Nanoscale freezing of the 2D spin liquid Pr₃Ga₅SiO₁₄

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In this letter, we report on the single crystal growth and physical characterization of the distorted kagomé system Pr₃Ga₅SiO₁₄. It is found that at zero magnetic field the system shows no magnetic order down to 0.035 K and exhibits a T² behavior for the specific heat at low temperatures, indicative of a gapless 2D spin liquid state. Application of an applied field induces nanoscale islands of ordered spins, with a concomitant reduction of the T² specific heat term. This state could be a possible ferro-spin nematic ordering stabilized out of an unusual spin liquid state.

One of the desired targets of modern materials science is the realization of model magnetic systems to test physical laws. In the field of geometrically frustrated magnetism, the Hamiltonians for many lattices have been expressed for various two dimensional and three dimensional sublattices, such as the triangular lattice and the pyrochlores, and experimental analogues have been well studied[1]. However, the two dimensional kagomé lattice has proved to be more difficult to synthesize, as many examples found in the literature (such as SrGa₄₋ₓGa₄+xO₁₉, or SCGO) have site disorder issues, or are difficult to produce in single crystalline form[2]. Jarosites, Such as (D₃O)Fe₃(SO₄)₂(OH)₆ (OD), have a similar problem with a significant amount of Fe vacancies for many species of this family[3]. Recently, the paratetramate family Zn₂Cu₄₋ₓ(OH)₆Cl₁₂[4], which shows a spin liquid state, was reported. These materials not only have “structurally perfect” bond angles for the kagomé lattice - they are also composed of s = 1/2 Cu²⁺ spins. It has been shown that these materials are excellent testing grounds for the resonating-valence-bond state predicted by Anderson[5], which has relevance not only for the study of quantum spin liquids, but also for studies of high-temperature superconductors and other low-dimensional magnetic systems. However, the issue of site disorder of the paratetramate still needs to be addressed.

Many quantum and classical theories for the kagomé lattice predict ordered ground states (typically with a √3 × √3 structure). The exceptions to this trend include SCGO, the jarosite (D₃O)Fe₃(SO₄)₂(OD), and the newly discovered paratetramates Zn₂Cu₄₋ₓ(OH)₆Cl₁₂. All of these compounds exhibit unconventional spin freezing at low temperatures. The former compounds exhibit, for example, a T² magnetic component to the specific heat (rather than linear component as expected for a spin glass)[2]. The paratetramate shows a sublinear T component that is believed to be the result of a Fermi surface of quantum excitations appearing at low temperatures, although this has yet to be confirmed with single crystals[6]. All of these samples show dynamics on slow time scales that can be resolved with high resolution inelastic neutron scattering[7], muon spin relaxation[8] or NMR[9]. The origin for these slow spin dynamics is thought to lie with persistent two dimensional quantum fluctuations which stabilize a spin liquid state, even in the case of the larger spins with Cr³⁺ (S = 3/2) and Fe³⁺ (S = 5/2).

In this letter, we report the single crystal growth and characterization of the distorted kagomé system Pr₃Ga₅SiO₁₄. This material has a two dimensional lattice of Pr³⁺ spins (J = 4) with weak antiferromagnetic coupling (θCW = -2.3 K). Neutron scattering experiments fail to show any ordering in zero applied magnetic fields down to 35 mK, despite the presence of a broad peak in the heat capacity at T = 6.7 K. The presence of a T² component in the heat capacity is correlated with low energy two dimensional spin excitations. Application of an external magnetic field perpendicular to the two dimensional layers induces a gap in the spin excitation spectrum, but magnetic Bragg peaks indicative of ordering do not appear. There is only diffuse scattering present up to H = 9 T which is modeled with the formation of nanoscale islands of ordered spins. This sort of ordering has been seen in other two dimensional systems such as NiGa₂S₄[10], but has only now been observed in a kagomé lattice with applied fields. This state could be a possible ferro-spin nematic ordering stabilized out of an unusual spin liquid state.

A single crystal of Pr₃Ga₅SiO₁₄ was grown by the traveling-solvent floating-zone technique. The room-temperature structure was determined with an X-ray diffractometer equipped with Cu Kα1 radiation. X-ray
Laue diffraction was used to orient the crystal. The magnetic-susceptibility measurements were made with a DC superconducting interference device (SQUID) magnetometer; the measurements were made on heating after cooling in zero field and with applied magnetic field (H = 1 T) parallel to the longest dimension of the sample. The specific heat and AC susceptibility measurements were made with a physical property measurement system on single crystals with applied fields parallel to the c axis. A dilution fridge was used to collect specific heat data below 0.4 K. Neutron scattering measurements were completed at the NIST CHRNS using the Disk Chopper Spectrometer with a wavelength of 5.0 Å. The crystal (total mass of 5 g) was aligned in the ab plane with a vertical magnetic field applied in the c direction. A dilution fridge was used which had a base temperature of 0.035 K.

