Magnetic Dilution in the Geometrically Frustrated $SrCr_{9p}Ga_{12-9p}O_{19}$ and the Role of Local Dynamics: A Muon Spin Relaxation Study

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We investigate the spin dynamics of $SrCr_{9p}Ga_{12-9p}O_{19}$ for p below and above the percolation threshold p_c using muon spin relaxation. Our major findings are as follows: (i) At $T \to 0$ 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^3 and $\lim_{p\to 0} U = 8$ 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.

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The $SrCr_{9p}Ga_{12-9p}O_{19}$ [SCGO(p)] compound has been intensely studied experimentally in recent years, as it is believed to be a model compound for a "superdegenerate" antiferromagnet [1–9]. By "superdegenerate" 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. Until now, this question was addressed only theoretically in two of the most famous superdegenerate magnets, the Kagomé [10] and the pyrochlore [11], 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 (μSR) rates as a function of temperature T, magnetic field H, and, most importantly, magnetic ion concentration p above and below 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 led us to another finding regarding the spin Hamiltonian in SCGO. For a long time it was suspected that this Hamiltonian must contain terms other than the Heisenberg one. This is because SCGO shows a spin-glass-like effect in susceptibility experiments, such as a cusp at a temperature $T_f \simeq 4p$ K [2], and a hysteresis between the field cooled and zero field cooled measurements. Neither of these could be understood in terms of Heisenberg spins on Kagomé or pyrochlore lattices [12]. 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 1350C from the stoichiometric mixtures of Cr_2O_3, Ga_2O_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 [3]. The p_c for the Kagomé lattice is 0.6527 and for a pyrochlore slab is not known. Nevertheless, the Curie-Weiss temperature Θ_{cw} in SCGO(p) is a linear function of p with a slope which is different below and above $p = 0.61(5)$ [2], 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) [2].

Our μSR 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 "flat" 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 presented on a log scale. Clearly, at high temperatures the relaxation is closer to exponential. Therefore,

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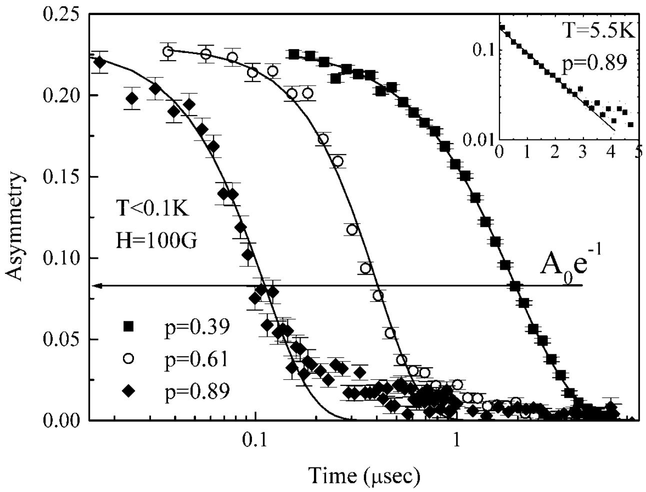

FIG. 1. The asymmetry in the emission of muon decay positrons $\propto P_z(t)$ as a function of time, for three different samples at base temperature, is presented on a semilog scale by the symbols. The solid lines are fits to Eq. (1). The inset shows the asymmetry at high temperature, again on a semilog scale. The solid line represents exponential decay.

the asymmetry waveform is temperature dependent, as was first found in the $p = 0.89$ sample by Uemura *et al.* [5], 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

$$A(t) = A_0 \exp[-(\lambda t)^{\beta}]. \tag{1}$$

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 initial 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 λ and β 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 lifetime (2.2 μs). Therefore, we concentrate here on the early time behavior of $A(t)$.

In Fig. 2 we show λ 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 μSR work [4,5] and more recent NMR measurements [6] on the $p = 0.89$ sample. In Fig. 3a, we depict β versus T for the different p's. As demonstrated previously,

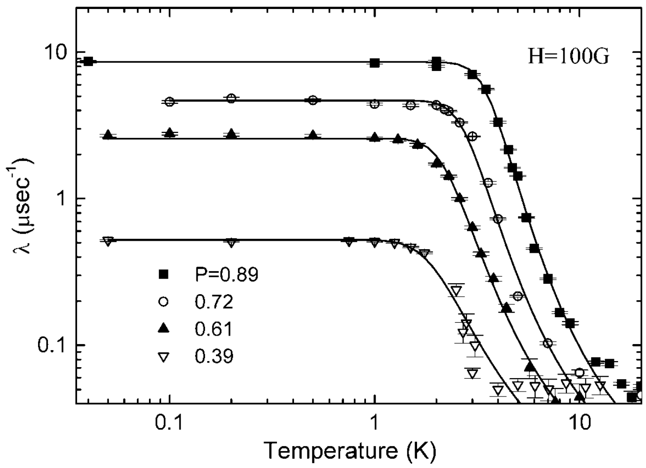

FIG. 2. Muon spin relaxation rates λ as obtained from fits of raw data to Eq. (1) for various values of p. The solid lines are fits to Eq. (3).

