hole introduced by doping is expected to prevent the formation of one singlet and make a localized spin 1/2. Resistivity measurements performed by Liu *et al.*[10] on La- and Na-doped polycrystalline samples verify the localized nature of these carriers. The prevention of some singlet formation by the different dopants is supported by dc susceptibility measurements performed on our single crystals with an applied field $H=1$ kG$\|ab$ plane.[21] All three doped samples had much larger Curie tails than the pure sample, indicating the presence of many more free spin-1/2 Cu's in the singlet regime. We have calculated the spin gap, Curie constant, and the resulting fraction of free spins by fitting this data to Eq. (1); the results are shown in Table I. In all the doped cases, the spin gap has been supressed. Also, the fraction of free spins is at least 5 times as great as in the pure case, but still lower than what we expect considering the concentration of our starting materials. This is likely due to difficulties involved in doping this system and suggests that our doping concentrations should be viewed as nominal values.

TABLE I. Estimated spin gaps, Curie constants, and fraction of free Cu spins by fitting susceptibility data with $H=1$ kG$\|$ab plane.

Sample	Spin gap (K)	Curie constant (K)	Estimated fraction of free Cu spins (%)
$SrCu_2(BO_3)_2$	27.8(8)	$3.4\times10^{-5}(8)$	0.0585(1)
$SrMg_{0.05}Cu_{1.95}(BO_3)_2$	20.4(6)	$5.5\times10^{-4}(1)$	0.95(2)
$Sr_{0.96}La_{0.04}Cu_2(BO_3)_2$	23.2(6)	$3.09\times10^{-4}(1)$	0.53(2)
$Sr_{0.95}Na_{0.05}Cu_2(BO_3)_2$	24.4(5)	$1.67\times10^{-4}(1)$	0.29(2)

Our μSR results complement the susceptibility measurements by providing microscopic evidence that some singlet formation is prevented in this system when doping both in and out of the $CuBO_3$ planes. There appear to be three distinct possibilities for muons in the doped samples. The muon can either stop at the sites in or out of the superexchange path as before. If the muon stops at the site in the superexchange path, it will perturb the Cu-Cu interaction and create two quasifree spins in close proximity. However, in some cases the formation of a local singlet will have already been prevented as a result of doping. In this case, the muon will only be in close proximity to one quasifree spin and so a smaller frequency shift will be measured with decreasing temperature, giving us the middle branch. In fact, Figs. 4(b)–4(d) show that this middle branch gives about half the shift of the upper branch.

IV. CONCLUSION

We determined there are two different muon sites in $SrCu_2(BO_3)_2$, which we associate with muons located adjacent to the two inequivalent O sites in the system. One site exhibits a large increase in the frequency shift with decreasing temperature that is unaffected by the onset of the singlet ground state, indicating that the muon resides in the Cu-O-Cu superexchange path and has essentially removed the interaction between the two neighboring Cu spins, thus preventing the formation of a local singlet. The frequency shift of the other site is considerably smaller and negative. It roughly scales with the dc bulk susceptibility, indicating the lack of a strong perturbation effect in this case.

We also observe a large relaxation increase for the site in the superexchange path in the singlet regime, which is in contrast to the weak, practically temperature-independent relaxation expected in such a state. Analysis of LF-μSR data has shown that this relaxation is likely due to slow but dynamic fluctuations of the liberated spins that persist down to our base temperature of 20 mK.

Finally, all three doped samples studied have remarkably similar frequency shifts. In each case, there are now three branches at low temperatures instead of two as observed in the pure sample. The upper and lower branches map on to the two branches in the pure sample very well, and so the third branch is attributed to the dopants. Specifically, this third branch represents the case when the muon resides at a site in the superexchange path where a local singlet cannot form as a result of doping. Our results demonstrate that electron or hole doping of $SrCu_2(BO_3)_2$ by substituting on the Sr site gives the same result as substitution of Cu by nonmagnetic Mg: namely, the prevention of a local singlet from forming and the liberation of a single Cu spin. We find that the number of free spins is significantly less than expected from the nominal dopant concentration and that reaching doping levels sufficient for metallic (and superconducting) behavior may be difficult in this system.

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