Ground State of the Easy-Axis Rare-Earth Kagome Langasite $Pr_3Ga_5SiO_{14}$

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We report muon spin relaxation and ^{69,71}Ga nuclear quadrupolar resonance local-probe investigations of the kagome compound $Pr_3Ga_5SiO_{14}$. Small quasistatic random internal fields develop below 40 K and persist down to our base temperature of 21 mK. They originate from hyperfine-enhanced ^{141}Pr nuclear magnetism which requires a nonmagnetic Pr^{3+} crystal-field (CF) ground state. In addition, we observe a broad maximum of the relaxation rate at ≃10 K which we attribute to the population of the first excited magnetic CF level. Our results yield a Van Vleck paramagnet picture, at variance with the formerly proposed spin-liquid ground state.

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In magnetic systems, coupled spins are generally expected to condense in an ordered state at low temperatures. Deviations from this paradigm are found in systems possessing substantial frustration, such as the celebrated geometrically frustrated kagome antiferromagnet. This corner-sharing triangular-based lattice indeed yields macroscopically degenerate spin configurations and tends to destabilize any Néel ordered state in favor of a liquid phase. Experimental realizations have been, until very recently, exclusively limited to transition-metal-based magnetism. For spins $S > 1/2$, small perturbations to the purely Heisenberg model, such as magnetic-anisotropy or minute off-stoichiometry, were found to stiffen the spin system in an ordered or glassy ground state [1,2]. Remarkably, in the $S = 1/2$ case, realized in the unique herbertsmithite compound [3], the quantum fluctuations seem to help stabilize the liquid phase [4,5] against such perturbation. The opposite limit of the Ising kagome lattice has been far less investigated due to the scarcity of suitable systems. For large spins ($S > 3/2$) the case of strong, yet finite, easy-axis anisotropy has been shown to be of particular interest. Beyond the Ising model on the kagome lattice, transverse quantum dynamics favor an unconventional semiclassical spin liquid at low temperatures [6]. Additionally, under applied magnetic field, a broad magnetization plateau is predicted [7].

The discovery of new members, $RE_3Ga_5SiO_{14}$ (RE = rare earth) [8], of the langasite family has provided unique realizations of the easy-axis kagome antiferromagnet for RE = Nd, Pr. Both $Nd_3Ga_5SiO_{14}$ (NGS) and $Pr_3Ga_5SiO_{14}$ (PGS) possess the same magnetic net, topologically equivalent to the kagome lattice. The magnetic anisotropy changes to easy-axis-like at low temperature (at 33 K in NGS and at 135 K in PGS). In NGS a fluctuating ground state was evidenced down to 40 mK [9,10], which remains to be fully understood [11]. PGS has been recently argued to be a spin liquid on the verge of spin freezing, which could be induced by increasing the chemical pressure [12]. The spin-liquid ground state was proposed on the basis of the absence of neutron magnetic Bragg peaks and a T^2 low-T dependence of the specific heat [13]. However, no neutron diffuse scattering, characteristic of short-range correlations in spin liquids, was observed. Further, when the magnetic field was applied, magnetic excitations [13] and spin dynamics [14] were drastically affected.

In order to unambiguously determine the zero-field (ZF) ground state of PGS, ZF local techniques—muon spin relaxation (μSR) and nuclear quadrupolar resonance (NQR)—have been used. We report the development of small random static magnetic fields below ~40 K, which persist at least down to 21 mK. We propose that they originate from hyperfine-enhanced ^{141}Pr nuclear moments. This implies that the crystal-field (CF) ground state of Pr^{3+} ions is *nonmagnetic* with a small energy gap to the first magnetic CF level estimated to be 18(3) K from relaxation measurements. We stress that a nonmagnetic ionic ground state is allowed for the non-Kramers Pr^{3+} ions ($J = 4$), at variance with the Kramers Nd^{3+} ions ($J = 9/2$). Our findings contradict the formerly proposed spin-liquid picture [12]. Instead, PGS should be regarded as a Van Vleck paramagnet.

μSR experiments were carried out on polycrystalline samples on the GPS and the LTF spectrometers at PSI, Switzerland, and on the MuSR spectrometer at ISIS, England. The samples were prepared by a solid state reaction. Their purity was verified by x-ray powder diffraction and magnetization measurements. μSR is well established for its unique sensitivity in detecting local magnetic fields, determining their distributions and dynamics [15]. Muons implanted into a sample are initially almost 100% polarized along the beam direction and get depolarized in local magnetic fields.