the waveform in all our samples is exponential ($\beta \to 1$) at high T but tends to be Gaussian ($\beta \to 2$) 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 semilog scale for all our samples, and in Fig. 3b the field dependence of β. The field dependence of λ 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 $T \to 0$, the value of λ is 10 μs^{-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, for instance, 2 kG, would have been nearly parallel to the initial

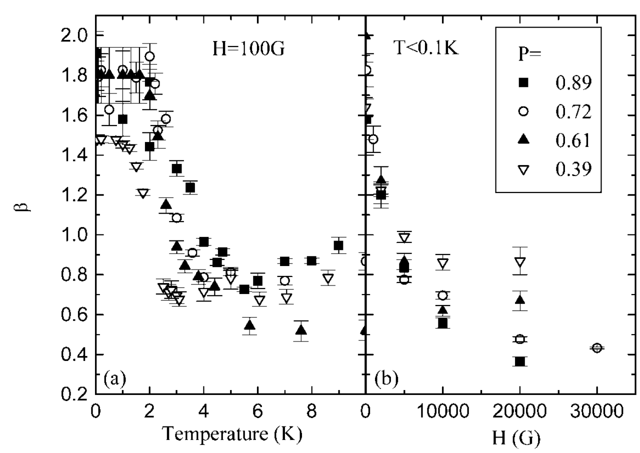

FIG. 3. The exponent β as obtained from a fit of the raw data to Eq. (1) for various values of p, (a) as a function of T at $H = 100$ G, and (b) as a function of H at base temperature.

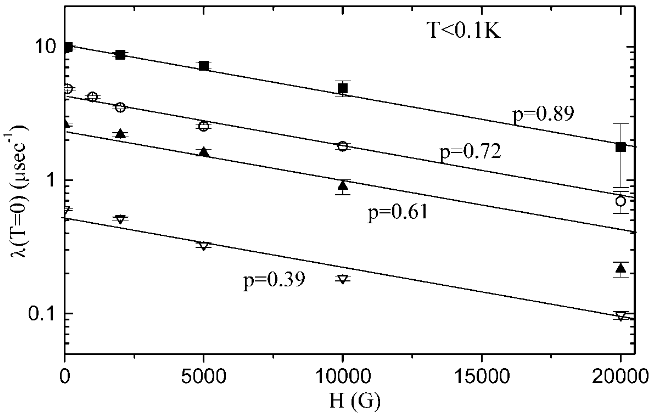

FIG. 4. The field dependence of the muon relaxation rate, plotted on a semilog scale, for various values of p. The solid lines are parallel and are described in the text.

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 random fields, and seems to be due to dynamic field fluctuations.

On the other hand, the waveform is a Gaussian with a λ 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 μSR in SCGO [5]. 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 autocorrelation 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 ν is related to the muon relaxation rate by

$$\nu \propto \langle B^2\rangle \lambda^{-1}, \qquad (2)$$

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

$$\lambda^{-1}(p,T) = Q(P) + C\exp[-U(p)/T], \qquad (3)$$

where $C = 150(10)$ μs 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 molecule system $CrNi_6$ where high-T dynamics is due to over-the-barrier motion, and low-T dynamics is due to quantum fluctuations [13]. 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. 5. This result, together with the field dependence of λ, 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.* [7]. 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.* [1] 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 ω's are k independent.

An extrapolation of $Q^{-1}(p)$ in Fig. 5 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 λ 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

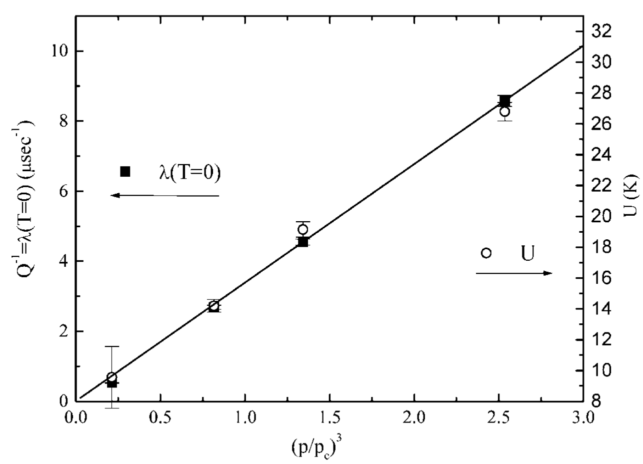

FIG. 5. The parameters Q^{-1} and U of Eq. (3) plotted vs $(p/p_c)^3$.

single crystal [8], but disagrees with Ohta *et al.* who found a single ion energy 2 orders of magnitude smaller using EPR [14].

The conclusions drawn until 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 λ shows a weak p dependence (see Fig. 2). We assume that $\lambda \propto p^{\epsilon}$ for large T, where ϵ is a small number. In addition, it is natural to expect $\nu \propto Jp^{1/2}$ (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 $\nu \propto p^{\epsilon-2.5}$, and since we cannot rule out small values of ϵ 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^2. Both of the dynamical properties are impartial to the percolation threshold and indicate the local nature of the fluctuations.

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