Easy-Axis Kagome Antiferromagnet: Local-Probe Study of $Nd_3Ga_5SiO_{14}$

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We report a local-probe investigation of the magnetically anisotropic kagome compound $Nd_3Ga_5SiO_{14}$. Our zero-field muon spin relaxation (μSR) results provide direct evidence of a fluctuating collective paramagnetic state down to 60 mK, supported by a wipeout of the Ga nuclear magnetic resonance (NMR) signal below 25 K. At 60 mK a dynamics crossover to a much more static state is observed by μSR in magnetic fields above 0.5 T. Accordingly, the NMR signal is recovered at low T above a threshold field, revealing a rapid temperature and field variation of the magnetic fluctuations.

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The kagome antiferromagnet (KAF), a 2D net of corner-sharing triangles, is one of the most intensively studied examples of geometrically frustrated lattices. In the classical case, extensive degeneracy—a hallmark of frustration—is present in the ground state (GS) manifold, both in the Heisenberg and the Ising limit [1,2]. For the Heisenberg case, "flexible" coplanar configurations which allow for zero-energy weathervane modes, are likely selected by thermal fluctuations [1]. Frustration is even more severe in the Ising limit, where there are minimal spin degrees of freedom to accommodate the competing individual interactions. The system remains disordered at all temperatures, with exponentially decaying pair spin correlations [2]. In the intermediate case, various anisotropy terms [3–5] adding to the Heisenberg Hamiltonian can become important in selecting a particular GS subspace. Anisotropy and an additional magnetic field H, favoring collinear spin configurations, may lead to particularly rich phase diagrams, as, e.g., predicted for the spin-1 KAF [6]. In this context the exciting and mostly unexplored field of KAF with a sizable easy-axis anisotropy, could well yield novel original states.

In the recently discovered $Nd_3Ga_5SiO_{14}$ (NGS) [7], Nd^{3+} ($S = 9/2$) magnetic moments occupy a network of corner-sharing equilateral triangles, topologically equivalent to the perfect kagome lattice if the nearest-neighbor exchange is considered [inset (b) to Fig. 1]. Susceptibility curves [7] display an interesting crossover from an easy-plane to an easy-axis (c axis, perpendicular to kagome planes) behavior below 33 K, as shown in the inset to Fig. 2. Because of this anisotropy and large Nd^{3+} moments, NGS is unique among kagomelike compounds intensively studied in the recent past [8]. The easy-axis low-T behavior, originating from single-ion anisotropy and/or exchange anisotropy due to crystal-field (CF) effects, opens a route to experimental investigation of large-spin Ising-like KAF. The analysis of the high-T susceptibility yielded a Curie-Weiss temperature $\theta_{\mathrm{CW}} = -52$ K, although no irregularities were observed down to 1.6 K [7]. Interestingly, at this low T, a magnetization plateau was observed at around $1/2$ of the saturated (free-ion) value in external fields $\mathbf{H}\|\mathbf{c}$ of only few Tesla [7].

In this Letter we report a series of complementary local-probe measurements, including nuclear magnetic resonance (NMR) and muon spin relaxation (μSR). Our results give a direct evidence of the fluctuating nature of the ground state and the absence of any static order in zero magnetic field. In addition, we investigate a dynamics crossover of the magnetic fluctuations when $\mathbf{H}\|\mathbf{c}$ is applied, toward a more static polarized state. Our findings prove persistent spin fluctuations in the zero-field ground state down to 60 mK, characteristic of a spin-liquid state, which has been recently suggested from the absence of neutron magnetic Bragg peaks and the presence of a weak

