Structures & Dynamics

Absence of long-range magnetic ordering in the spin-liquid candidate, $Pr_3Ga_5SiO_{14}$

H.J. Silverstein,[1] H.D. Zhou,[3] R.L. Donaberger,[4] and C.R. Wiebe[1,2]

[1] Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada
[2] Department of Chemistry, University of Winnipeg, Winnipeg, MB, Canada
[3] National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, USA
[4] NRC Canadian Neutron Beam Centre, Chalk River Laboratories, Chalk River, ON, Canada

Materials with a 2D kagomé substructure widely regarded by physicists for their vast display of physical properties displayed by these systems as a result of being geometrical frustrated. Examples of these materials include natural minerals herbertsmithite ($ZnCu_3(OH)_6Cl_{12}$, S = 1/2) [1] and jarosite ($KFe_3(OH)_6(SO_4)_2$, S = 5/2) [2], as well as synthetic compounds $Ba_3NbFe_3Si_2O_{14}$ [3] and $Nd_3Ga_5SiO_{14}$ (S = 3/2) [4]. The latter two are part of a vast series of compounds called the langasites; the former is a multiferroic while the latter, a previous spin-liquid candidate, was shown to have surprisingly small exchange interactions between moments. Spin-liquids are systems with highly degenerate, dynamic ground states. Studied because of their apparent violation of the third law of thermodynamics, these systems are few in number but may include herbertsmithite, $Tb_2Ti_2O_7$ [5], $Yb_2Ti_2O_7$ [6] and quite possibly $Pr_3Ga_5SiO_{14}$ [7].

Magnetic susceptibility measurements on $Pr_3Ga_5SiO_{14}$, a non-Kramers ion antiferromagnet (J = 4), show no signs of magnetic ordering down to at least 1.8 K, while the specific heat capacity has a T^2 dependence characteristic of two-dimensional systems (Figure 1). In the past, it has been argued using μSR that the absence of long-range order rather reflects a Van-Vleck paramagnetic state while EPR and NMR studies seem to indicate that this compound is, indeed, magnetic (Figure 2) [7-9]. If weak, dynamic correlations do exist in this system, one would expect to see diffuse scattering around Bragg peaks as the temperature decreases. A weak magnetic field should induce some of the spins to order parallel to it. Neutron scattering measurements were taken on the Disc Chopper Spectrometer on single crystalline $Pr_3Ga_5SiO_{14}$ aligned in the *ab* plane with a 9T magnetic field applied in the *c* direction. Figure 3 shows 'rod-like' Bragg peaks and diffuse scattering around (010) and (100) peaks by taking advantage of the upper and lower banks of detectors covering a range of ±2.9° out of the plane. This is indicative of weak, magnetic correlations within 2D kagomé layers. Diffuse scattering can be induced in fields as low as 2 T.

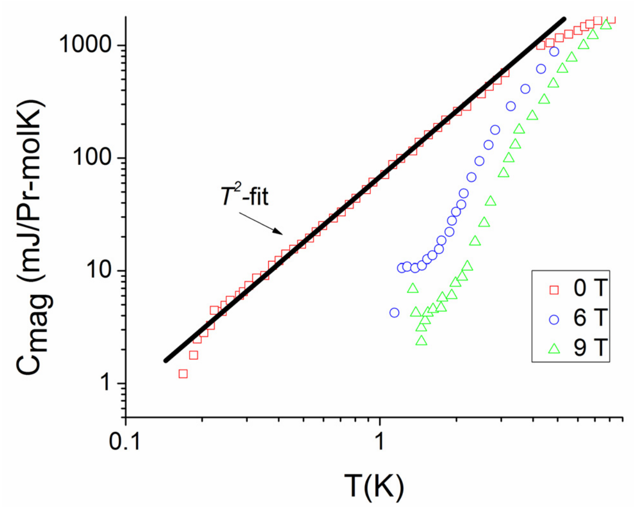

Fig. 1 The magnetic specific heat was obtained by subtracting the Schottky anomaly and lattice component. Data taken from L.L. Lumata et al, Phys. Rev. B (2010) [7].

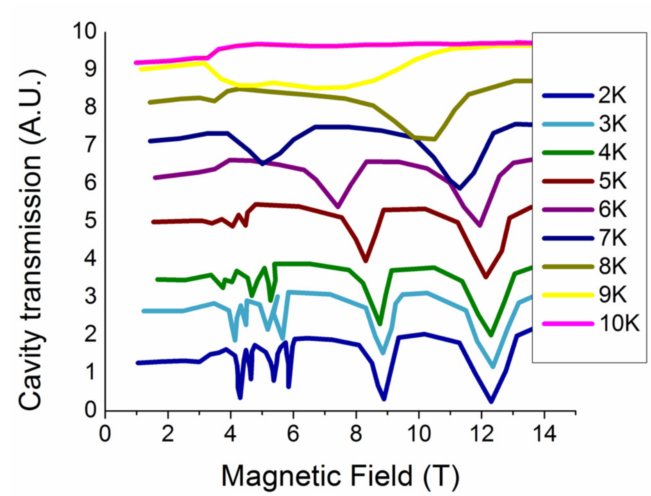

Fig. 2 127 GHz EPR spectrum for $Pr_3Ga_5SiO_{14}$. The complex pattern shifting with temperatures is highly unusual for paramagnetic compounds. Data taken from S. Ghosh *et al* EPR (2011) [9].