Pr$_3$Ga$_5$SiO$_{14}$ crystallizes in the trigonal space group P321 with lattice parameters $a = 8.0661(2)$ Å and $c = 5.0620(2)$ Å (Fig. 1(c)). The Pr$^{3+}$ magnetic ions in Pr$_3$Ga$_5$SiO$_{14}$ are organized in corner sharing triangles in well-separated planes perpendicular to the c axis. Within each plane, the Pr$^{3+}$ ions form a distorted kagomé lattice (Fig. 1(a)), which is topologically equivalent to the ideal kagomé when only the shortest atom bridging interactions are considered. The nearest Pr-Pr separation in the ab plane is 4.2 Å (Fig. 1(a)).

Figure 1(b) shows the temperature dependences of the specific heat $C_p(T)$ and the magnetic susceptibility $\chi(T)$ for Pr$_3$Ga$_5$SiO$_{14}$ and La$_3$Ga$_5$SiO$_{14}$. (d) Magnetic contribution of specific heat after subtracting the Schottky anomaly and lattice contribution.

The specific heat data, $C_p(T)$, also shows no evidence of a phase transition down to 0.1 K in zero field (Fig. 2(a)) and (c). The magnetic specific heat $C_{mag}(T)/T$ after subtraction of the lattice contribution ($C_p(T)$ of La$_3$Ga$_5$SiO$_{14}$ with no magnetic ions) exhibits a broad peak at $T_{peak} = 6.7$ K. The integration of $C_{mag}(T)/T$ gives an entropy $S_{mag} = 8.5$ J/mol-K (circles in Fig. 2(b)) near 200 K, which is approaching Rh3 ($R$ is the gas constant). This value suggests that the crystal field scheme of Pr$^{3+}$ below 200 K could be (i) three singlet levels, (ii) a dou-blet ground state and a singlet excitation level, or (iii) a singlet ground state and a doublet excitation level. These three possibilities have been tested with the experimen-
tal data - the best fit is obtained from the three singlet level scheme with $\Delta_1 = 25$ K and $\Delta_2 = 117$ K. This is in good agreement with earlier studies on the related garnet structure Pr$_3$Ga$_5$O$_{12}$, which has three singlets with an energy separation of $\Delta_1 = 26$ K and $\Delta_2 = 68$ K.[11] It would be unusual if Pr$_3$Ga$_5$SiO$_{14}$, of lower site symmetry, would have doublets if the cubic garnet structure is already composed of low temperature singlets. The next singlet of Pr$_3$Ga$_5$O$_{12}$ is at $T = 780$ K, and this is not seen in our specific heat data. The calculated data (the line in Fig. 2(b)) fits experimental data well at high temperatures; but at low temperatures the experimental data shows a more broad peak and larger value of specific heat below $T_{\text{peak}}$. The origin for this feature is the broadening of the crystal field levels due to correlation effects, as seen in other spin liquid candidates such as Tb$_2$Ti$_2$O$_7$.[12]

At low temperatures (Fig. 2(c)), the nuclear Schottky anomaly introduces an upturn in the specific heat, which can be fit with a $T^{-2}$ term. After the substraction of this anomaly and the lattice contribution, the magnetic contribution of the specific heat at zero field exhibits power-law behavior at low temperatures (Fig. 2(d)). The data between 0.1 K and 4 K are well fitted by a power law $C_{\text{mag}} = AT^\alpha$, where $A$ is a constant and $\alpha = 1.98(2)$. Two dimensional (2D) spin excitations would give $C \sim T^2$. This quadratic temperature dependence without long-range magnetic order indicates the presence of gapless linear modes in 2D, similar to other 2D kagome systems such as SCGO.[2]

In general, a peak in $C(T)/T$ results from a peak in the density of states, $g(w)$, defined as $U = \int dw g(w)n(w)w$, where $U$ is the internal energy, $n(w)$ is the Bose population factor, and the integral is taken over the excitation bandwidth. Usually, the temperature of the $C(T)/T$ peak is roughly half the mode energy. Applying this rule here, a peak in $g(w)$ is expected at $\hbar\omega_0 \sim 13$ K. In order to confirm this prediction, inelastic neutron scattering experiments were completed. In Fig. 3(c), the results of the integrated intensity scans are shown as a function of applied field. Note that at zero field there is a broad peak at $E = 1.2$ meV $\sim 13$ K, which is consistent with the temperature of the specific heat peak.

