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A local study of dynamic and static magnetism in the Kagomé bilayer compound $Ba_2Sn_2ZnCr_{6.8}Ga_{3.2}O_{22}$

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Abstract

We present a survey of an NMR and μSR magnetic study of the so called 'QS ferrite' frustrated antiferromagnet $Ba_2Sn_2ZnCr_{6.8}Ga_{3.2}O_{22}$ (BSZCGO(0.97)). We compare our results to the archetype of highly frustrated magnets, $SrCr_{8.6}Ga_{3.4}O_{19}$ (SCGO(0.95)), which has a very similar Kagomé bilayer structure. These two compounds show a spin glass like transition at a temperature T_g, much lower than the Curie–Weiss temperature, despite a strong frustration of the Cr^{3+} ($S = 3/2$) Kagomé bilayer lattice. Although there is a large difference between these transition temperatures, T_g (BSZCGO(0.97)) $\approx$ T_g (SCGO(0.95))/2.5, the evolution of the dynamics of the Cr^{3+} spins around T_g, as probed by μSR, is very similar in both samples, with a persistent dynamical magnetic ground state under $\approx 0.4T_g$. This suggests that the spin glass like state and the dynamical properties are closely linked. A brief report of our NMR results is also given, where a maximum in the Cr bilayer susceptibility is observed around 45 K, similar to SCGO(p), and the existence of new dilution independent defects is evidenced.

$SrCr_{9p}Ga_{12-9p}O_{19}$ (SCGO(p)) was the first Kagomé antiferromagnet to be discovered, and it is considered as one of the best representatives of geometric frustration induced physics. In this compound, 7/9 of the Cr^{3+} $S = 3/2$ ions arrange themselves into a Kagomé bilayer with an isotropic exchange and negligible single-ion anisotropy, which leads to a simple canonical Heisenberg Hamiltonian on a frustrated lattice. Although extensively studied, it has a major drawback in that 2/9 of the Cr^{3+} ions occupy unfrustrated sites which are however believed to have no impact on the low T physics, since they form pairs with a 216 K gapped singlet ground state [1]. The crystal structure of $Ba_2Sn_2ZnGa_{10-7p}Cr_{7p}O_{22}$ (BSZCGO(p)) is very similar to the SCGO(p) one, but displays a larger intra-bilayer distance ($\approx$9.4 Å) and slightly

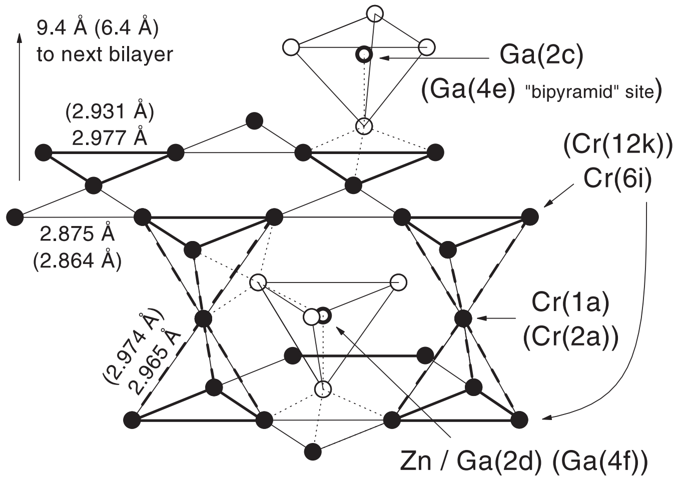

Figure 1. The BSZCGO Cr^{3+} network showing the oxygen environments and Ga^{3+} sites. The corresponding site labelling and bonds are also given in brackets for SCGO.

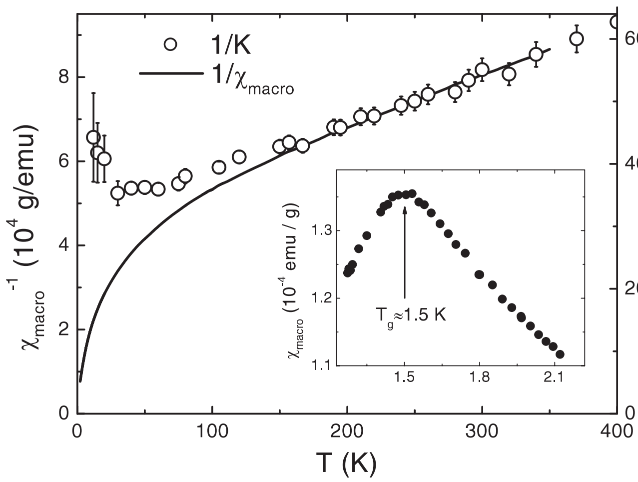

Figure 2. The inverse of the BSZCGO(0.97) macroscopic susceptibility under 100 G, $\chi_{\mathrm{macro}}^{-1}$ (left scale), and the inverse of the shift, K^{-1} (right scale), versus T. Inset: ac susceptibility versus T. T_{g} is the spin glass like transition temperature.

