Magnetic dilution in the geometrically frustrated $\text{SrCr}_p\text{Ga}_{12-9p}\text{O}_{19}$ and the role of local dynamics: a $\mu$SR study

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(March 21, 2022)

We investigate the spin dynamics of $\text{SrCr}_p\text{Ga}_{12-9p}\text{O}_{19}$ for $p$ below and above the percolation threshold $p_c$ using muon spin relaxation. Our major findings are: (I) At $T \rightarrow 0$ the relaxation rate is $T$ independent and $\propto p^3$, (II) the slowing down of spin fluctuation is activated with an energy $U$ which is also a linear function of $p^{a}$ and $\lim_{p \to 0} U \approx 8$ K; this energy scale could stem only from a single ion anisotropy, and (III) the $p$ dependence of the dynamical properties is identical below and above $p_c$, indicating that they are controlled by local excitation.

The $\text{SrCr}_p\text{Ga}_{12-9p}\text{O}_{19}$ (SCGO($p$)) compound has been intensely studied experimentally in recent years, as it is believed to be a model compound for a "super-degenerate" antiferromagnet $^{[1][2][3]}$. By "super-degenerate" we mean that the classical ground state energy is invariant under a local rotation of a small number of spins, a symmetry which leads to local zero energy excitations in addition to the more common collective ones. One of the open questions in this area of research is which type of excitations will dominate in low temperatures. To date, this question was addressed only theoretically in two of the most famous super-degenerate magnets, the kagomé $^4$ and the pyrochlore $^5$, where it was found that the dynamical properties are mostly controlled by the local excitations. Here we examine this question experimentally. We do so by measuring muon spin relaxation ($\mu$SR) rates as a function of temperature $T$, magnetic field $H$, and, most importantly, magnetic ion concentration $p$ below and above the percolation threshold $p_c$. Our major finding is that the dynamical properties of the system are impartial to $p_c$, suggesting that they could not emerge from a collective phenomenon.

Unexpectedly, our measurements also lead us to another finding regarding the spin Hamiltonian in SCGO. For long it was suspected that this Hamiltonian must contain terms other than the Heisenberg one. This is because SCGO shows spin glass like effect in susceptibility experiments, such as a cusp at a temperature $T_f \approx 4p$ K $^6$, and a hysteresis between the field cooled (FC) and zero field cooled (ZFC) measurements. Neither of these could be understood in terms of Heisenberg spins on kagomé or pyrochlore lattices $^7$. Our data indicate the presence of a single ion anisotropy with an energy scale of $\sim 8$ K which might be the origin of the susceptibility effects.

Our samples were prepared by solid state reaction at 1350°C from the stoichiometric mixtures of Cr$_2$O$_3$, Ga$_2$O$_3$ and SrCO$_3$. X-ray examination revealed the absence of foreign phase in the prepared samples and a slight smooth lattice expansion as $p$ is decreased. Our intention was to have $p$ values both above and below the $p_c$ of the lattice. However, there is a controversy whether SCGO represents a kagomé lattice or a pyrochlore-slab $^8$. The $p_c$ for the kagomé lattice is 0.6527 and for a pyrochlore-slab is not known. Nevertheless, the Curie-Weiss temperature $\Theta_{cw}$ in SCGO($p$) is a linear function of $p$ with a slope which is different below and above $p = 0.61(5)$ $^9$, in agreement with $p_c$ for the kagomé lattice. Therefore we assume that $p_c = 0.6527$ and prepare samples with $p$ in the range 0.39 to 0.89. The value of $p$'s in our samples is determined from their Curie constant. This method was found to be in agreement with the stoichiometric ratio in the sample preparation, the Curie-Weiss temperature, and $T_f$ (when measurable) $^3$.

Our $\mu$SR experiments were done in both TRIUMF and ISIS. In these experiments one follows the time evolution of the spin polarization $P_z(t)$ of a muon implanted in a sample, through the asymmetry $A(t) \propto P_z(t)$ in the positron emission of the muon decay. In addition, an external field $H$ is applied along the initial muon spin (longitudinal) direction which defines the $z$ axis. $A(t)$ for three different samples at base temperature and $H = 100$ G is shown by the symbols in Fig. 1 where time is presented on a log scale. The small field of 100 G could be considered as zero field; it is applied in order to decouple the nuclear spin contribution to the muon spin relaxation. As can be seen from the figure, there is a strong variation in the time scale of relaxation between the different samples. In addition, the asymmetry for all samples has a "bat" beginning similar to Gaussian. In the inset of Fig. 1 we depict the asymmetry for the $p = 0.89$ at high temperature (5.5 K) where $A$ is pre-
sented on a log scale. Clearly at high temperatures the relaxation is closer to exponential. Therefore, the asymmetry waveform is temperature dependent, as was first found in the $p = 0.89$ sample by Uemura et al. [8], but depends weakly on the most important variable in this paper, namely, $p$.