In Fig. 1(a) we show typical ZF μ^+ relaxation curves, which were measured in a broad T range covering 4 orders of magnitude. The relaxation gradually increases as the temperature is lowered. Below ≃2 K it becomes

T-independent. In the ground state the relaxation curve displays a marked dip at $t_{dip} \simeq 1\ \mu$s [Fig. 1(b)] followed by a slowly decaying tail at longer times which amounts to about 1/3 of the full polarization. The 1/3 tail in powder-sample μSR is regarded as one of the firmest evidences of static magnetism while the lack of oscillations points to frozen disorder [15]. In PGS muons thus experience a broad distribution of randomly oriented static internal fields. Slow fluctuations that, nevertheless, persist down to the base temperature (21 mK) give rise to a slow decay of the 1/3 tail. The width of the static field distribution Δ/γ_μ can be estimated directly from the dip position, $\Delta/\gamma_\mu \simeq 2/(\gamma_\mu t_{dip}) \simeq 20$ G, where $\gamma_\mu = 2\pi \times 135.5$ MHz/T is the muon gyromagnetic ratio. Accordingly, Fig. 1(b) shows that the muon relaxation is mostly suppressed by applying, in the direction of the initial muon polarization, an external field $\simeq 10$ times larger than the internal random static fields. On the other hand, the residual decay observed on the 1/3 tail in zero field demands much higher fields to be suppressed, which confirms its dynamical origin.

The low-T magnetic state in PGS is therefore drastically different from that in NGS, where ZF muon relaxation was monotonic down to the lowest temperatures [10]. Moreover, we stress that the low-T width $\Delta/\gamma_\mu \simeq 20$ G is neither typical for nuclear nor electronic field distributions, the former usually being in the 1 G and the latter in the 1 kG range. For the cases of nuclear ^{141}Pr magnetic moments ($\mu_I = 4.25\mu_N$, where μ_N is the nuclear magneton) and full Pr^{3+} electronic moments ($\mu_J = 3.57\mu_B$, where μ_B is the Bohr magneton) we calculated the dipolar-field-distribution width [16] at the three nonequivalent oxygen sites, in the vicinity of which muons are most likely to reside. The corresponding values for the nuclear and electronic fields are $\Delta_I/\gamma_\mu = 1.5$–1.7 G and $\Delta_J/\gamma_\mu = 2.3$–2.7 kG, respectively. We will address this important issue that severely constrains the nature of the ground state in PGS later on.

In order to track accurately the T dependence of the static magnetism, the ZF data were fitted to the relaxation function $G(t) = G_{VKT}(t)\exp[-(\lambda t)^\alpha] + G_0$ [Fig. 1(a)], where $G_0 = 0.07$ accounts for a constant fraction in our time window, the stretched exponential term $\exp[-(\lambda t)^\alpha]$ accounts for dynamical μ^+ relaxation causing the decay of the 1/3 tail, and $G_{VKT}(t) = \frac{1}{3} + \frac{2}{3}[1-(\Delta t)^\beta)] \times \exp[-(\Delta t)^\beta/\beta]$ is the Voigtian Kubo-Toyabe relaxation expected for random static fields with a distribution that interpolates between a Gaussian ($\beta = 2$) and a Lorentzian ($\beta = 1$) [17]. This model fits nicely the ZF data up to 40 K with a T-independent $\beta = 1.3(1)$, which indicates that the shape of the local field distribution does not change with temperature. It is close to the Lorentzian distribution, which is regularly the case in diluted canonical spin glasses [18], but was observed also in magnetically dense spin glasses [19,20]. The distribution shape may also be affected by the existence of at least three nonequivalent muon sites. The VKT model was adapted to the longitudinal field (LF) case [15] and fits equally well the LF data taken at 1.6 K with fixed values of $\beta = 1.3$ and $\Delta/\gamma_\mu = 26$ G [Fig. 1(b)].

