Dynamical Behavior of Spins in the Rare-Earth Kagomé \textit{Pr}_3\textit{Ga}_5\textit{SiO}_{14}

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We report on the use of $^{69,71}$Ga nuclear magnetic resonance to probe spin dynamics in the rare-earth kagomé system \textit{Pr}_3\textit{Ga}_5\textit{SiO}_{14}. We find that the spin-lattice relaxation rate $^{69}/T_1$ exhibits a maximum around 30 K, below which the $^{Pr^{3+}}$ spin correlation time $\tau$ shows novel field-dependent behavior consistent with a field-dependent gap in the excitation spectrum. The spin-spin relaxation rate $^{69}/T_2$ exhibits a peak at a lower temperature (10 K) below which field-dependent power-law behavior close to $T^2$ is observed. These results point to field-induced formation of nanoscale magnetic clusters consistent with recent neutron scattering measurements.

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Various two-dimensional (2D) triangular lattices, including kagomé systems, exhibit intriguing low-temperature spin dynamics induced by a geometrical frustration \cite{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11}. The prototypical kagomé examples are ZnCu$_3$(OH)$_6$Cl$_{12}$ \cite{6}, SrCr$_{8-2x}$Ga$_{4+x}$O$_{19}$ \cite{6}, and the jarosite \cite{3, 4}. These are all 3d transition metal based compounds in which the exchange interactions and geometrical frustration are of dominant importance while Dzyaloshinsky-Moriya interactions, single-ion anisotropies, and off-stoichiometry serve as small perturbations. Nonetheless, investigation of the predicted spin-liquid state is complicated by the presence of these perturbations.

For rare-earth (RE) compounds, the situation might be less complicated: the single-ion anisotropies govern the overall magnetic behavior, while frustration-induced spin dynamics is expected to emerge at energies well below the crystal field splitting. The recently discovered RE based kagomé compounds R$_3$Ga$_5$SiO$_{14}$ (R=Nd or Pr) do show a disordered state at low temperatures \cite{7, 8, 9, 10}. The cooperative magnetic correlations depend on the RE ion involved and the crystal field environment. However, this issue has not yet been fully addressed. It is therefore desirable to study the spin dynamics of \textit{Pr}_3\textit{Ga}_5\textit{SiO}_{14} and to compare the behavior with its isostructural counterpart Nd$_3$Ga$_5$SiO$_{14}$ which has different magneto-crystalline anisotropy \cite{9}. \textit{Pr}_3\textit{Ga}_5\textit{SiO}_{14}, which belongs to the langasite family, has a trigonal crystal structure (P321) with lattice parameters $a = 8.0661(2)$Å and $c = 5.0620(2)$Å. The RE $Pr^{3+}$ ions (5$^2f^2: J = 4$) are networked by corner sharing triangles in well-separated planes to form a distorted lattice (see the inset of Fig. 1) topologically equivalent to the kagomé lattice. Analysis of the specific heat suggests that

the crystal field energy level structure of $Pr^{3+}$ consists of three singlets with gaps $\Delta_1 = 25$ K and $\Delta_2 = 68$ K, and $\Delta_3 = 780$ K \cite{8}. At high temperatures the magnetic susceptibility $\chi$ obeys the Curie-Weiss law with a Curie-Weiss temperature of $\theta_{CW} = -2.3$ K that points to weak antiferromagnetic (AF) correlations between the $Pr^{3+}$ spins \cite{8}. At zero external field \textit{Pr}_3\textit{Ga}_5\textit{SiO}_{14} shows (i) no long-range magnetic ordering at temperatures down to 35 mK, (ii) a $T^2$ dependence of the specific heat at low $T$, and (iii) spin excitations consistent with a highly degenerate state \cite{8}. These suggest that \textit{Pr}_3\textit{Ga}_5\textit{SiO}_{14} has

FIG. 1: (color online). NMR field-scan spectra of \textit{Pr}_3\textit{Ga}_5\textit{SiO}_{14} at 92 MHz showing quadrupolar split $^{69}$Ga ($I = 3/2$) and $^{71}$Ga ($I = 3/2$) components for the three non-equivalent Ga sites. Resolved peaks are labelled central (C) and $\alpha$Ga nuclear magnetic resonance to probe spin dynamics in the rare-earth kagomé system \textit{Pr}_3\textit{Ga}_5\textit{SiO}_{14}. We find that the spin-lattice relaxation rate $^{69}/T_1$ exhibits a maximum around 30 K, below which the $^{Pr^{3+}}$ spin correlation time $\tau$ shows novel field-dependent behavior consistent with a field-dependent gap in the excitation spectrum. The spin-spin relaxation rate $^{69}/T_2$ exhibits a peak at a lower temperature (10 K) below which field-dependent power-law behavior close to $T^2$ is observed. These results point to field-induced formation of nanoscale magnetic clusters consistent with recent neutron scattering measurements.