In order to show the existence of a spin liquid state, one must first show the absence of long-range order in the system. Since the single crystal sample was aligned in the *ab* plane, the possibility of magnetic ordering in the *ac* plane cannot be ruled out, even with scattering data from the upper and lower banks of detectors on the DCS instrument. To solve this issue, we crushed single crystal $Pr_3Ga_5SiO_{14}$ into a powder and preformed a neutron scattering experiment on the C2 diffractometer using a novel mounting method for sub-kelvin diffraction developed at Chalk River [10]. Figure 4 shows no long range order down to at least 300 mK. This neutron diffraction work, coupled with previous NMR, EPR, and neutron measurements, provide a compelling case for spin liquid behaviour in this compound rather than a non-magnetic ground state.

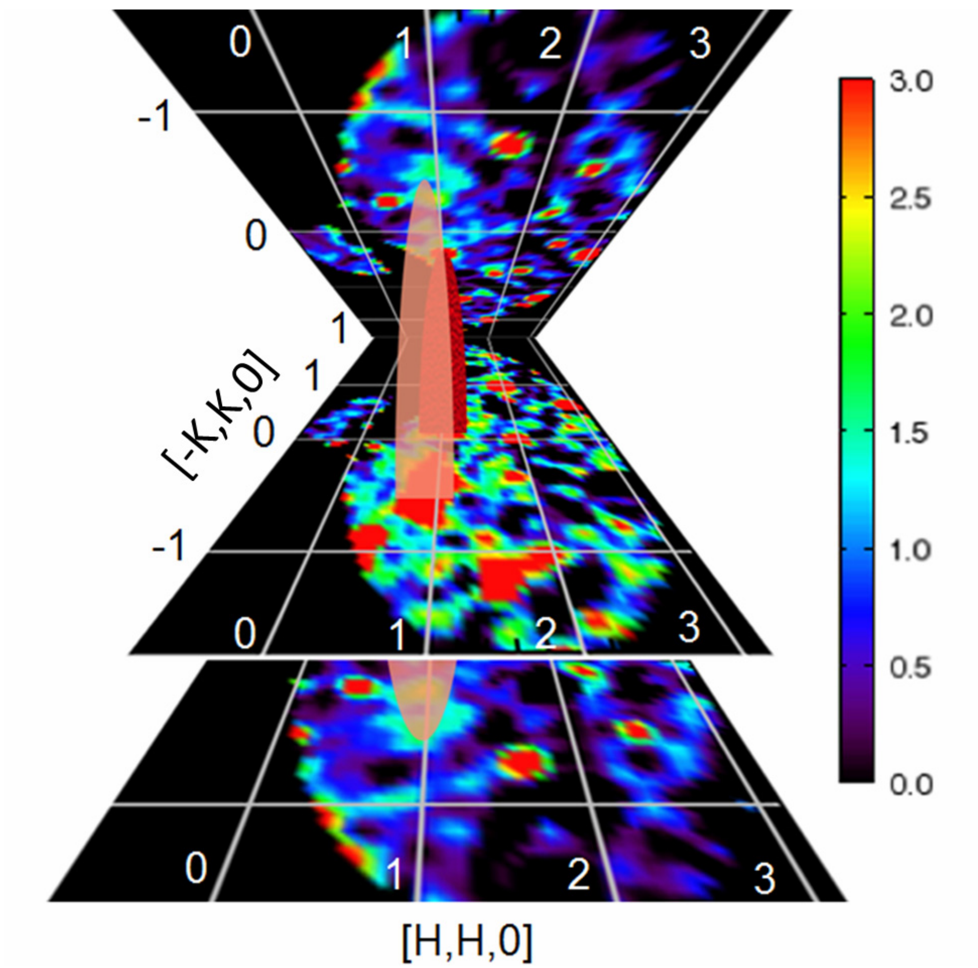

Fig. 3 Elastic diffuse scattering is observed at low temperatures using a 9T magnetic aligned in the c direction. Although the crystal was aligned in the *ab* plane, *ac* interactions can be observed using the upper and lower detector banks at the Disc Chopper Spectrometer (NIST) which are ±7° outside of the plane. These rod like Bragg peaks are indicative of fluctuating spins within the *ab* plane only.

