Partial Field-Induced Magnetic Order in the Spin-Liquid Kagomé $Nd_3Ga_5SiO_{14}$

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The distorted kagomé system $Nd_3Ga_5SiO_{14}$ has been investigated with neutron scattering down to 0.046 K with no evidence of magnetic long range order of the Nd^{3+} moments in a zero field. Substantial diffuse scattering is observed which is in agreement with nearest-neighbor correlations between the fluctuating spins. Upon the application of a field in the *c* direction, the diffuse scattering is reduced in intensity while the magnetic Bragg peaks grow in intensity to saturate by 1 T to 1/2 of the expected magnetization. These measurements suggest that a unique spin-liquid state develops in $Nd_3Ga_5SiO_{14}$ with a frustration index of $f \sim |\theta|/T_C \geq 1300$.

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Spins on a kagomé lattice (corner-sharing triangles) remain a celebrated example of strongly geometrically frustrated magnetism in two dimensions [1,2]. These systems have received an increasing amount of attention over the last few decades due to the novel physics they offer. Arguably the best studied of these is SCGO ($SrCr_{12-x}Ga_xO_{19}$) [3], which still has a controversial magnetic ground state due to the question of disorder on the chromium sites, and the jarosites, which tend to order at low temperatures [4]. However, even though most of the jarosites order, a new spin excitation, the "lifted zero energy" mode, has been recently verified in $KFe_3(OH)_6 \times (SO_4)_2$ [5]. The search still continues for new 2D spin systems which may be true spin liquids in the limit of zero temperature. The new discovery of the "perfect" kagomé system of quantum, $S = 1/2$, Cu spins [$ZnCu_3(OH)_6Cl_2$] on a lattice of equatorial triangles might be such a candidate [6].

The discovery of the new distorted kagomé system $Nd_3Ga_5SiO_{14}$ has renewed interest in the search for these exotic ground states [7,8]. $Nd_3Ga_5SiO_{14}$ does not have the typical kagomé-like structure of Nd^{3+} spins, but the topology of the magnetic sublattice is equivalent to isolated kagomé planes stacked in the *c* direction if one considers the connectivity of nearest-neighbor spins (Fig. 1). The first Letter on this material suggested that $Nd_3Ga_5SiO_{14}$ could be a spin-liquid candidate [7]. However, there were no data presented on the properties below 1.6 K, where typically many rare earth oxides tend to show magnetic ordering [1]. Furthermore, a recent erratum published indicates that the previous inelastic neutron scattering results were erroneous, and further investigation is needed to find the identity of the ground state [9].

In this Letter, we detail new neutron scattering measurements on single crystals of $Nd_3Ga_5SiO_{14}$ to determine the nature of the ground state of this new material. We find that there are no new magnetic Bragg peaks down to 0.046 K, but there is distinct diffuse scattering which follows a liquidlike form factor. Upon applying a field of 0.5 T in the *c* direction (perpendicular to the *ab* planes), an ordered state is induced with a reduced magnetic moment of $1.5(1)\mu_B$. The lack of long-ranged-magnetic order, coupled with a high frustration index, makes this system a good candidate for a spin-liquid ground state.

Single crystals of $Nd_3Ga_5SiO_{14}$ with typical sizes of 5 cm long and 1 cm in diameter were grown by the floating-zone technique. dc susceptibility (χ) was mea-