The T dependence of the distribution of frozen fields, as fitted from the ZF data, is presented in Fig. 2. Above 150 K the relaxation is T-independent. As such, it can be assigned to nuclear dipolar fields with a typical Gaussian Kubo-

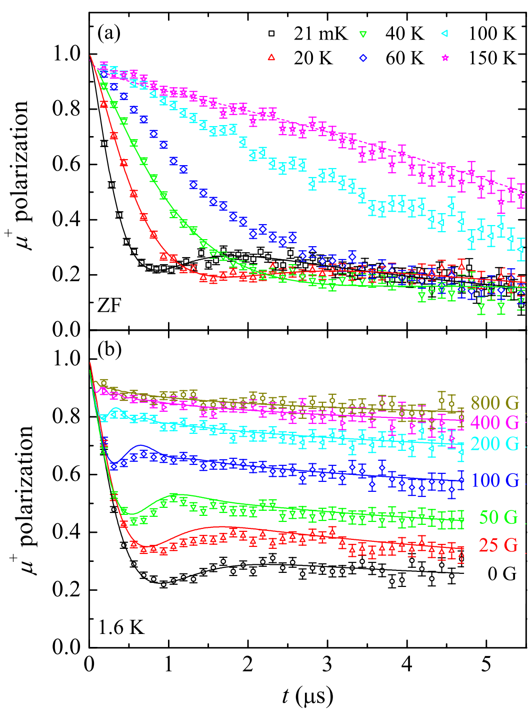

FIG. 1 (color online). (a) T dependence of zero-field (ZF) μ^+ depolarization. Solid lines are fits to the model $G_{VKT}\exp[-(\lambda t)^\alpha]$ with $\beta = 1.3$, while dashed lines correspond to the Gaussian Kubo-Toyabe model. (b) Longitudinal-field decoupling (see text) at 1.6 K. Solid lines show the agreement with the LF Voigtian Kubo-Toyabe model for the same $\beta = 1.3$. The data have been corrected for muons stopping in the sample holder.

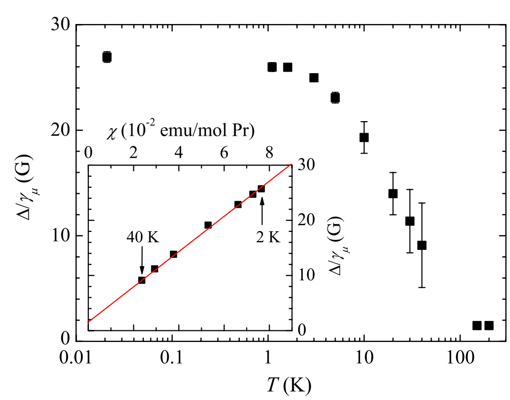

FIG. 2 (color online). Temperature evolution of the width of the static-random-internal-field distribution. The inset proves its linear scaling with bulk susceptibility measured in 10 G.

Toyabe decay corresponding to $\Delta_I/\gamma_\mu = 1.5(3)$ G, in agreement with our calculation, $\Delta_I/\gamma_\mu = 1.5$–$1.7$ G, for ^{141}Pr nuclear spins.

The static magnetism which develops below 40 K is surprisingly weak, which likely justifies the failure of other less sensitive techniques to detect it [12–14]. If the frozen fields were to be ascribed to the Pr^{3+} electronic moments the concentration c and/or the magnitude μ_e of the moments would have to be strongly reduced. From the measured width Δ/γ_μ of the frozen field distribution and the relation $c\mu_e = \sqrt{2/\pi}\mu_J\Delta/\Delta_J$ [18], we compute $c = 0.007$ for $\mu_e = \mu_J$. In principle, it is possible that the ground state of the non-Kramers Pr^{3+} ion in PGS is nonmagnetic, except at some rare sites where, because of the random Ga^{3+}/Si^{4+} disorder on one of the Ga sites [8], the CF would favor a magnetic ground state. This scenario, however, can be ruled out since (i) PGS is an insulator so there exists no long-range interaction that could induce a spin-glass state at 40 K for a concentration of moments far below the site percolation threshold $c_p = 0.65$ of the kagome lattice. The main interaction should be the short-range exchange coupling, which is in praseodymium oxides usually in the sub-Kelvin range [21]. (ii) In the diluted electronic spin-glass scenario, one would expect a Schottky peak at 170 mK [22] due to the hyperfine splitting of the ^{141}Pr nuclear levels, which is not observed experimentally [13]. (iii) The random Ga^{3+}/Si^{4+} distribution would not yield such a small concentration c.