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a spin-liquid-like ground state corresponding to a high frustration index \( f = \frac{\theta_{CW}}{T_c} \geq 60 \). Application of an external field parallel to the \( c \)-axis leads to the formation of nanoscale magnetic clusters, whose size increases with \( H \). This behavior is accompanied by reduction of the \( T^2 \) component of the specific heat and the opening of a spin gap in the excitation spectrum \[18\].

\( \mu \)SR and NMR measurements on the sister RE kagomé compound Nd\(_3\)Ga\(_5\)SiO\(_{14}\) reveal that a disordered state persists down to low \( T \) in zero field \[19\], \[20\]. Spin fluctuations are suppressed by an applied field and for \( H = 0.5 \) T a field-induced transition is found at 60 mK. Although the two isostructural compounds R\(_3\)Ga\(_5\)SiO\(_{14}\) (R = Pr\(^{3+}\) or Nd\(^{3+}\)) share, to some extent, common physics, detailed cooperative spin dynamics varies with the RE ions. This is because Pr\(^{3+}\) and Nd\(^{3+}\) have different crystal field splittings, single-ion anisotropies, and exchange interactions leading to a substantial difference in low-energy spin dynamics both at zero field and in external field.

In this Letter we present \(^{69,71}\)Ga NMR lineshape and relaxation rate measurements made on Pr\(_3\)Ga\(_5\)SiO\(_{14}\) as a function of temperature in applied fields in the range 2 – 17 T. The objective is to follow the spin dynamical behavior with temperature in the spin liquid regime and to determine how the dynamical behavior depends on large applied magnetic fields. We find that spin-spin relaxation rate is sensitive to field-induced short-range magnetic ordering. This enables us to separate frustration-induced cooperative phenomena from single-ion physics.

Single crystal samples of Pr\(_3\)Ga\(_5\)SiO\(_{14}\) were grown using the traveling floating-zone technique and characterized by X-ray diffraction as described previously \[18\]. The NMR spectra and relaxation rate measurements were obtained using a pulsed spectrometer with quadrature detection.

Figure 2(a) shows the NMR field sweep spectrum obtained by integrating spin-echo signals. Multiple peaks are found corresponding to three non-equivalent sites for the \( I = 3/2 \) \(^{69}\)Ga and \(^{71}\)Ga isotopes each having quadrupolar splittings which give rise to a central line and two satellites due to non-cubic site symmetry. The resulting spectrum consisting of eighteen overlapping lines is similar to that of Nd\(_3\)Ga\(_5\)SiO\(_{14}\) \[20\]. Two Ga sites lie parallel to the kagomé planes and site 3 is randomly occupied by Ga\(^{3+}\) and Si\(^{4+}\) ions \[20\]. The principal components of the spectrum are denoted as C(1) and C(2) for each isotope.

Figure 2(a) plots the measured spectral NMR shift \(^{69}K\) for \( H = 9 \) T along \( c \) versus \( \chi \parallel \) with \( T \) as the implicit parameter while Fig. 2(b) shows the spectra in a stacked plot. The linewidth increases significantly as \( T \) is lowered below 100 K reaching a plateau value of 0.22 T below 10 K. For \( T > 30 \) K a linear relationship between \(^{69}K\) and \( \chi \parallel \) is found. However, departures from this relationship become apparent below 30 K where spin correlation effects become increasingly important.

In order to study the Ga\(^{3+}\) ion spin dynamics, spin-lattice (1/\(T_1\)) and spin-spin (1/\(T_2\)) relaxation rates were measured as functions of temperature for the central \(^{69}\)Ga spectral component corresponding to \(^{69}\)C(1) (see Fig. 2(b)). Relaxation rate measurements were made in several different applied magnetic fields directed parallel to the \( c \)-axis and the results are given in Figs. 3 and 4. Similar results were found for the other spectral components. At low \( T \) the magnetization recovery curve showed stretched exponential form \( M = M_0[1 - \exp(-t/T_2)β] \) where \( β \approx 0.7 \) indicating a distribution of relaxation rates. In contrast to the sister compound Nd\(_3\)Ga\(_5\)SiO\(_{14}\) \[21\] and other transition metal based frustrated 2D antiferromagnets such as NiGa\(_2\)S\(_4\) \[13\], in which the lowest energy gap \( \Delta_1 \) \[14\], in which wipe-out of the NMR signal occurs at low temperatures due to low frequency magnetic fluctuations, the NMR signal in Pr\(_3\)Ga\(_5\)SiO\(_{14}\) could be observed in all applied fields over the temperature range 300 mK to 290 K. As a result, the relaxation rates could be measured over the entire temperature range showing well defined maxima below 30 K, as seen in Figs. 3 and 4 permitting detailed analysis of the data.

