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Spin-freezing in the two-dimensional spin-gap systems $SrCu_{2-x}Mg_x(BO_3)_2$ ($x = 0, 0.04, 0.12$)

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Abstract

The magnetic properties of the two-dimensional dimer spin-gap system $SrCu_2(BO_3)_2$ were investigated by the μ^+SR technique. The relatively slow fluctuations of spin-dimers slow down with decreasing temperature and an unusual spin-freezing process is unraveled at $T_f < 3.75$ K, well within the spin-gap temperature range ($T_{SG} \approx 20$ K). This quasi-static phase displays a Gaussian field distribution with a remarkable stability with applied longitudinal fields. In support of the criticality of the $SrCu_2(BO_3)_2$ spin-gap ground state towards an antiferromagnetic transition, Knight-shift measurements suggest that implanted muons may liberate spin density at $T < T_{SG}$ that undergoes spin-freezing at very low temperatures. On the other hand, non-magnetic impurity-doping of the copper sublattice does not suppress the spin-gap ground state and does not lead to magnetic ordering effects of static nature.

Keywords: Low-dimensional solids; Spin gap; Knight shift

Recent years have seen a great deal of research exploring complicated quantum mechanical phenomena associated with the mechanism of high-T_c superconductivity in two-dimensional (2D) copper oxides. Prominent features of these systems include the presence of a pseudo-gap and its evolution with doping [1]. Low-dimensional chemical analogues of the cuprates with spin-gap ground states offer opportunities to study prototypical systems with unconventional low-temperature behavior.

$SrCu_2(BO_3)_2$ is a spin-gap ($\Delta \approx 30$ K) system [2] in which the Cu^{2+} ions form a 2D network of rectangular CuO_4 units with triangular BO_3 group connectivity [3]. Nearest-neighbor Cu^{2+} ($S = 1/2$) ions form dimers ($d \approx 2.90$ Å), arranged orthogonally to each other, while the sheets are separated by non-magnetic Sr^{2+} ions. An illustration of the tetragonal unit cell of the structure [3] is presented in Fig. 1. The magnetic exchange pathways in $SrCu_2(BO_3)_2$ are topologically similar to the dimer model of Shastry and Sutherland [4]. In this, a 2D Heisenberg model allowing for nearest-neighbor (NN; J) and next-nearest-neighbbor (NNN; J') magnetic exchange interactions was employed, leading to the conclusion that the singlet dimer state is an exact eigenstate of the spin Hamiltonian. At $T < T_{SG} \approx 20$ K, the bulk magnetic susceptibility of $SrCu_2(BO_3)_2$ (shown in the inset of Fig. 4) shows a characteristic thermally activated

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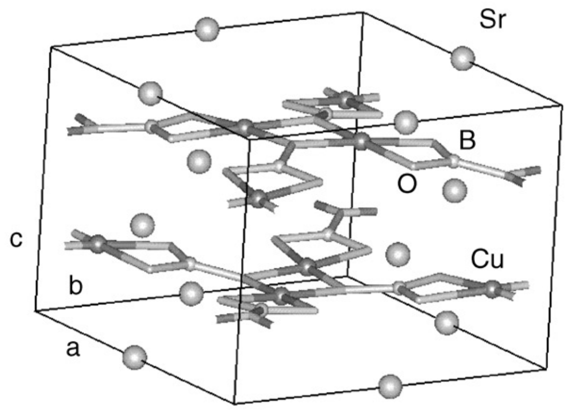

Fig. 1. Layered arrangement of the Cu^{2+} ions in the tetragonal unit cell of $SrCu_2(BO_3)_2$.

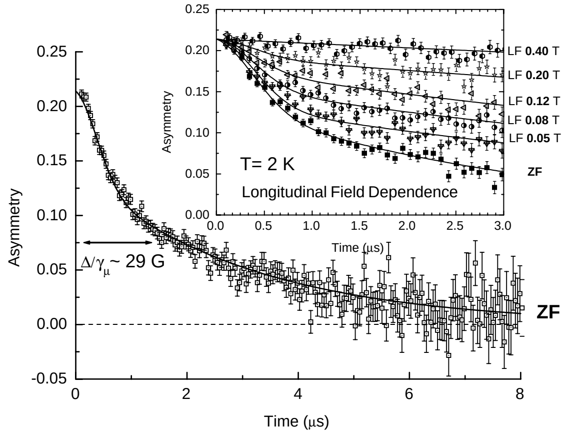

Fig. 2. Zero field μ^+SR time spectrum of $SrCu_{1.96}Mg_{0.04}(BO_3)_2$ at 2 K ($<T_{SG}$). The line is the fit to Eq. (3). Inset: Longitudinal-field μ^+SR decoupling experiment ($T = 2$ K) showing the persisting character of the Gaussian field distribution.