We therefore propose an alternative scenario—enhanced nuclear magnetism—which is well documented for materials based on non-Kramers rare earths with a nonmagnetic CF ground state and a strong hyperfine coupling A [23–25]. Although these materials are nonmagnetic, they do possess a large Van Vleck susceptibility χ due to the proximity of low-lying magnetic CF levels. The electronic shell can thus be polarized by the nuclear magnetic moments through the hyperfine coupling, and the nuclear moments μ_I become effectively enhanced by a factor $1 + K = 1 + A\chi$ [25]. On the muon time scale, the nuclear magnetism is static and disordered. This yields the usual nuclear Kubo-Toyabe relaxation but with an enhanced width of the field distribution $\Delta/\gamma_\mu = (1 + A\chi)\Delta_I/\gamma_\mu$ as compared to the bare-nuclei width Δ_I/γ_μ.

In PGS the field-distribution width indeed scales linearly with bulk magnetic susceptibility below 40 K (inset of Fig. 2). The width of 1.8(2) G obtained by extrapolation to zero susceptibility is in agreement with the 1.5(3) G value deduced from ZF data above 150 K and with our calculations, 1.5–1.7 G. The slope $A\Delta_I/\gamma_\mu = 314$ G mol/emu yields the hyperfine coupling constant $A = 174(20)$ emu/mol, in perfect agreement with 187.7 emu/mol reported for Pr^{3+} [21,23]. The enhancement factor thus reaches the value $K = 15$ at low temperatures, very similar to other Pr-based compounds [21,26,27]. Our ZF μSR results can therefore be perfectly explained in the framework of the enhanced nuclear magnetism, which proves that the ground CF state in PGS is nonmagnetic. At higher temperatures, for $T \gtrsim \Delta_{CF}$, where Δ_{CF} is the gap to the first exited magnetic CF level, the Pr^{3+} ions acquire a spontaneous fluctuating electronic moment. The hyperfine field is then motivationally narrowed in ZF and nuclear enhancement is suppressed [24]. Accordingly, our ZF data above 40 K show a combination of static nuclear magnetism, observed above 150 K, and T-dependent electronic spin dynamics.

Since static internal fields are small in PGS, one can easily decouple muons from them by applying moderate longitudinal fields (500 G). The remaining relaxation is then due to spin dynamics only. As shown in Fig. 3, the relaxation was fitted satisfactorily using a stretched exponential model with a T-independent stretch exponent $\alpha = 0.40(3)$. The dynamical μ^+ relaxation rate λ exhibits a maximum around 10 K (Fig. 4), which points to a substantial T dependence of the magnetic fluctuations. The latter persist down to the lowest temperatures, since the decay of the 1/3 tail in ZF μSR is present even at 21 mK [Fig. 1(a)].

In the context where recent NMR experiments suggested that the magnetic fluctuations in PGS are drastically affected by the applied field [14], we performed a complementary ZF study using ^{69}Ga ($I = 3/2$) NQR. The μSR and NQR T dependences of the relaxation rate are similar. In passing we note that this similarity excludes the possibility that the μ^+ charge has any appreciable effect on the near-neighbor Pr^{3+} CF levels in PGS, as observed in few other Pr-based compounds [28,29].

The decrease of the NQR relaxation rate below 10 K can be fitted to the spin-gap expression $1/T_1 = 1/T_1^0 + B\exp[-\Delta_{CF}/T]$ (Fig. 4), with $\Delta_{CF} = 18(3)$ K and a residual relaxation $1/T_1^0 = 0.075\ \mathrm{ms}^{-1}$ for $T \to 0$. The gap Δ_{CF} is in agreement with the inelastic neutron scattering (INS) peak observed at 1.3–1.4 meV [13,30] and with CF calculations [30]. The INS peak is rather broad suggesting distributed CF energy levels [30], which one can attribute to random Ga^{3+}/Si^{4+} disorder [8]. This is reflected in a broad distribution of local environments and leads to very