As noted above, magnetic contributions to the specific heat are accounted for by assuming low-lying crystal field split states for the Pr\(^{3+}\) ions \[18\]. Following this model, we may expect that, for \( T < 30 \) K, the temperature dependence of the correlation time due to transitions between the ground state and the first excited state should be given by \( \tau = \tau_0\exp(\Delta_1/T) \) with \( \Delta_1 \) the lowest energy gap and the pre-exponential factor \( \tau_0 \sim 10^{-11} \) s. This predicts that for \( T < \Delta_1 \) the correlation time for spin fluctuations will increase rapidly with decreasing \( T \). Behavior of this kind has been found in \( \mu \)SR and Ga NQR relax-
Similarly, we have rate measurements in the quasi-2D AF NiGa$_2$S$_4$ NMR as a function of $T$ at 9 T, together with magnetic specific heat at 9 T whose peak is close to the maximum of $1/\tau_2$. The similarity in behavior of $1/\tau_1$ and $C_{\text{mag}}$ is striking and points to a common underlying mechanism. Inset: log-log plot of points to a common underlying mechanism. Inset: log-log plot of $1/\tau_1$ versus $T$ and $C_{\text{mag}}$ is striking and points to a common underlying mechanism.

Spin-lattice relaxation is attributed to fluctuating hyperfine fields, produced by the electron moments on nearby Pr$^{3+}$ ions, which induce nuclear spin state transitions. The fluctuating local field $H_L$ at a Ga nuclear site is mainly due to dipolar interactions with neighboring electron spins and any transferred hyperfine interaction plays a subsidiary role. The dipolar interaction induces nuclear transitions at the Larmor frequency $\omega_L$ while an isotropic hyperfine interaction will induce mutual electron-nucleus transitions at the much higher frequency $|\omega_L + \omega_S|$ where $\omega_S$ is the electron frequency. For long correlation times the dipolar process is dominant and we can neglect any contributions due to the hyperfine coupling. Assuming that the spin correlation function decays exponentially, the spin-lattice relaxation rate may be written as $1/\tau_1 = C_L(\tau_2 / (1 + \omega_1^2 \tau_2^2))$ where $\tau_2$ is the transverse correlation time for electron spins and $C_L = \gamma^2(H_L^2)$ is the transverse component of the local field $H_L$. Similarly, we have $1/\tau_2 = C_L(\tau_1 / (1 + \omega_2^2 \tau_1^2)) + C_\parallel \tau_1$ with $\tau_1$ being the longitudinal correlation time, $C_\parallel = \gamma^2(H_\parallel^2)$, and $H_\parallel$ the $z$-component of the local field. The expression for $1/\tau_2$ holds provided $\tau_1 < 1/\Delta \omega$ where $\Delta \omega$ is the NMR linewidth of the selected spectral component. For $\tau_1 < 1/\Delta \omega$, $1/\tau_2$ is expected to saturate. The introduction of both transverse and longitudinal electron spin correlation times allows for the possibility of different mechanisms being of dominant importance for $\tau_1$ and $\tau_2$, respectively. A maximum in $1/\tau_1$ occurs for $\omega_1 \tau_2 = 1$ while for higher $T$, in the short correlation time case ($\omega_2 \tau_1 < 1$) the dipolar mechanism leads to $1/\tau_1 \sim C_L \tau_2$ and $1/\tau_2 \sim 1/2 C_L \tau_2 + C_\parallel \tau_1$. Inspection of Fig. 3 shows that for $T > 30$ K, the $1/\tau_1$ and $1/\tau_2$ curves lie close together suggesting that the transverse fluctuations are of dominant importance, corresponding to $C_L > C_\parallel$, for both relaxation rates in this interval. It is likely that $\tau_1 = \tau_2$ at high $T$. Use of the condition for the maximum in $1/\tau_1$ permits $\tau_2$ values to be obtained as a function of $T$ as shown in Fig. 3. Assuming the Arrhenius relation holds in the high-$T$ ($T > 30$ K) region the fitted curve gives $\tau_0 \sim 10^{-11}$ s and the energy gap for spin excitations $\Delta = 98$ K. This is consistent with the crystal field splittings $(\Delta_1 + \Delta_2)$ given by the specific heat results [14]. The energy gap obtained from the slopes of the curves in the low $T$ region of Fig. 3, denoted $\Delta_{\text{NMR}}$, is clearly field-dependent with values plotted versus $H$ in the upper inset. The fitted curve in this plot has the form $\Delta_{\text{NMR}} = \Delta_0 + aH$ where the slope $a \approx g \mu_B$ with $\mu_B$ the Bohr magneton and $g = 3.32$ close to the $g$ value for the Pr$^{3+}$ ion. The magnitude of the zero-field gap, $\Delta_0 = 3.5$ K (see Fig. 3 caption), obtained from the low temperature ($T < 10$ K) NMR relaxation data is much smaller than the high-$T$ NMR value or that from the specific heat results. We note that integrated inelastic neutron scattering data at 35 mK [18] give a field-dependent spin gap in the excitation spectrum strikingly similar to the gap derived from the NMR correlation time behavior as shown in the upper inset in Fig. 3. It is likely that field-suppressed magnetic fluctuations are responsible for the observed field-dependence.