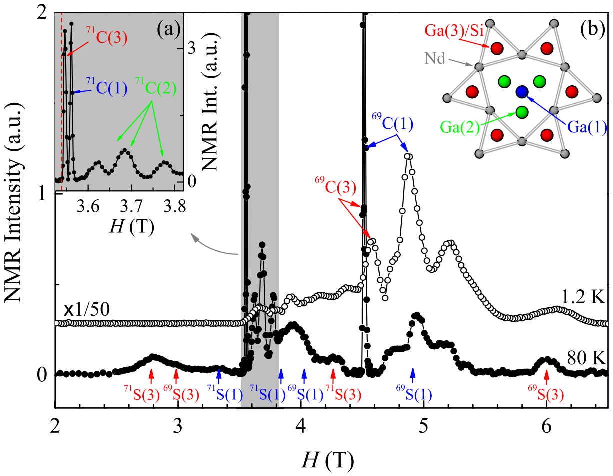

FIG. 1 (color online). ^{69,71}Ga NMR spectra of NGS at 46.01 MHz and $\mathbf{H}\|\mathbf{c}$. The 1.2 K spectrum is translated vertically. Arrows indicate the satellite (S) lines at 80 K. The inset (a) highlights central (C) peaks of the three crystallographically nonequivalent Ga sites at 80 K; the vertical dashed line corresponds to a reference field. The inset (b) shows the network of Nd^{3+} magnetic moments and the location of the in-plane Ga(1) sites and Ga(2, 3) sites separating kagome planes.

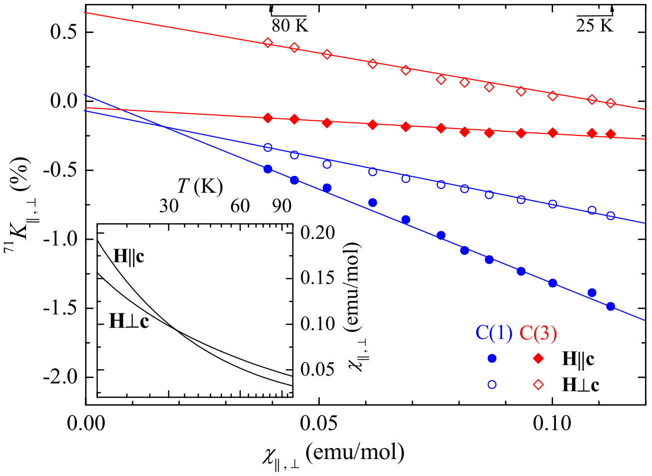

FIG. 2 (color online). Scaling of the ^{71}Ga NMR shift with bulk susceptibility. Inset: The susceptibility crossover at 1 T.

diffuse scattering down to 46 mK [9]. Partial ordering has been also reported under applied field at low T.

Polycrystalline $Nd_3Ga_5SiO_{14}$ samples were synthesized by a solid state reaction and a single crystal of cylindrical shape (2 mm in diameter and 8 mm in length) was grown by a floating zone technique [7]. NMR measurements were performed at various fixed frequencies by sweeping the magnetic field. Nuclear quadrupolar resonance (NQR) was also measured at zero field. Powder μSR measurements were performed on the LTF and GPS spectrometers at PSI, Switzerland.

We first report our Ga NMR investigation. The local magnetic coupling with the Nd^{3+} moments is different for the three crystallographically nonequivalent gallium sites Ga(1, 2, 3) [inset (b) to Fig. 1]. In addition, both ^{69,71}Ga isotopes contribute to the NMR spectrum. Through their sizable quadrupolar moments they are sensitive to local charge distributions, creating crystal electrostatic field gradients (EFG). We assigned all the observed peaks shown in Fig. 1—three sets of central (C) and two satellite (S) lines for each isotope—by performing frequency and angular dependent measurements. We took advantage of the EFG tensors symmetry [10], known gyromagnetic ratios ($^{69}\gamma/^{71}\gamma = 0.7871$), and the ratio of the quadrupolar moments ($^{69}Q/^{71}Q = 1.583$). Since the Ga(3) site is randomly occupied by Ga^{3+} and Si^{4+} [7], a large distribution of quadrupolar frequencies is expected. This results in broad S lines and a broad NQR spectrum [10]. Surprisingly, the distribution of local environments does not lead to glasslike behavior at low T.

In order to eliminate the quadrupolar broadening and get the best accuracy on the local magnetic properties, the magnetic field was applied perpendicular to the kagome planes (**H**$\|$**c**), along a local threefold rotational axis for the Ga(1, 3) sites. This results in narrow C(1, 3) lines, on which we now focus. Their shift $K = (H_0 - H_c)/H_c = A\chi_l + K_0$ of a resonance field H_c from a reference field H_0 is proportional to the local susceptibility χ_l. It has three contributions, which need to be considered in the coupling constant $A = A_{hf} + A_{dd} + A_{dm}$: a hyperfine ($hf$) and a dipolar ($dd$) coupling between Nd^{3+} moments and Ga nuclei, and a macroscopic demagnetization (dm) field. K_0 is a T-independent chemical shift. Our calculation of the dipolar field [11] yields that all these contributions are of a similar magnitude and that the hyperfine coupling is almost isotropic [10]. In Fig. 2 we show the linear scaling of the shift with bulk susceptibility between 80 and 25 K. This proves that the local and the bulk magnetic response are identical and, in particular, the 33 K crossing is also detected by our local-probe measurement. On the contrary, in formerly studied 3d metal kagomelike compounds the intrinsic susceptibility is regularly overshadowed by magnetic defects contributions at low T [8].