behavior consistent with the opening of an excitation gap, Δ. In addition, high-temperature susceptibility measurements [2,5] find that the NN Cu^{2+} interactions are strongly antiferromagnetic, $J \approx -100$ K, while the NNN interactions are sizeable ($J' \approx 0.68J$) and with important consequences for the stability of the ground state. Theory predicts [5] that the $SrCu_2(BO_3)_2$ dimer ground state is at the borderline of the transition from disordered spin-gap to antiferromagnetically (AF) ordered state with the quantum critical phase transition expected to occur at $(J'/J)_c \approx 0.7$.

Bearing the above in mind, we employed the μ^+SR technique to authenticate the nature of the magnetic ground state in $SrCu_{2-x}A_x(BO_3)_2$ ($A = Mg^{2+}$; $x \leqslant 0.12$), search for static magnetic order, follow the T-dependence of small moment spin fluctuations, investigate the spatial inhomogeneity of the ground state, find out if the spin-gap is modified by non-magnetic impurity dopants (Mg^{2+}), and answer questions regarding possible muon-induced break-up of the dimer spin-singlets.

μ^+SR measurements were carried out at the Paul Scherrer Institute (PSI), Villigen, Switzerland. Datasets were collected in the zero-field (ZF), longitudinal-field (LF = 10 mT to 0.4 T), and transverse-field (TF = 0.6 T) variants of the technique. Polycrystalline samples were pressed into pellets (∅ 13 mm) and mounted on a silver sample holder which was then attached on the sample stick of a continuous flow cryostat operating between 1.7 and 300 K.

Fig. 2 shows the ZF-μ^+SR spectrum of $SrCu_{1.96}Mg_{0.04}(BO_3)_2$ at 2 K which is representative of all samples studied. This is very unusual for systems with disordered non-magnetic singlet ground states for which the only means of μ^+ spin depolarization is through the disordered nuclear moments [6]. In the present cases, the low-temperature ZF-μ^+SR data were described well by two-component depolarization functions, incorporating a strongly relaxing Gaussian (σ_1) and a slow exponential (λ_2) component.[1] The following functional forms were employed in the analysis of ZF time-spectra for different temperature ranges:

$$P_\mu(t) = A\exp(-\lambda t)\exp(-\tfrac{1}{2}\sigma^2 t^2) \quad 4.5 \leqslant T < 10\,\mathrm{K}, \tag{1}$$

$$P_\mu(t) = A\exp(-\lambda t) \quad 3.75 \leqslant T < 4.5\,\mathrm{K}, \tag{2}$$

$$P_\mu(t) = A_1\exp(-\tfrac{1}{2}\sigma_1 t^2) + A_2\exp(-\lambda_2 t) \quad T < 3.75\,\mathrm{K}. \tag{3}$$

Fig. 3 compiles the temperature dependence of the fitted parameters. We find that at high

[1] Similar behavior has been observed by A. Fukaya et al. (this conference) on a different batch of samples.