There are two ways to obtain a relaxation rate in a situation where the waveform is changing: (I) using the $1/e$ criteria where we define the time $T_1$ by $A(T_1) = A(0)/e$, or (II) fitting all data sets to a stretched exponential

$$A(t) = A_0 \exp \left(-\left(\frac{t}{\lambda}\right)^\beta \right).$$

Representative fits are depicted in Fig. 1 by the solid lines. However, in our case, where the stretched exponential fits the data well for more than $1/e$ of the internal asymmetry, as demonstrated by the arrow in Fig. 1, one finds that $\lambda = 1/T_1$. Therefore, both methods lead to the same relaxation rate although in (II) both $\lambda$ and $\beta$ are functions of $T$, $H$, and $p$ whereas in (I) these parameters impact only $T_1$. We therefore continue the discussion using the stretched exponential fit approach which is more informative and accurate. Finally, in the samples with large $p$, Eq. 1 accounts only for early times where the asymmetry drops by $\sim$80%. At later times a second component with low relaxation rate dominates. However, this second component is not observable in the small $p$ samples due to experimental limitations imposed by the muon life time ($2.2$ μsec). Therefore, we concentrate here on the early time behavior of $A(t)$.

In Fig. 2 we show $\lambda$ in $H = 100$ G as a function of temperature for various values of $p$. All samples show critical slowing down starting at $T = 20 - 5$ K, followed by a saturation of the muon relaxation rate, in agreement with earlier $\mu$SR work [1] and more recent NMR measurements [3] on the $p = 0.89$ sample. In Fig. 3a, we depict $\beta$ versus $T$ for the different $p$’s. As demonstrated before, the waveform in all our samples is exponential ($\beta \rightarrow 1$) at high $T$ but tends to be Gaussian ($\beta \rightarrow 2$) at low $T$.

There are two possible mechanisms which can be responsible for the loss of the muon polarization: static field distribution, or dynamic field fluctuations. It is possible to distinguish between these two by measuring the field dependence of the muon spin relaxation rate. In Fig. 4 we show $\lambda(H)$ on a semi-log scale for all our samples, and in Fig. 3b the field dependence of $\beta$. The field dependence of $\lambda$ allows us to rule out the possibility of relaxation due to static field distribution as the following argument shows. In the $p = 0.89$ sample, when $H = 100$ G, and $T \rightarrow 0$, the value of $\lambda$ is $10$ μsec$^{-1}$. If this relaxation would have been due to static field distribution it would have implied an internal magnetic field $[B]$ at the muon site in the order of 100 G (using $\lambda \sim \gamma_\mu [B]$ where $\gamma_\mu = 85.16$ MHz/kG). The vector sum of this internal field and an external longitudinal field of, say, 2 kG, would have been nearly parallel to the initial muon spin direction. Therefore, if the internal fields were static, we would expect a complete quenching of the relaxation rate in 2 kG and above, in contrast to observation. This line of argument applies to all other samples as well. Thus, the decay of $P_z(t)$ is not due to static field distribution, or dynamic field fluctuations.

On the other hand, the waveform is a Gaussian with a $\lambda$ that has a very weak field dependence for $H$ up to 2 kG; a field that obeys $\gamma_\mu H/\lambda \gg 1$. This stands in strong contrast to all theories known to us of relaxation from dynamical fluctuations. These theories yield exponential relaxation when there is weak field dependence for $\gamma_\mu H/\lambda \gg 1$. A dynamical Gaussian waveform is also very unusual experimentally, and is one of the ongoing puzzles of $\mu$SR in SCGO [3]. Nevertheless, we interpret our data using a dynamical model, since the argument regarding the vector sum of internal and external fields seems more fundamental than the exact waveform.

In dynamical models $\lambda(H)$ is proportional to the Fourier transform of the local field dynamical auto correlation function $\langle B_i(t)B_j(0) \rangle$ (i = x, y, z) at the frequency $\omega = \gamma_\mu H$. We find that for all samples $\lambda(H) \propto \exp(-H/H_0)$ where $H_0 = 1.16$ T, as demonstrated by the solid line in Fig. 4. This fact indicates that the spectral density is not modified by magnetic dilution, apart from an overall factor, and that it is impartial to percolation.