different bonds (see figure 1) [2]. 100% of the Cr^{3+} ions here belong to the frustrated lattice *without* Cr pairs. Nonetheless, as in SCGO(p), one cannot reach a perfect lattice ($p = 1$), and Cr^{3+}/Ga^{3+} substitutions always occur leading to $p \leqslant 0.97$, a limit above which some parasitic phases are detected by x-ray diffraction. In this paper, we present a susceptibility, NMR and μSR study of BSZCGO(p) powder samples.

The macroscopic susceptibility χ_{macro} was measured with a commercial SQUID magnetometer between 1.8 and 350 K, under an external field of 100 G. We observe the same behaviour as reported in [2], characteristic of a frustrated antiferromagnet. The linearity at high T of $\chi_{\mathrm{macro}}^{-1}$ extends down to 100 K, well below the Curie–Weiss temperature $\theta_{\mathrm{CW}} = 350 \pm 10$ K determined from a linear fit in the high T range (see figure 2). From the mean field formula $\theta_{\mathrm{CW}} = \langle z\rangle S(S+1)J/3$, where $\langle z\rangle = 5.14$ is the average *nn* coordination of the Kagomé bilayer

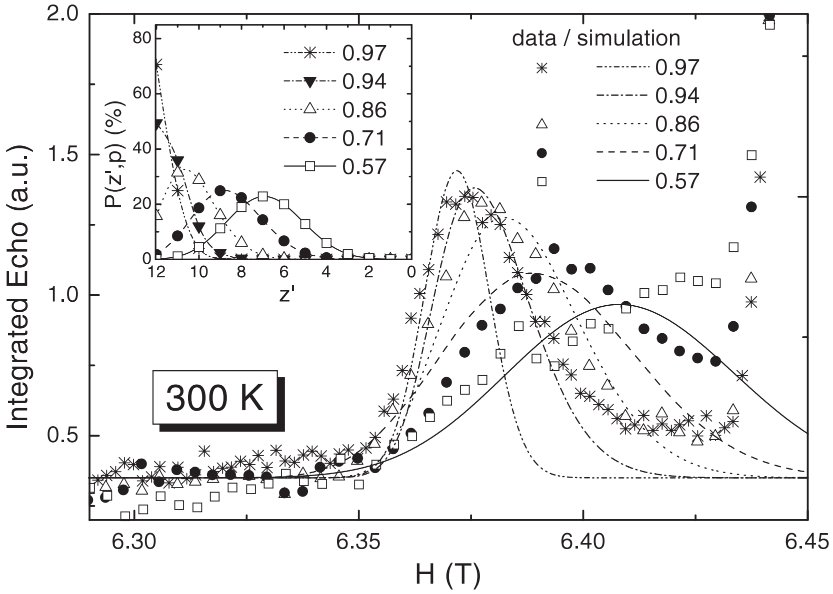

Figure 3. ^{71}Ga spectra at 300 K for several values of p. Ga(2d)(p) spectra are compared with simulations (curves) using the number of $Cr^{3+}nn$. The ^{71}Ga non-shifted position is $H_{ref} \approx 6.5$ T. The rise at 6.45 T corresponds to the low field edge of the Ga(2c) line.

geometry, we determine an average Cr–Cr exchange interaction of $J \sim 55$ K. At temperatures lower than 100 K, a paramagnetic Curie term is evident in χ_{macro}. Finally, in order to determine the spin glass like transition T_g, additional susceptibility measurements were performed using an ac technique down to 1.2 K, where $T_g \approx 1.5$ K was found (see the inset of figure 2). By comparison, $T_g \approx 3.6$ K was observed in SCGO(0.95) [3]. The frustration ratio defined by Ramirez [4] is $f = \theta_{CW}/T_g \sim 250$, for BSZCGO(0.97), higher than in SCGO(0.95). Taking into account all these considerations, this makes BSZCGO(p) one of the best candidates for studying 2D frustrated antiferromagnets.