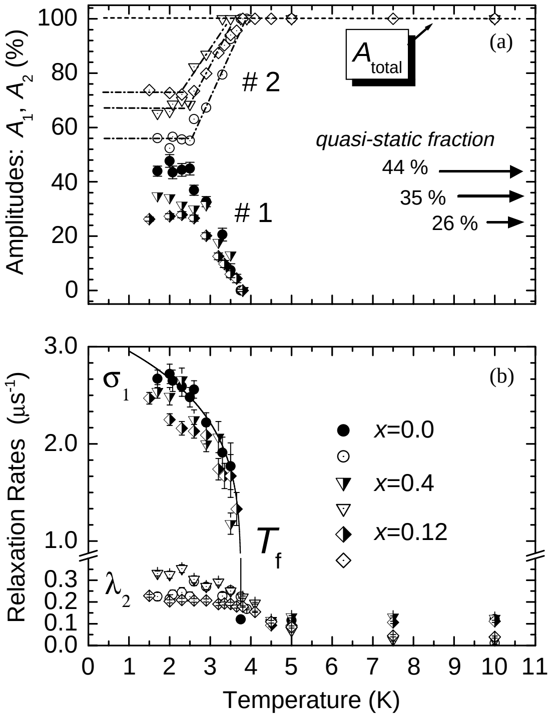

Fig. 3. Temperature dependence of the fitted parameters (Eqs. (1)–(3)) for $SrCu_{2-x}Mg_x(BO_3)_2$ ($x = 0, 0.04, 0.12$) in zero field: (a) the sample volume fractions ($A_1 + A_2 = A_{total}$) involved in the μ^+ spin-depolarization and (b) the corresponding relaxation rates. At $T > 3.75$ K, σ is on average $\sim 0.12\,\mu s^{-1}$, whereas λ becomes smaller with increasing temperature—the line through σ_1 is a power-law fit to determine T_f (≈ 3.75 K).

temperatures the Cu nuclei of $SrCu_{2-x}Mg_x(BO_3)_2$ dominate the depolarization ($\sigma = 0.121(6)\,\mu s^{-1}$) behavior (Eq. (1)), while relatively fast spin fluctuations that are already present above 4.5 K appear to slow down (Eq. (2)) as we approach the characteristic temperature of 3.75 K from above, with the exponential relaxation rates (Eqs. (1)–(3)) increasing smoothly from $0.168(4)\,\mu s^{-1}$ at 5 K to $0.23(2)\,\mu s^{-1}$ at 2.1 K.

On the other hand, below 3.75 K the Gaussian depolarization component begins to grow quickly at the expense of the exponential one. The corresponding relaxation rate, σ_1 approaches saturation at the lowest temperatures ($\sim 2.7(1)\,\mu s^{-1}$) and gives rise to a sizeable field width which varies little among the different compositions, i.e. $\langle \Delta B^2 \rangle^{1/2} = 31_{x=0}$, $29_{x=0.04}$, and $26.5_{x=0.12}$ G at 2 K. The rapid growth of the relaxation rate and the Gaussian field spread are consistent with component #1 of Eq. (3) reflecting a quasi-static volume fraction (A_1) which diminishes with increasing Mg-content from 44% in the parent compound to $\approx 26\%$ for $x = 0.12$. Component #1 cannot arise from paramagnetic $S = 1/2$ impurities present in the samples, as magnetic susceptibility measurements put an upper limit of 0.1% to such impurities. By fitting a power-law expression to the T-dependence of the Gaussian (Eq. (3)) depolarization rate, $\sigma_1 = \sigma_0[1 - (T/T_f)]^{\beta}$, a freezing temperature, $T_f = 3.75(2)$ K ($\beta \approx 0.22-0.3$) for the electronic magnetic moments can be extracted. In order to explore further the nature of the Gaussian component of Eq. (3), we performed additional LF-μ^+SR experiments at $T < T_f$. The time-dependence of the muon spin depolarization at applied LFs is similar for all compositions. A good description of the LF spectra at $T < 3.75$ K was achieved with Eq. (3), while at higher-Ts Eq. (2) was more appropriate. The inset of Fig. 2 shows a typical decoupling experiment. The exponential component (A_2) represents the dominant volume fraction in the presence of an applied LF and the corresponding relaxation rates appear to diverge when approaching T_f. The maximum depolarization rate is reached at about 3.5 K (e.g. for $x = 0$: $\lambda \sim 0.23\,\mu s^{-1}$ in ZF and $\lambda \sim 0.08\,\mu s^{-1}$ in 0.2 T LF) and then diminishes at lower temperatures (e.g. at 2 K: $\lambda_{ZF} \sim 0.22\,\mu s^{-1}$, $\lambda_{0.1\,T} \sim 0.06\,\mu s^{-1}$, $\lambda_{0.2\,T} \sim 0.02\,\mu s^{-1}$). Very surprisingly though, the Gaussian component, σ, survives even after the application of $H_{LF} \sim 0.05$ T ($\gg \Delta/\gamma_\mu$), while its volume fraction appears to shrink somewhat. Only when fields of the order of $H_{LF} \sim 0.2$ T are reached, component #1 of Eq. (3) is completely decoupled. Such a very unusual, persisting Gaussian relaxation has been seen before in other systems with spin-singlet ground states. For example, in the frustrated Kagomé lattice system $SrCr_8Ga_4O_{19}$, a similar behavior was observed and was attributed to a dilute source of a magnetic local field, which migrates spatially through the lattice [7].