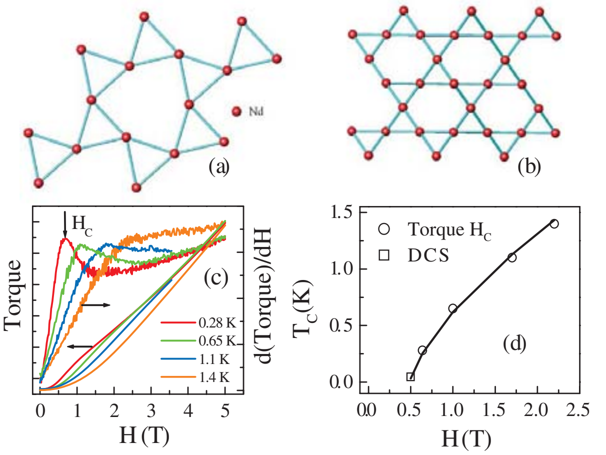

FIG. 1 (color). (a) The distorted kagomé lattice of Nd^{3+} ions in the ab plane of $Nd_3Ga_5SiO_{14}$; (b) A perfect kagomé lattice; (c) The field dependence of the magnetic torque and its derivatives at different temperatures; (d) The phase diagram for the magnetic ordered state in $Nd_3Ga_5SiO_{14}$, as determined by magnetic torque measurement and DCS neutron data. The solid line is fit to $T_C \sim |H - H_C|^\alpha$ with $H_C = 0.51(1)$ T and $\alpha = 0.68(2)$.

sured with a SQUID magnetometer with an applied field of 0.1 T. The linear fit of $1/\chi$ to the high temperature data (100 K and above) yields a Curie-Weiss constant $\theta = -62(2)$ K and an effective moment $\mu_{\mathrm{eff}} = 3.5(1)\mu_B$ in good agreement with previous results [8]. The magnetic torque was measured by using a thin film CuBe cantilever with thickness of 0.0125 mm with an applied field parallel to the c axis of the crystal. Neutron scattering measurements were completed at the NIST CHRNS using the disk chopper spectrometer (DCS) with wavelengths of 4.8 and 1.8 Å and also using the neutron spin echo (NSE) spectrometer. On the DCS at 4.8 Å, elastic data were obtained by integrating from -0.1 meV to 0.1 meV energy transfer. The crystals were aligned in the ab plane (total mass of 5 g) with a vertical magnetic field applied in the c direction. A dilution fridge was used which had a base temperature of 0.046 K.

Torque magnetometry was first used to map out the phase diagram at low temperatures. Experiments on samples oriented with the magnetic field along the c direction demonstrate that there is a transition in low-fields to an ordered state at 0.6 T at 0.28 K (Fig. 1), as evidenced through the derivative of the torque function. Note how there is no transition to a long-ranged ordered state beneath fields of 0.5 T above 0.046 K. The ordering transition increases as a function of increasing applied magnetic field, similar to the spin-liquid—spin-solid transition in the frustrated pyrochlore $Tb_2Ti_2O_7$ [10]. The phase diagrams look remarkably similar for fields applied along the [110] direction in $Tb_2Ti_2O_7$ [10] compared to fields applied in the [001] direction in $Nd_3Ga_5SiO_{14}$. There is also a similar field-driven transition in the related system $Gd_3Ga_5O_{14}$ (GGG), which has a transition to a long-ranged order state above 0.67 T [11]. The values of $H_C = 0.51(1)$ T and $\alpha = 0.68(2)$ can be obtained by fitting our phase-boundary data to $T_C \sim |H - H_C|^{\alpha}$ (T_C and H_C are the ordering temperatures and fields, respectively). Since there is not sufficient evidence to distinguish this boundary as either a true second order phase transition or as crossover behavior, the exponent should be treated as an empirical fit to the data.

Figure 2 shows the elastic neutron scattering intensity for samples oriented with the ab plane defining the scattering plane of the experiment, and with the c axis vertical for the application of a magnetic field. No new Bragg peaks are found down to 0.046 K in zero field. Note that this gives a "frustration" index of $f \sim |\theta|/T_C \geq 1300$, a large value compared to other kagomé systems [2]. There is a possibility that crystal-field effects are masking the true Curie-Weiss constant (i.e., it could be lower than -62 K) which would result in a lower effective frustration index. It is worth stressing at this point, however, that there is no concern that we are dealing with exotic moment-induced physics, since Nd^{3+} is a Kramers ion.