While $1/\tau_1$ decreases at temperatures below the maximum shown in Fig. 3, $1/\tau_2$ continues to increase as $T$ is lowered before passing through a maximum and then decreasing dramatically below 7 K. The behavior is strongly field-dependent and this again points to field suppression of magnetic fluctuations. Fig. 3 compares the behavior of $1/\tau_2$ at 9 T with that of the specific heat at 9 T with the scales adjusted to allow comparison. The magnetic specific heat $C_{\text{mag}}(T)$, which is obtained from the measured $C_P(T)$ by subtracting the lattice contribution using La$_3$Ga$_5$SiO$_{14}$ as a reference, shows $T^2$ behavior for $H = 0.15$ T. The entropy saturates at $R \ln 3$ as expected for a system with three low-lying crystal field states. The temperature dependence of $1/\tau_2$ is strikingly similar to that of $C_{\text{mag}}(T)$ as seen in Fig. 3 (for $H = 9$ T) and this similarity in form points to a common underlying process involved in both observed behaviors linked to the spins entering the singlet ground state at low $T$. Similar behavior is observed in NiGa$_2$S$_4$ where the estimated spin “freezing” temperature $T_f$ is coincident with the peak in $C_{\text{mag}}$, but NMR washout prevents detailed comparison.
with $1/T_2$ [14]. Pr$_3$Ga$_5$SiO$_{14}$, however, allows this comparison to be made over a complete temperature range. Below 7 K occupation of the singlet ground state by the electron spins rapidly increases with decreasing $T$ and both $1/T_2$ and $C_{mag}$ drop to low values. The behavior of $1/T_2$ below 7 K can be accounted for in terms of $\tau_1$ and/or $H_\parallel$. While it is unlikely that $\tau_1$ will shorten at low $T$, local ordering of spins could result in a reduction in $H_\parallel$ leading to a change in the “static” field contribution to $1/T_2$. This effect will be particularly marked if spin ordering occurs in the a-b plane. The NMR spectra for $T < 10$ K show little change in linewidth and the Knight shift is roughly constant (Fig. 2).

The quadratic $T$-dependence of $C_{mag}$ for $H = 0$ T is interpreted as evidence for gapless Goldstone modes. For $H > 0$ T, $C_{mag}(T)$ has a minimum at 80 mK with the low-$T$ upturn ascribed to nuclear contributions to the specific heat [18]. Elastic neutron scattering measurements for $T < 1$ K show that nanoscale ordering occurs in the presence of an applied field consistent with 2D short-range order and give a correlation length of 29 Å ($\sim$ 6 to 7 in-plane lattice spacings) for $H = 9$ T [18]. The present relaxation rate results suggest that at low temperatures the spin correlation time $\tau$ becomes long as shown in Fig. 4 and a possible reduction in the c-axis component of the dipolar field at Ga sites results from in-plane short range ordering leading to the anomalous behavior of $1/T_2$.

In conclusion, we have investigated the spin dynamics in the rare-earth kagomé system Pr$_3$Ga$_5$SiO$_{14}$ via $^{69}$Ga NMR measurements over a complete temperature range without the NMR wipeout effect seen in the sister compound Nd$_3$Ga$_5$SiO$_{14}$. The correlation time $\tau$ for spin fluctuations extracted from the spin-lattice relaxation rate values exhibits novel features; $\tau$ increases with decreasing $T$ and below 30 K the results are consistent with a field-dependent energy gap in the excitation spectrum. The spin-spin relaxation rate shows a maximum close to that in the specific heat and the form of the temperature dependence of these two quantities is very similar below 10 K. This result warrants theoretical attention. The drop in $1/T_2$ below 7 K is attributed to a decrease in the local field at Ga sites linked to field-induced nanoscale ordering of the electron spins in the a-b plane.

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