To access the local susceptibility of the Kagomé bilayers, we performed ^{71}Ga NMR experiments for various dilutions p. We focused our study on the Ga(2d) site, which is strictly identical to Ga(4f) previously studied in SCGO(p) [3, 5], although they are not labelled in the same manner (see figure 1 for details of these sites). It is located inside the bilayer, and coupled to 12 p Cr^{3+} sites of the bilayer through hyperfine coupling, hence making it a very good probe of this magnetic network. Typical spectra taken at 300 K are presented in figure 3. The line observed between 6.35 and 6.45 T corresponds to the Ga(2d) resonance [6]. At high T, where the magnetic Curie-like contribution of the substitution defects to the linewidth is negligible [3], the line shape directly reflects the distribution of the magnetic environment around a given Ga^{3+}. In the inset of figure 3 we plot the probability $P(z', p)$ for a Ga(2d) to have $z'Cr^{3+}$ neighbours at various p, in the case of homogeneous substitutions. Our experimental data agree with the Ga(2d) lines simulated from these probability distributions for $p \leqslant 0.86$ (curves in figure 3), assuming that the Ga(2d)–Cr(1a) and the Ga(2d)–Cr(6i) hyperfine couplings are the same order of magnitude. Figure 3 also shows that the $p = 0.97$ sample is closer to the simulation for $p = 0.94$. These measurements prove that the actual Cr contents in our samples are of the order of the nominal concentrations.

The $p = 0.97$ sample was used to perform a refined study of the local susceptibility since the Ga(2d) site is mostly surrounded by Cr^{3+} ions. The shift, K, of the *position* of the Ga(2d) line is proportional to the intrinsic susceptibility χ_{NMR} of the Kagomé bilayer Cr network, whereas the low T *linewidth* ($\propto 1/T$) was previously shown to be the landmark of extended magnetic perturbations around a substitution defect [3]. χ_{NMR} is very close to the SCGO(0.95) bilayer susceptibility [3, 5], showing a maximum around 45 K (see figure 2). Its decrease at lower T is most likely linked to the increase of the magnetic correlations observed in neutron scattering [7]. This is consistent with numerical computations based on a mean field approach on spin clusters, which find a maximum of χ_{NMR} around $0.2\theta_{CW}$ [8]. The variation of χ_{NMR} is in contrast with the Curie term observed in χ_{macro}, reflected in the linewidth and linked to defects, as first reported in SCGO(p) [5]. Surprisingly the low T linewidth is larger than in SCGO($p \geqslant 0.8$), and due to new p independent defects in this sample [6]. The very small difference between χ_{NMR} in SCGO(0.95) and BSZCGO(0.97) is a clear indication that the T dependence of the intrinsic susceptibility is very robust to the presence of defects.

μSR experiments consist of implanting 100% spin polarized muons (μ^+, $S = 1/2$) in a sample and measuring their polarization $G(t) = A(t)/A\ (t = 0)$ along the z axis, where $A(t)$ is the asymmetry of the positron emission of the μ^+ decay. As the muon lifetime is close to 2.2 μs, its polarization can be observed in a typical time window of 10 μs. The relaxation of the muon polarization is due to magnetic fluctuations and/or to a distribution of static local fields in the μSR timescale. The advantage of BSZCGO(p) as compared to SCGO(p) is that $G(t)$ is only linked to the magnetic Kagomé bilayer structure. The nuclear dipole contribution has been decoupled with a weak longitudinal field $H_{LF} = 100$ G, which only has a weak effect on electronic spins.

Figure 4 (left) shows the T dependence of $G(t)$ for the $p = 0.97$ sample. For $T > 5$ K the relaxation shape fits well to an exponential $\exp(-\lambda t)$ (curves in figure 4 (left)). It is actually expected in the case of fast fluctuations in the paramagnetic regime ($T \gg T_g$), with a weak external longitudinal field H_{LF}, and for a dense distribution of magnetic moments. In this case, $\lambda = 2\Delta^2\nu/(\nu^2+(\gamma_\mu H_{LF})^2) \sim 2\Delta^2/\nu$ where ν is the Cr^{3+} spin fluctuation rate, and Δ/γ_μ is the width of the random Gaussian field distribution on the muon sites [9] ($\gamma_\mu = 85.14$ MHz kG^{-1} is the gyromagnetic ratio of the muon). Above 20 K, the relaxation barely evolves with T and is mainly due to spin lattice relaxation processes in the pure paramagnetic regime, with $\lambda(100\text{ K}) \sim 0.01\ \mu\text{s}^{-1}$ and $\nu = \sqrt{z}Jk_BS/\hbar \sim 2 \times 10^{13}$ s^{-1}, leading to $\Delta/\gamma_\mu \sim 4$ kG. These results are of the same order of magnitude as in SCGO [10].