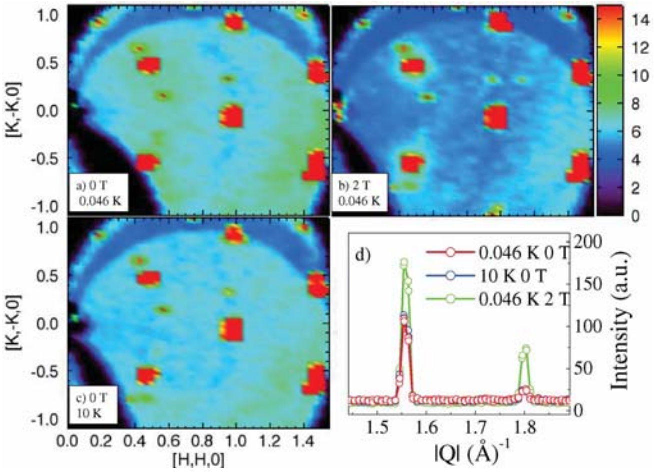

FIG. 2 (color). Neutron scattering ($\lambda = 4.8$ Å) within the (H, K, 0) plane of $Nd_3Ga_5SiO_{14}$ at (a) $T = 0.046$ K, $H = 0$ T; (b) $T = 0.046$ K, $H = 2$ T; (c) $T = 10$ K, $H = 0$ T; (d) Neutron diffraction patterns at $T = 0.046$ K, $H = 0$ T, $T = 0.046$ K, $H = 2$ T, and $T = 10$ K, $H = 0$ T (fields applied in the c direction). Note the appearance of rings of diffuse scattering as a function of Q in (a)–(c). The dark ring of scattering in (a)–(c) is due to the "dark angle" of the dilution fridge.

Superimposed upon the chemical or nuclear Bragg peaks are rings of diffuse scattering (in zero field) which are isotropic in intensity as a function of Q within the scattering plane [12]. The lack of prominent features in the diffuse scattering is due to the distortion of the kagomé lattice, which results in a nearly featureless set of rings as a function of $\mathbf{Q}$ [7]. The development of the magnetic diffuse scattering is clear comparing the 10 K data set to the 0.046 K data set (Fig. 3).

Upon the application of a small field in the [001] direction, magnetic Bragg peaks grow in intensity while the diffuse scattering decreases (Figs. 2 and 3). The intensities of several Bragg peaks as a function of applied field is shown in Fig. 3. The intensities of these peaks are consistent with a net ferromagnetic moment along the c axis of $1.5(1)\mu_B$. This is also consistent with the saturation of the signal through dc magnetometry measurements [8]. However, it is a reduced moment from the free Nd^{3+} spin, which is expected to be $3.5\mu_B$. Reduced moments are typical in frustrated systems [1], but in this case there could be some spins still within a paramagnetic state since there is still some diffuse scattering intensity even after the magnetic Bragg peaks saturate by 2 T (see Figs. 2 and 3).

The diffuse scattering was analyzed using the spin-liquid form factor from the distorted kagomé model of Robert *et al.* [7]. The diffuse scattering intensity has been summed from -0.4 r.l.u (reciprocal lattice units) to 0.4 r.l.u. in the (K-K0) direction to obtain a cross section of the rings of scattering. The 10 K data was used as a subtraction to extract only the diffuse scattering, and Bragg peaks were removed to improve the analysis. The resulting intensity was divided by the magnetic form factor, $F(Q)^2$, for Nd^{3+} spins. The data fit well to a model using first-neighbor spin correlations in the distorted kagomé lattice [7] [Fig. 3(c)].

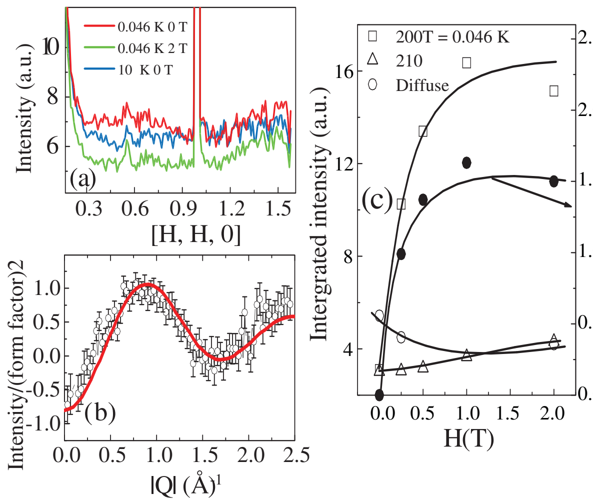

FIG. 3 (color). (a) The diffuse scattering of $Nd_3Ga_5SiO_{14}$ at $T = 0.046$ K, $H = 0$ T, $T = 0.046$ K, $H = 2$ T, and $T = 10$ K, $H = 0$ T. (b) The difference between patterns taken at $T = 0.046$ K, $H = 0$ T and that taken at $T = 10$ K, $H = 0$ T. The solid line is calculated from a model described in the text. (c) The field dependence of the integrated intensity of the (2, 0, 0) and (2, 1, 0) Bragg peaks, and the diffuse scattering (integrated from -0.4 r.l.u. to 0.4 r.l.u. in the *ab* plane) at $T = 0.046$ K, along with the calculated magnetic moment of per Nd. All lines shown in (c) are guides for the eye.