Next, we investigate the Nd^{3+} spin dynamics. In Fig. 3(a) we show the T dependence of the ^{71}C(3) spin-lattice relaxation rate $1/T_1$ for **H**$\|$**c**. Its values were obtained by fitting a magnetization recovery curve after saturation to the relaxation function $M_z(t) = M_z[1 - 0.4\exp(-t/T_1) - 0.6\exp(-6t/T_1)]$, suited for magnetic relaxation of the central line in spin-3/2 nuclear systems [12]. The relaxation is rather fast, proving that it is due to rapidly fluctuating dipolar and hyperfine fields, originating from Nd^{3+} moments. With lowering T the magnetic fluctuations are found to slow down considerably, which significantly enhances $1/T_1$ below 100 K and wipes out completely the signal below 25 K. The wipeout is depicted in Fig. 3(b), displaying the T dependence of the NMR intensity. It is caused by the increase of both the spin-lattice and the spin-spin relaxation rate. In a conventional

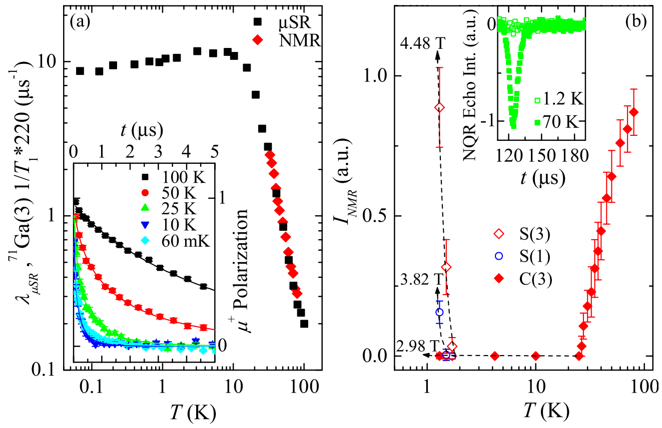

FIG. 3 (color online). (a) Zero-field (ZF) muon spin relaxation rate λ and ^{71}C(3) NMR spin-lattice relaxation rate $1/T_1$ measured at 46.01 MHz (3.55 T) and **H**$\|$**c**. Inset: ZF relaxation of muon polarization. (b) Wipeout of the NMR intensity. The high-T (low-T) data were taken at 46.01 MHz (29.61 MHz) at different fields. Dashed lines are a guide to the eyes. Inset: absence of the NQR echo at 1.2 K and 15 MHz.

transition scenario to a frozen state one would expect the NMR/NQR signal to emerge again below the transition temperature. In contrast, the inset to Fig. 3(b) demonstrates the absence of the NQR signal at 1.2 K, which points to persistent magnetic fluctuations. Similarly, the NMR signal is not detected at 1.2 K in small applied fields ($H \lesssim 3$ T). Only in higher fields the NMR signal is recovered (Figs. 1 and 3). We will address this field-induced effect later.

Further insight into the Nd^{3+} dynamics is provided by zero-field (ZF) μSR measurements. The muon relaxation rate λ could be followed in the full T range from 100 K down to 60 mK and was extracted from a stretched-exponential fit $P(t) = P_0 \exp[-(\lambda t)^\alpha]$ of the muon polarization. The T-independent $\alpha = 0.6(1)$ likely reflects a variety of oxygen, hence μ^+ sites in NGS. In the simplified case of an exponential relaxation, λ is related to the Nd^{3+} magnetic fluctuation rate ν_e by [13]

$$\lambda = \frac{2\gamma_\mu^2 H_\mu^2 \nu_e}{\nu_e^2 + \gamma_\mu^2 H_{\mathrm{LF}}^2}, \tag{1}$$