Below $T \sim 4$ K, the μ^+ spin relaxation is no longer exponential and it becomes faster when T decreases. The dynamics of the Cr^{3+} spins is therefore slowed down, reaching a state which does not evolve below $T \sim 1.5$ K. The characteristic recovery of 1/3 of the asymmetry at long times for a static magnetic state is not observed. In such a state, the relaxation rate $\lambda \sim 2\ \mu\text{s}^{-1}$ would also lead to a completely decoupled asymmetry under an external longitudinal field of $H_{LF} \sim 5\lambda/\gamma_\mu \sim 100$ G, either in a dense (dashed curves in figure 4 (right)) or a dilute magnetic system [9, 11]. Figure 4 (right) shows decoupling experiments performed at 0.03 K. A field of 100 G and even of 1000 G weakly affects $G(t)$. The magnetic state reached under 1.5 K is then dynamical, although a spin glass like transition is observed in χ_{macro}.

Below 1.5 K, the shape of the asymmetry is nearly Gaussian at early times as in SCGO(p) [10, 12]. In a dynamical state, this is characteristic of slow fluctuating dense magnetic systems with the associated dynamical Kubo–Toyabe (DKT) relaxation function, $G^{DKT}(t, \Delta, H_{LF}, \nu)$. We tried to fit our data with its analytical approximation derived by Keren for $\nu \geqslant \Delta$ and any longitudinal field H_{LF} [13]. The continuous curves in figure 4 (right) show good fits of the zero field and $H_{LF} = 50$ G data. Using the parameters obtained, the relaxation curves are calculated for $H_{LF} = 200$, 1000 and 5000 G (figure 4 (right)). The field has a weaker effect than expected and therefore the DKT function is not relevant here. Uemura *et al* observed first this *undecoupleable Gaussian* line shape in SCGO(0.89) and proposed a

