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 $\mu^+$ 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-neighbor (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...
behavior consistent with the opening of an excitation gap, $\Delta$. 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 $\mu^+\text{SR}$ technique to authenticate the nature of the magnetic ground state in SrCu$_{2-x}$A$_x$(BO$_3$)$_2$ ($A = \text{Mg}^{2+}; x \leq 0.12$), 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 ($\text{Mg}^{2+}$), and answer questions regarding possible muon-induced break-up of the dimer spin-singlets.

$\mu^+\text{SR}$ 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 $\sim 0.4$ T), and transverse-field (TF $= 0.6$ T) variants of the technique. Polycrystalline samples were pressed into pellets ($\varnothing 13$ 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-$\mu^+\text{SR}$ spectrum of SrCu$_{1.96}\text{Mg}_{0.04}$(BO$_3$)$_2$ at 2 K ($< T_{\text{SG}}$). The line is the fit to Eq. (3). Inset: Longitudinal-field $\mu^+\text{SR}$ decoupling experiment ($T = 2$ K) showing the persisting character of the Gaussian field distribution.

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temperatures the Cu nuclei of SrCu_{2−x}Mg_{x}(BO_{3})_{2} dominate the depolarization (σ = 0.121(6) μs⁻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) μs⁻¹ at 5 K to 0.23(2) μs⁻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, σ₁ approaches saturation at the lowest temperatures (∼2.7(1) μs⁻¹) and gives rise to a sizeable field width which varies little among the different compositions, i.e. ⟨ΔB²⟩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 (A₁) which diminishes with increasing Mg-content from 44% in the parent compound to ∼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, σ₁ = σ₀[1−(T/Tₐ)]², a freezing temperature, Tₐ = 3.75(2) K (β ≈ 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 < Tₐ. 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 (A₂) represents the dominant volume fraction in the presence of an applied LF and the corresponding relaxation rates appear to diverge when approaching Tₐ. The maximum depolarization rate is reached at about 3.5 K (e.g. for x = 0: λ ≈ 0.23 μs⁻¹ in ZF and λ ≈ 0.08 μs⁻¹ in 0.2 T LF) and then diminishes at lower temperatures (e.g. at 2 K: λ_{ZF} ≈ 0.22 μs⁻¹, λ_{0.1 T} ≈ 0.06 μs⁻¹, λ_{0.2 T} ≈ 0.02 μs⁻¹). Very surprisingly though, the Gaussian component, σ₁, survives even after the application of H_{LF} ≈ 0.05 T (≫ Δ/γₘ), while its volume fraction appears to shrink somewhat. Only when fields of the order of H_{LF} ≈ 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 SrCr₂Ga₉O₁₉, 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...
performed TF-\mu^+SR (at 0.6 T) measurements between 5 and 90 K. We find that at $T \leq 20$ K, while entering the spin-gap regime, the local field distribution, initially centered at $v_0 \sim 81.3$ 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:

$$K_{s,i} = \frac{\gamma \mu B_{s,i}}{v_0}
= \frac{v_i(T) - v_0}{v_0} - 4\pi \left( \frac{1}{3} - N_{xx} \right) \chi(T),$$

(4)

where $v_0$ is the frequency of the external field, $v_i$ ($i = 1, 2, 3$) 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 ($v_i = v_0 + C/T$) 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, \mu^+SR investigations of the SrCu$_2$(BO$_3$)$_2$ ground state indicate that the spins associated with the dimer singlet state are fluctuating relatively slowly ($v \sim 1/\langle \hat{\lambda} \rangle_{LF=0.1 T} \sim 66$ 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 mu^+-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 mu^+-associated perturbation of the SrCu$_2$(BO$_3$)$_2$ quantum critical ground state.
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