In an attempt to understand the origin of the slowing down and eventual freezing of the electronic magnetic moments at $T < T_{SG}$, we

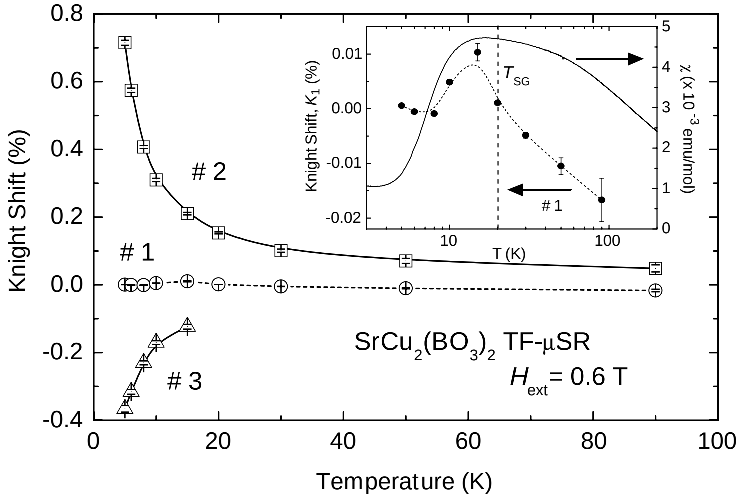

Fig. 4. Knight shifts of the muon precession frequencies observed in $SrCu_2(BO_3)_2$ as a function of temperature. The lines through the data for components #2 and #3 are Curie-law fits. Inset: Temperature dependence of the Knight shift, K_1, of component #1 and of the bulk molar dc susceptibility ($H = 1$T) in $SrCu_2(BO_3)_2$.

performed TF-μ^+SR (at 0.6 T) measurements between 5 and 90 K. We find that at $T \leqslant 20$ K, while entering the spin-gap regime, the local field distribution, initially centered at $\nu_0 \sim 81.3$ MHz, becomes broader and two additional lines (#2, #3) gradually separate out while approaching 5 K. We calculated the Knight shift (Fig. 4) for the three components according to the formula:

$$\begin{aligned} K_{s,i} &= \frac{\gamma_\mu B_{s,i}}{\nu_0} \\ &= \frac{\nu_i(T) - \nu_0}{\nu_0} - 4\pi\left(\frac{1}{3} - N_{xx}\right)\chi(T), \end{aligned} \qquad (4)$$

where ν_0 is the frequency of the external field, ν_i ($i = 1, 2, 3$) is the frequency of each component, N_{xx} is the demagnetization factor, and $\chi(T)$ is the volume susceptibility. The T-variation of the corresponding sample volume fractions and relaxation rates are similar to those shown in Fig. 3 for the ZF measurements, i.e. TF #1 is associated with the ZF exponential component, whereas TF #2 and #3 are related to the ZF Gaussian component. With ZF/LF and TF experiments probing effects of the same nature, we note the similarity of $K_1(T)$ to $\chi(T)$, as shown in the inset of Fig. 4. Assuming that component #1 of the TF data reflects roughly the bulk susceptibility around T_{SG}, then the Curie-like behavior ($\nu_i = \nu_{0,i} + C/T$) exhibited by the spins associated with components #2 and #3 may be ascribed to some spin-density, which is liberated by the muon itself.

In summary, μ^+SR investigations of the $SrCu_{2-x}Mg_x(BO_3)_2$ ground state indicate that the spins associated with the dimer singlet state are fluctuating relatively slowly ($\nu \sim 1/\langle\lambda\rangle_{LF=0.1\,T} \sim$ 66 MHz) at 7.5 K before slowing down ($\sim$9 MHz) at 3.5 K close to a characteristic temperature, T_f that is 5 times smaller than T_{SG}. Interestingly, this point is also marked by the appearance of a secondary process, which sets in abruptly and is consistent with the freezing of spins liberated from the dimer state. This transition is marked by a persisting (non-decouplable upon the application of H_{LF}) Gaussian field distribution and points to a μ^+-induced effect suggested before for other low-dimensional spin-gap systems [8]. It is presumably an indication of how close $SrCu_2(BO_3)_2$ is to a quantum critical phase transition from a spin-gap to an AF ordered state. In addition, Mg-dilution of the Cu-sublattice does not induce static magnetic order; instead, it decreases the volume fraction associated with the free-spins in accord with the picture of a μ^+-associated perturbation of the $SrCu_2(BO_3)_2$ quantum critical ground state.

Acknowledgements

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