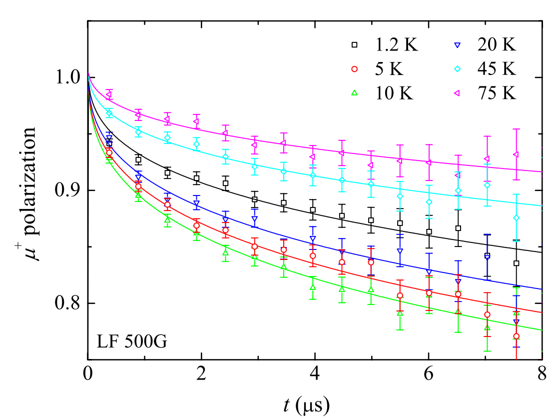

FIG. 3 (color online). T-dependent μ^+ depolarization in a 500 G longitudinal field.

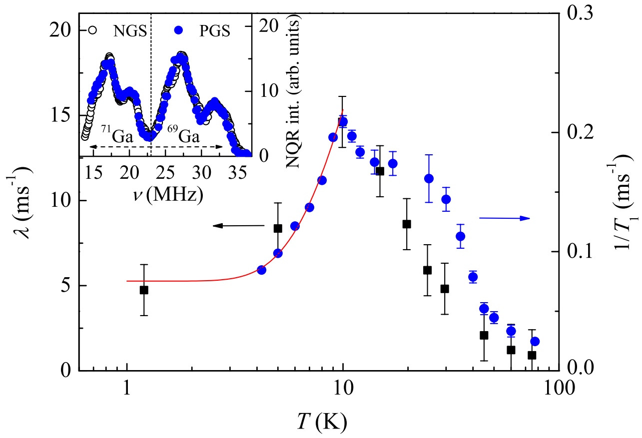

FIG. 4 (color online). μ^+ relaxation rate λ in LF 500 G (squares) and NQR spin-lattice relaxation rate $1/T_1$ measured at 27 MHz (circles). Solid line corresponds to the fit to the spin-gap model [$\Delta_{CF} = 18(3)$ K] with residual zero-temperatures relaxation. The inset shows comparison of the NQR spectra recorded in $Pr_3Ga_5SiO_{14}$ (PGS) and $Nd_3Ga_5SiO_{14}$ (NGS) at 80 K.

broad ^{69,71}Ga ($I = 3/2$) NQR spectra in PGS and NGS (inset of Fig. 4), instead of the expected pair of narrow lines [31]. This broad distribution could be at the origin of the Voigtian μ^+ decay instead of the expected Gaussian one.

Both μSR and NQR measurements point to residual dynamics at low T, extending down to at least 21 mK, as evidenced by the dynamical decay of the ZF μSR polarization [Fig. 1(a)]. Since the dynamics are present even for $T \simeq \Delta_{CF}/1000$, they are intrinsic to the nonmagnetic ground state and not due to fluctuations between the ground state and magnetic levels. The corresponding magnetic fluctuations rate $\nu \sim 100$ kHz gives an estimate of the ^{141}Pr-^{141}Pr coupling $J_n = h\nu \sim 5$ μK. This indirect nuclear coupling is mediated by the electronic coupling [23] $J_e = J_n(g_J\mu_B I/K\mu_I)^2 \sim 15$ mK. The latter admixes excited CF states into the ground CF singlet, which otherwise has a quenched total angular momentum in isolated ions. This is not in contradiction with the Van Vleck paramagnet picture, because in PGS J_e/Δ_{CF} is far below the critical value which would allow ground-state moments to form spontaneously [32].

In conclusion, we have found a very weak quasistatic magnetism in PGS which originates from hyperfine-enhanced ^{141}Pr nuclear magnetism. This enhancement unambiguously assigns PGS to be a Van Vleck paramagnet, which excludes the possibility of a collective spin-singlet ground state. Much like the rich family of pyrochlores, langasites seem to present a variety of physical behaviors associated with the nature of the rare-earth ion. Our study calls for future in-depth investigations of the single-ion properties of other members of the family; e.g., spin liquids should be found for Kramers ions with potentially enhanced exchange coupling. The langasite family certainly opens the way to a new confrontation between theory and experiments on kagome lattices with strong local anisotropy. Finally, our study serves as the zero-field basis to understand the surprising development of short-range spin correlations in PGS at much higher temperatures under an applied field [13].

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