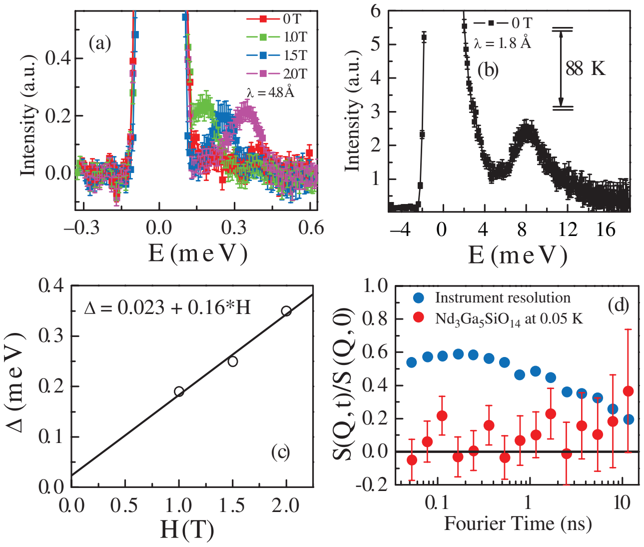

FIG. 4 (color). (a) Inelastic scattering integrated over Q at 0.046 K ($\lambda = 4.8$ Å). Note the excitation which develops as a function of magnetic field, presumably due to the split ground-state doublet. (b) Higher energy inelastic scattering at 0.046 K demonstrating a possible crystal-field level at 8 meV ($\lambda = 1.8$ Å). A crystal-field scheme of two doublets. (c) Linear dependence of the gap Δ as a function of field for the dispersionless mode in (a). (d) Neutron spin echo data of the normalized intermediate scattering function at 50 mK. This indicates that the system is still very dynamic within the NSE time window. The instrument resolution function shows the expected result for a static system.

This validates earlier predictions of slow spin fluctuations with only nearest-neighbor correlations, a signature of a highly correlated liquidlike state. Also note how the function has a negative value at $Q = 0$, indicative of antiferromagnetic correlations $\langle \boldsymbol{S} \cdot \boldsymbol{S} \rangle$.

Figure 4 displays the inelastic neutron scattering spectrum of $Nd_3Ga_5SiO_{14}$, integrated over $\mathbf{Q}$ in the *ab* plane. Note that the inelastic spin-liquid features observed by Robert *et al.* are not present (this was due to liquid He scattering) [9]. However, the absence of this response does not necessarily suggest that the spins are frozen [7]. Our energy resolution is $-0.1 < \Delta E < 0.1$ meV, which suggests that the moments are fluctuating at frequencies less than 20 GHz. This is within the range of NMR and muon spin relaxation experiments that have been used previously to verify the spin-liquid state in other frustrated systems [13]. NSE data presented in Fig. 4(d) shows that the system is essentially dynamic at $T = 50$ mK. The intermediate scattering function completely relaxes within the first 4 ps, similar to other dynamic systems such as $Yb_2Ti_2O_7$ [14].

The loss of the elastic spin-liquid-like scattering with applied field is correlated with the appearance of a nearly dispersionless mode (Fig. 4), which is reminiscent of the 0.3 meV mode that rises out of the quasielastic scattering in $Tb_2Ti_2O_7$ [10]. The linear magnetic field dependence suggests that this is due to a split ground-state doublet. However, the extrapolated splitting in zero field (0.02 meV) is too small for the expected energy difference between a ground-state doublet and the first excited state for a Kramers ion. Such a small splitting would naïvely appear too small for a single-ion crystal-field splitting between a ground-state doublet and first excited state when compared to other Kramers ions.