When no external field is applied the internal field fluctuation rate $\nu$ is related to the muon relaxation rate by

$$\nu \propto \langle B^2 \rangle \lambda^{-1}$$

where $\langle B^2 \rangle$ is the rms of the instantaneous field distribution at the muon site. We find that $\lambda^{-1}(T)$ could be well fitted to

$$\lambda^{-1}(p,T) = Q(P) + C \exp \left[-U(p)/T \right]$$

where $C = 150(10)$ μsec is a global parameter. The fit results are given in Fig. 2 by the solid lines. This fit suggests that the internal field fluctuation rate is controlled by two dynamical processes: a temperature independent quantum one, and an activated one. A similar behavior was observed in the high spin molecular system CrNi$_6$ where high $T$ dynamics is due to over-the-barrier motion, and low $T$ dynamics is due to quantum fluctuations [3]. Surprisingly, we find that $Q^{-1}(p)$ and $U(p)$ are linear functions of $(p/p_c)^3$ both below and above $p_c$ as demonstrated in Fig. 3. This result, together with the field dependence of $\lambda$, leads us to our first main conclusion, namely, that the fluctuations are impartial to whether the lattice percolates and supports collective excitations or not. Therefore, the excitations are of local nature.

It is interesting to compare this finding with other relevant experiments. Heat capacity measurements were performed by Ramirez et al. [3]. They found that $C(T) \sim T^2$ even when the percolation threshold for the kagomé lattice was crossed. They pointed out that this temperature dependence could result from collective antiferromagnetic excitations in two dimensions of the acoustic
type, namely, $\omega \propto k$. A similar indication was made by Broholm et al. \cite{Ref1} based on density of states $\rho(\omega) \propto \omega$ found in neutron scattering. However, no dispersion relation of the acoustic type was ever found. Our finding of local excitations indicates that at low $T$ the important $\omega$'s are $k$ independent.

An extrapolation of $Q^{-1}(p)$ in Fig. 1 to $p = 0$ suggests that $Q$ diverges upon dilution. In fact for $p \leq 0.05$ we expect $Q(p) \gg C$ and the muon relaxation rate $\lambda$ should be $T$ independent. In other words, SCGO($p \leq 0.05$) should behave as if its spins are isolated. A similar extrapolation of $U(p)$ to low $p$ gives 8 K. This leads to our second major finding, namely, that the activated part of the dynamics does not emerge only from coupling between neighboring spins, but also from on site (single ion) interactions. The energy scale of this interaction is 8 K. When comparing this result with other experiments we find that it agrees with the energy scale of the anisotropy found by Schiffer et al. in their susceptibility measurements on SCGO single crystal \cite{Ref2}, but disagrees with Ohta et al. who found a single ion energy two orders of magnitude smaller using EPR \cite{Ref3}.

The conclusions drawn up to now are based on gross features in the data. Now we would like to speculate on how the $p$ dependence of the muon relaxation rate $\lambda(p)$ is shared between the instantaneous field distribution $\langle B^2 \rangle (p)$ and the fluctuation rate $\nu(p)$ which determines it using Eq. 2. First we calibrate $\langle B^2 \rangle (p)$ from the high temperature data where $\lambda$ shows a weak $p$ dependence (See Fig. 2). We assume that $\lambda \propto p^\epsilon$ for large $T$, where $\epsilon$ is a small number. In addition, it is natural to expect $\nu \propto J p^{1/2}$ (where $J$ is a coupling constant) in the high temperature range. Therefore, our calibration leads to $\langle B^2 \rangle (p) \propto p^{1/2+\epsilon}$, an expression which is only slightly different from the dilute limit where $\langle B^2 \rangle (p) \propto p$ ($\epsilon = 1/2$). In SCGO the relation $\langle B^2 \rangle (p) \propto p^{1/2+\epsilon}$ should hold at all temperatures since no static moment develops. Therefore, at base temperature, where $\lambda \propto p^3$ we expect $\nu \propto p^{3-2.5}$, and since we can overrule small values of $\epsilon$ there is a reasonable chance that $\nu \propto p^{-2}$.

In summary the dynamical spin fluctuations in SCGO are controlled by both quantum and activated dynamical processes. The activation energy is a linear function of $p^3$, and indicates the presence of single ion anisotropy with an energy scale of 8 K. This anisotropy might be responsible for the spin glass like behavior of SCGO. The quantum fluctuation time ($1/\nu$) is most likely proportional to $p^3$. Both of the dynamical properties are impartial to the percolation threshold and indicate the local nature of the fluctuations.

We are grateful for the technical support of J. Lord from ISIS and C. Ballard from TRIUMF, A. Keren, Y. J. Uemura, and G. Luke would like to thank the Israel - U. S. Binational Science Foundation and Y. J. Uemura and G. Luke appreciate the NSF-DMR-98-02000 (Columbia), and NEDO International Joint Research Grants for supporting their research.

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Asymmetry

\[ A_0 e^{-t} \]

Time (\(\mu\)sec)

T<0.1K
H=100G

\[ T=5.5K \]
\[ p=0.89 \]

\[ p=0.39 \]
\[ p=0.61 \]
\[ p=0.89 \]

Keren et al. Fig. 1
$\lambda(T=0)$ (\(\mu\text{sec}^{-1}\))

$H$ (G)

$T<0.1\text{K}$

$p=0.89$

$p=0.72$

$p=0.61$

$p=0.39$

Keren et al. Fig. 4