where $H_\mu = 0.2$ T is the average dipolar field created by the Nd^{3+} spins at the muon sites, $\gamma_\mu/2\pi = 135.5$ MHz/T is the muon gyromagnetic ratio, and H_{LF} stands for the applied longitudinal field if any. The thermal evolution of $\lambda \propto 1/\nu_e$ in zero field, plotted in Fig. 3(a) [14], reflects a strong slowing down of the Nd^{3+} spin fluctuations—from ~200 GHz at 100 K, in agreement with paramagnetic fluctuations governed by the magnitude of the exchange, to ~4 GHz at 10 K. The saturation of λ below 10 K indicates that the slow magnetic fluctuations, likely associated to strongly short-range coupled Nd^{3+} spins, persist in NGS down to 60 mK, which is a fingerprint of a dynamical ground state, observed in many kagomelike [15–19] and pyrochlore [20–22] lattices. In most of these materials the dynamical plateau though coexists with a spin-glass-like transition or even long-range order. Such transitions are regularly observed at the temperature of the plateau onset [15–18,21,22]. Supported by a lack of anomalies in the magnetic susceptibility of NGS [7], the muon relaxation curves, which relax to zero down to 60 mK [inset to Fig. 3(a)], provide direct evidence of the absence of any static magnetic fields emerging from the Nd^{3+} moments. Our μSR data thus support a collective paramagnetic state in NGS, stabilized below 10 K, which makes it together with the recently discovered spin-1/2 Heisenberg system $\mathrm{ZnCu_3(OH)_6Cl_2}$ [23] the only KAF potentially displaying a pure spin-liquid ground state [24].

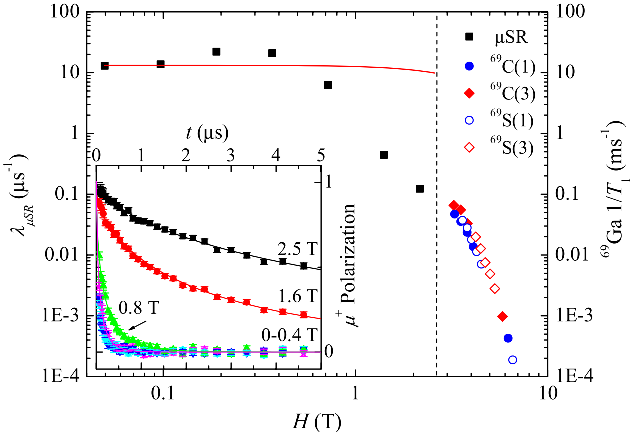

FIG. 4 (color online). Field dependence of the muon relaxation rate λ at 60 mK and the ^{69}Ga NMR $1/T_1$ at 1.2 K on several C and S lines. The solid line gives the predicted H dependence of λ in the dynamical case [Eq. (1)]. Inset: relaxation of muon polarization in various LF fields at 60 mK.

When applying the longitudinal field (LF) at 60 mK, λ varies moderately up to 0.5 T and then suddenly decreases by more than 2 orders of magnitude for $H_{\mathrm{LF}} = 2.5$ T, as visible already in raw relaxation curves (Fig. 4). Such a strong response to H_{LF}, not observed in any other kagome-like compound [16,17,19], cannot be explained within a fast fluctuation regime. Equation (1) predicts a smooth and much slower decrease of λ with the upward shift of the Larmor frequency $\omega_L = \gamma_\mu H_{\mathrm{LF}}$ with respect to the fixed fluctuation rate ν_e [solid line in Fig. 4]. The observed decrease of λ above $H_{\mathrm{LF}} > 0.5$ T demands that the spin dynamics itself, ν_e, is strongly reduced by H_{LF}, which suppresses the spectral density of fluctuations at ω_L. Assuming $H_\mu = 0.2$ T, Eq. (1) gives $\nu_e \approx 10$ MHz at 2.5 T. Therefore, our data point to a field-induced crossover from a dynamical to a more static state for $H_{\mathrm{LF}} > 0.5$ T at 60 mK, in agreement with the recent detection of a static, net-ferromagnetic, state in the same T and H range [9].