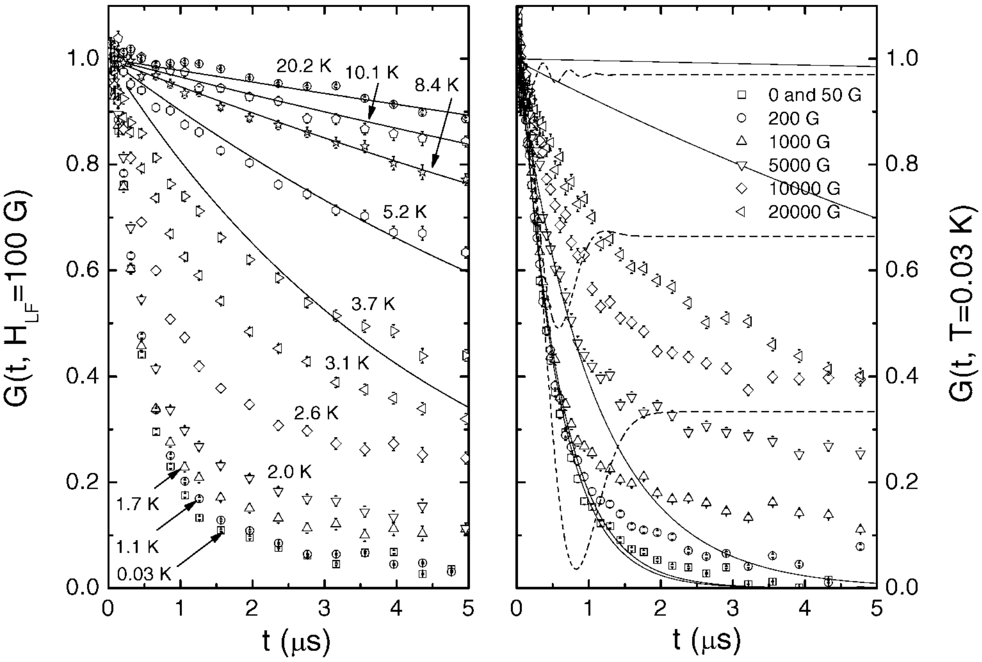

Figure 4. Left: The T dependence of $G(t)$ under $H_{\mathrm{LF}} = 100$ G. The continuous curves are exponential fits. Right: The H_{LF} dependence of $G(t)$ at $T = 0.03$ K. The dashed curves are static Kubo–Toyabe functions with an internal field distribution $\Delta = 2.1\ \mu\mathrm{s}^{-1}$, in zero external field, $H_{\mathrm{LF}} = 50$ and 200 G, from bottom to top. The continuous curves are dynamical Kubo–Toyabe functions with $\nu \approx 16.7\ \mu\mathrm{s}^{-1}$ and $\Delta \approx 4\ \mu\mathrm{s}^{-1}$, under zero field, $H_{\mathrm{LF}} = 50$, 200, 1000 and 5000 G, from bottom to top (see text).

model based on a spin liquid ground state [10], with a relaxation function derived from the DKT function. Without an extra term which might be related to the novel defects evidenced by NMR, we could not fit our data with this model [6].

Since even stretched exponentials do not fit our low T data, we just define the muon relaxation rate $\lambda(T)$ as $G(1/\lambda(T)) = 1/\mathrm{e}$, as proposed in [12]. As we are in a fast fluctuating regime, $\lambda \sim 2\Delta^2/\nu$ is still characteristic of the magnetic fluctuations. $\lambda(T/T_{\mathrm{g}})$ is presented in figure 5. The increase of $\lambda(T)$ by two orders of magnitude at low T shows the slowing down of the Cr^{3+} spin fluctuations around T_{g}. $\lambda(T)$ presents an unconventional plateau below $T \approx 0.6$ K $\approx 0.4T_{\mathrm{g}}$. In spin glasses [11] or even other Kagomé samples [14], $\lambda(T)$ decreases below the divergence at T_{g} as a consequence of a *static* magnetic ground state in the μSR time window of 10 μs. A comparison with SCGO(0.95), for which $T_{\mathrm{g}} \approx 3.6$ K, is presented in figure 5. A strikingly similar evolution of $\lambda(T/T_{\mathrm{g}})/\lambda_{T\to 0}$ is observed between the two samples. The factor $\sim$7.5 in $\lambda_{T\to 0}$ between both samples may be explained by different muon sites in the lattice, but is still to be understood.

In conclusion, we find that despite the presence of new p independent defects in BSZCGO(p), lots of properties remain similar to SCGO(p). BSZCGO(0.97) and SCGO(0.95) present the same T dependence of the bilayer susceptibility, with a maximum at 45 K, as well as a dynamical magnetic ground state reached under T_{g}. The similarity of the evolution of the dynamics crossing the spin glass like transition is singled out, suggesting that this strange coexistence is an intrinsic Kagomé bilayer property which remains to be understood on a theoretical ground. A study of the T dependence of the magnetism dynamics in BSZCGO(p)

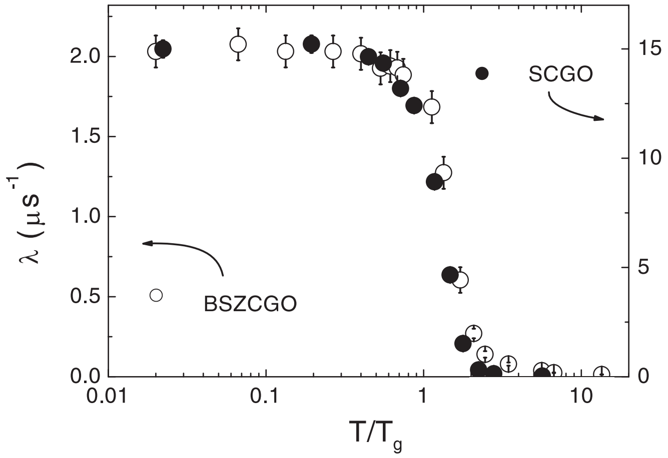

Figure 5. The μSR relaxation rate λ plotted as a function of T/T_g for SCGO(0.95) and BSZCGO(0.97).

with $0 < p < 1$ and its comparison with a former SCGO(p) study [12] will be presented in a separate paper [6].

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