Larger moment systems such as $Tb_2Ti_2O_7$ and $Ho_2Ti_2O_7$ show exotic ground states (spin-liquid [13] and spin ice states [15] respectively) due to the interplay between magnetic exchange and dipolar interactions. It may be possible that $Nd_3Ga_5SiO_{14}$ does not order because mangetic exchange dominates over the dipolar interactions. The spin-liquid state in $Nd_3Ga_5SiO_{14}$ may be stabilized by other terms in the Hamiltonian such as the admixing of higher crystal-field states (as in the case of $Tb_2Ti_2O_7$) [16,17]. The next doublet beyond the ground-state has to occur at energies higher than 8 meV, where a dispersionless excitation is seen in the neutron scattering spectra (Fig. 4) [17]. The value of 8 meV $\sim$ 88 K is similar to the Curie-Weiss constant, which may suggest that the frustration index may be skewed in a nontrivial manner by crystal-field effects [17]. It is also worth noting that there are three other Kramers doublets which have been unobserved, which may either be at high temperatures or have a small matrix element with respect to neutron scattering experiments. Recent heat capacity experiments under applied fields have revealed that the low temperature ($0.1\ \mathrm{K} < T < 10\ \mathrm{K}$) data is well described by a single ground-state doublet [18]. This eliminates the possibility that a level crossing to a low level crystal field on the order of 1 meV (that would be invisible to neutrons) is the root of the spin ordering under applied fields.

The observation of an ordered moment of nearly $1/2$ the full Nd^{3+} moment for fields applied along the c direction [8] brings up some interesting questions. For other triangular based 2D lattices, $1/3$ magnetization plateaus have been predicted and observed for Ising [19], XY [20] and Heisenberg [20,21] interactions between the spins which can be understood with a 2 spin-up/1 spin-down configuration on each triangle. It is difficult to envision a scenario where three spins give rise to a net ferromagnetic moment of $1/2$, and this has not been predicted for the kagomé lattice. However, in corner-shared tetrahedral lattices, these features have been observed due to subtle quantum effects [22] for the $S = 3/2$ chromate spinels $HgCr_2O_4$ [23] and $CdCr_2O_4$ [24]. For fields applied along the [111] direction, the spinel magnetic sublattice lattice can be described as a kagomé network with layers connected by corner-shared tetrahedra, so it is perhaps not completely surprising that a similar state could exist in $Nd_3Ga_5SiO_{14}$. However, in the spinels, a 3:1 spin configuration on each tetrahedra results in the $1/2$ magnetization plateau [24]. It is not clear how this moment sum would be possible with the triangular plaquette system in $Nd_3Ga_5SiO_{14}$. One would expect that if this is an ordered state, the $q = 0$ or the $q = \sqrt{3}x\sqrt{3}$ structure would be stabilized at low temperatures, which is determined by the relative strength of nearest and next-nearest-neighbor interactions. Ferromagnetic second nearest neighbors favor the $q = \sqrt{3}x\sqrt{3}$ ordering, for example [25]. Since there are no new magnetic reflections within the Q-space sampled within this experiment, the magnetic unit cell is identical to the chemical unit cell with only three magnetic spins. Only the $q = 0$ structure would then be expected to be stable, and this structure is not consistent with the intensities of the observed Bragg peaks. The identity of this phase would have to be consistent with the coexistence of diffuse scattering and magnetic Bragg peaks. This could be analogous to the ordered state of the garnet $Gd_3Ga_5O_{14}$ (GGG) which at low temperatures has a mixed ground state in zero field [11]. There could also be a field-stabilized nematic spin-liquid state present which would result in both diffuse scattering and magnetic Bragg peaks forming at low temperatures [26]. These scenarios are being investigated in further detail.

The identity of the fluctuating moment ground state in $Nd_3Ga_5SiO_{14}$ is a mystery. All evidence so far points towards a highly frustrated system ($f > 1300$) which results in a spin liquid down to at least 46 mK. A partially ordered phase appears with applied fields that is characterized by the coexistence of magnetic Bragg peaks and diffuse scattering at low temperatures. These features cannot be explained through conventional magnetic behavior and demand a new perspective on the possibility of a unique spin-liquid state developing in $Nd_3Ga_5SiO_{14}$.

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