In summary, the zero field data on single crystalline Pr$_3$Ga$_5$SiO$_{14}$ shows the following low temperature properties: (i) the absence of long-range magnetic order; (ii) the absence of magnetic diffuse scattering; (iii) a $T^2$ dependence of the specific heat; and (iv) the existence of spin excitations related to a highly degenerate state as $T$ approaches zero. These properties place strong constraints on possible ground states. Observations (i), (iii), and (iv) are consistent with a spin liquid with no conventional long-range magnetic order, such as observed in the triangular lattice NiGa$_2$S$_4$[10] and hyper-kagome Na$_2$Ir$_3$O$_8$[13]. However, the absence of magnetic diffuse scattering is unusual. One possibility is that the spins are truly dynamic on the neutron time scale. The AC susceptibility (Fig. 3(a, b)) shows no anomaly, nor any frequency dependence down to 1.8 K, which also indicates that the characteristic fluctuation rate is beyond the kHz region. The featureless AC susceptibility data also excludes the possibility that Pr$_3$Ga$_5$SiO$_{14}$ is a spin glass at low temperatures.

![Figure 3: Temperature dependences of the AC susceptibility.](image-url)

The specific heat measured at magnetic fields (Fig. 2(d)) shows that the absolute value becomes smaller and $T^2$ behavior disappears. These field-dependent behaviors can be related to the inelastic spin excitation (Fig. 3(c)), which is clearly suppressed by applied fields. The suppression of the density of states of the 2D spin excitations in higher fields is clear from the neutron scattering data. The elastic neutron pattern at 0.035 K with $H = 9$ T (Inset of Fig. 1(c)) shows no extra peak and intensity compared to the zero field pattern, which means no long-range magnetic order is stabilized. However, significant diffuse scattering appears near $Q = 0.78$ Â (Fig. 4(a)) with $H = 9$ T. The form of this diffuse scattering of a broad asymmetric peak (a sharp rise at low $Q$ and a slow fall off toward high $Q$) is characteristic of two-dimensional short-range order. The scattering from Pr$_3$Ga$_5$SiO$_{14}$ can be described analytically by a modified Warren function for 2D magnetic correlations[14]. The structure factor $F_{2g}$, around the peak is expressed by:
clusters induces a spin gap in the excitation spectrum, and subsequently reduces the $T^2$ component of the specific heat.

For the studied geometrically frustrated systems, such as SCGO[2], NiGa$_2$S$_4$[10], and Na$_2$Ir$_3$O$_8$[13], one common feature is that the $T^2$ behavior of specific heat is independent of the applied magnetic field, suggesting that the ground state consists of moment free spin clusters. In contrast, Pr$_3$Ga$_5$SiO$_{14}$ studied here has a $T^2$ behavior which is sensitive to magnetic fields with a gap opening in the spin excitation spectrum. One of the possible states which could correspond to such behavior is the recently predicted spin nematic that should appear in two dimensional triangle-based lattices[15, 16]. However, most of these models in the literature lack terms in the Hamiltonian to express the crystal field effects of the Pr$^{3+}$ sites (they are modeled on Heisenberg like transition metal systems with quenched orbital angular momentum). Despite this, we can rule out the presence of a non-collinear spin nematic[15], since much of the spin excitation spectrum is gapped out within the $ab$ plane. A ferro-nematic state, as mentioned by Bhattacharjee et al.[16], in which the moment is spatially uniform and the excitations are polarized, is a more likely possibility. Future experiments are clearly needed to verify or refute this scenario.

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[1] J. E. Greedan, J. Mater. Chem. 11, 37 (2001).
[2] R. J. Ramirez et al., Phys. Rev. Lett. 84, 2957 (2000).
[3] A. S. Wills et al., Europhys. Lett. 42, 325 (1998).
[4] J. H. Helton et al., Phys. Rev. Lett. 98, 107204 (2007).
[5] S. H. Lee et al., Nature Materials 6, 853 (2007).
[6] M. Hermele et al., Phys. Rev. B 77, 224413 (2008).
[7] B. D. Gaulin et al., Phys. Rev. Lett. 69, 3244 (1992).
[8] Y. J. Uemura et al., Phys. Rev. Lett. 73, 3306 (1994).
[9] A. Olariu et al., Phys. Rev. Lett. 100, 087202 (2008).
[10] S. Nakatsuji et al., Science 309, 1697 (2005).
[11] F. N. Hooge, J. Chem.Phy. 45, 4504 (1966).
[12] M. J. P. Gingras et al., Phys. Rev. Lett. 62, 6496 (2000).
[13] Y. Okamoto et al., Phys. Rev. Lett. 99, 137207 (2007).
[14] A. S. Wills et al., Chem. Mater. 11, 1936 (1999).
[15] H. Tsunetsugu and M. Arikawa, J. Phys. Soc. Jpn. 75, 083701 (2006).
[16] S. Bhattacharjee et al., Phys. Rev. B 74, 092406 (2006).