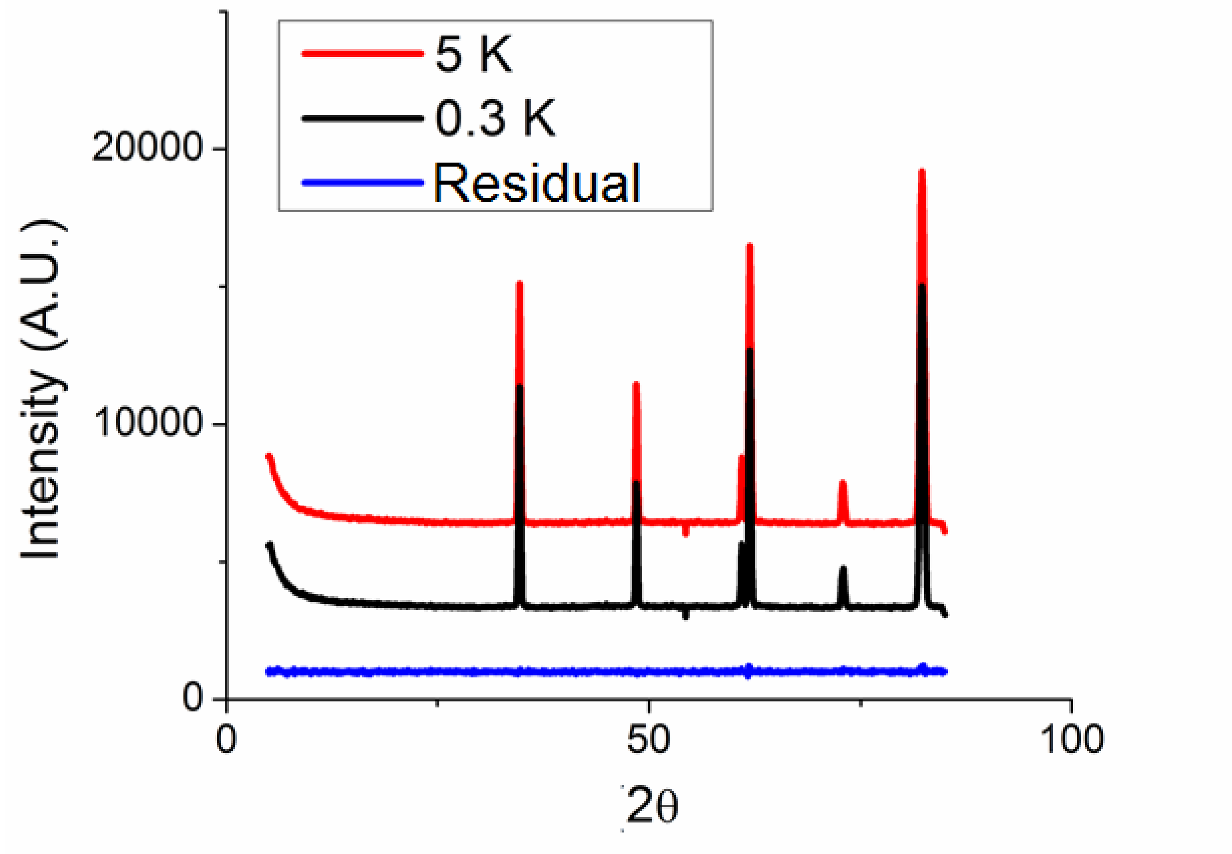

Fig. 4 C2 data taken at 5 K and 300 mK on powder $Pr_3Ga_5SiO_{14}$ show no signs of long range ordering.

References

[1] M.P. Shores, E.A. Nytko, B.M. Bartlett and D.G. Nocera, J. Am. Chem. Soc. 127, 13462 (2005).

[2] B. Fak, F.C. Coomer, A. Harrison, D. Visser and M.E. Zhitomirsky, EPL 81, 17006 (2008).

[3] H.D. Zhou, L.L. Lumata, P.L. Kuhns, A.P. Reyes, E.S. Choi, N.S. Dalal, J. Lu, Y.J. Jo, L. Balicas, J.S. Brooks and C.R. Wiebe, Chem. Mater. 21, 156 (2009).

[4] H.D. Zhou, B.W. Vogt, J.A. Janik, Y.J. Jo, L. Balicas, Y. Qiu, J.R.D. Copley, J.S. Gardner and C.R. Wiebe, Phys. Rev. Lett. 99, 236401 (2007).

[5] H. Takatsu, H. Kadowaki, T.J. Sato, J.W. Lynn, Y. Tabata, T. Yamazaki and K. Matsuhira, J. Phys. Condens. Mat. 24, 052201 (2012).

[6] K.A. Ross, L. Savary, B.D. Gaulin and L. Balents, Phys. Rev. X 1, 021002 (2011).

[7] L.L. Lumata, T. Besara, P.L. Kuhns, A.P. Reyes, H.D. Zhou, C.R. Wiebe, L. Balicas, Y.J. Jo, J.S. Brooks, Y. Takano, M.J. Case, Y. Qiu, J.R.D. Copley, J.S. Gardner, K.Y. Choi, N.S. Dalal and M.J.R. Hoch, Phys. Rev. B 81, 224416 (2010).

[8] A. Zorko, F. Bert, P. Mendels, K. Marty and P. Bordet, Phys. Rev. Lett. 104, 057202 (2010).

[9] S. Ghosh, S. Datta, H.D. Zhou, M.J.R. Hoch, C.R. Wiebe and S. Hill, J. Appl. Phys. 109, 07E137 (2011).

[10] D.H. Ryan and I.P Swainson, NRC Canadian Neutron Beam Centre Scientific Reports, 87 (2008).