The field-suppressed magnetic fluctuations are further reflected in a pronounced H dependence of the NMR spin-lattice relaxation rate $1/T_1$ at 1.2 K, as measured at various fields in the spectra and at various frequencies (Fig. 4). $1/T_1$ is lowered by almost 3 orders of magnitude in a narrow H window between 3 and 6.5 T. This enhanced effect of H on the magnetic fluctuations is responsible for only partial observability of the NMR spectrum at low T. The 3.5 T threshold field at 1.2 K and 46.01 MHz is easily extracted from the missing S(1, 3) lines below this field, as evidenced in Fig. 1. The observed peaks are significantly shifted and broadened with respect to the high-T spectrum. Using the shift of the narrowest ^{71}C(1) line and its high-T coupling constant A, the Nd^{3+} magnetic moment of $1.6\mu_B$, ca. half a value of the full moment, is extracted. Note that this is the mean value of the six moments on the kagome star, to which the Ga(1) is coupled. Individual Nd^{3+} moment could be larger than $1.6\mu_B$ in a nonferromagnetic arrangement on the star. This value is constant above the threshold field, in accordance with previous magnetization measurements [7]. The static line shift and the dynamical relaxation thus exhibit strikingly different H dependence at 1.2 K. When lowering the temperature below the wipeout the NMR signal reappears in a rather narrow low-T range.

In Fig. 3(b) we show that the intensity is completely recovered between 1.7 and 1.2 K at 4.5 T, while at lower fields it is not fully recovered yet at 1.2 K. This points to a rapid temperature variation of the threshold field, which is a strong indication of a field-induced transition in NGS.

On the theoretical side, considerable attention has been recently devoted to the magnetic-field effects on the ground state of the Ising-like KAF, either due to easy-axis single-ion anisotropy (SIKAF) [5,6] or anisotropic exchange (AEKAF) [6,25,26]. Since the CF symmetry on the Nd^{3+} site is low in NGS [7], one expects that the lowest Kramer's doublet essentially describes the low-T physics. *A priori*, one cannot discard single-ion or exchange anisotropy. If the exchange $J = 3|\theta_{\mathrm{CW}}|/4S(S+1) \approx 1.5$ K is much lower than the CF splitting between the ground and excited states the SIKAF picture will apply, otherwise the exchange anisotropy may be important. For this latter AEKAF case, an "exotic ferromagnetic" phase, showing finite magnetization but no conventional order, was predicted at $H = 0$ with a transition temperature $T_c \lesssim 0.08 J_z S/A$, which depends on the asymmetry level $A = J_z/J_{xy}$ [3]. To comply with the absence of transition above 60 mK in NGS, this model would yield a strong easy-axis scenario with $A \gtrsim 10$ which does not fit well with the moderate magnetocrystalline anisotropy observed at low T [7]. NGS is thus likely best described in the SIKAF model with finite single-ion anisotropy D. The susceptibility crossing at 33 K suggests that D is of the order of 10 K. Our NMR results at 1.2 K together with magnetization data at 1.6 K [7] point to a magnetization plateau with $1.6\mu_B$ per Nd^{3+}. It is worth noting that the expectation value of the total angular momentum operator within the ground Kramer's doublet is likely reduced with respect to the full free-ion value ($3.27\mu_B$). Therefore, the magnetization fraction M/M_f on the observed plateau is not accurately known, but $M/M_f \gtrsim 1/2$. In striking contrast, all anisotropy models on the kagome lattice predict a 1/3-magnetization plateau [5,25,26]. This plateau should be stable up to a field of ca. 10 T ($H \sim JS$) [5], in contrast with the experiment.

In conclusion, our results point to the persistence of the fluctuating disordered state in NGS down to 60 mK in zero field. The rather slow fluctuations, $\nu_e \approx 4$ GHz, witness a collective paramagnetic state below 10 K, which is a new relevant energy scale in the system. NGS and $\mathrm{ZnCu_3(OH)_6Cl_2}$ thus enable an experimental verification of theoretical predictions of a spin-liquid ground state for quite different Hamiltonians. The fluctuations in NGS are considerably suppressed by the applied field and signify an unpredicted field-induced phase transition above 0.5 T at 60 mK. Much like in rare-earth based pyrochlores, our results speak in favor of competing single-ion anisotropy and exchange interaction. Such a competition may lead to the observed collective paramagnetism and to its instability against the applied magnetic field.

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