Spin-Liquid Correlations in the Nd-Langasite Anisotropic Kagomé Antiferromagnet

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Dynamical magnetic correlations in the geometrically frustrated $Nd_3Ga_5SiO_{14}$ compound were probed by inelastic neutron scattering on a single crystal. A scattering signal with a ring shape distribution in reciprocal space and unprecedented dispersive features was discovered. Comparison with calculated static magnetic scattering from models of correlated spins suggests that the observed phase is a spin liquid inherent to an antiferromagnetic kagomé-like lattice of anisotropic Nd moments.

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Geometrically frustrated magnets are at the forefront of research because of their diverse exotic ground states but also because the concept of frustration plays a major role in fields beyond magnetism [1]. One prototype is the kagomé antiferromagnet, a two dimensional lattice of corner sharing triangles of antiferromagnetically interacting spins, which attracts strong attention as a promising candidate for possessing a disordered ground state. At the quantum limit of spins-1/2, there are converging arguments towards the stabilization of a type II spin liquid [2] consisting in a disordered ground state breaking neither spin nor lattice symmetry, and realizing a quantum spin-liquid state. Its search traces back to the suggestion of a resonating valence bond state in the triangular lattice Heisenberg model [3]. At the classical limit of large spins, the basic signature of the geometric frustration is the infinite degeneracy of the ground state. A disorder phase with short-range magnetic correlations, transposable to the superposition of ground state spin configurations, can be expected, with an intrinsic dynamical nature associated with zero-point motions, localized or extended [4–8]. Subtle differences exist according to the spin degrees of freedom. With planar *XY* or isotropic Heisenberg spins, because of the continuous extensive entropy, thermal fluctuations play a crucial role in selecting a subspace within the ground state manifold [6] through the *order out of disorder* mechanism [9]. Whether nonlinear effects may even push forward this selection to a unique ground state is still an open question. With Ising spins, a cooperative paramagnet is predicted at all temperatures with a discrete extensive ground state degeneracy and exponentially decaying spin-spin correlations [4,10].

A disorder phase is experimentally easily destabilized by any kind of small perturbation [1], like second order interactions, structural imperfections, or off stoichiometry. Accordingly, most of the few materializations of kagomé antiferromagnets available to date do order at low enough temperatures, though often into unconventional magnetic states (noncollinear, noncoplanar, multipropagating, or incommensurate orderings, disorder-free spin glassiness, ...) that are in some cases sustaining large magnetic fluctuations. Of interest is that these compounds (for instance the jarosites [11], the Cr kagomé bilayers [12], the volborthite [13], and the kagomé-staircase compounds [14]) are best described by Heisenberg spin models and that, up to now, there was no example of a kagomé antiferromagnet with a strong magnetocrystalline anisotropy calling for an Ising or an *XY* description. Another point was the absence of large enough single crystals for three-axis inelastic neutron scattering in all cases of kagomé antiferromagnets in which a spin-liquid state was suspected. This unique technique allows one to probe the dynamical magnetic correlations both in space and time and was earlier successfully used in evidencing signatures of spin-liquid phases in compounds containing a 3D pyrochlore net of magnetic moments: the itinerant-electron $Y_{0.97}Sc_{0.03}Mn_2$ [15] and the insulating $ZnCr_2O_4$ [16].

Nd-langasite, $Nd_3Ga_5SiO_{14}$, crystallizes in the trigonal space group *P*321 and belongs to a family of materials that attracted strong interest for showing better piezoelectric properties than quartz or lithium niobate and tantalate [17]. We recently discovered that some members of this family could be also of interest as geometrically frustrated magnets [18]. The Nd^{3+} magnetic ions in $Nd_3Ga_5SiO_{14}$ are organized in corner sharing triangles in well-separated planes perpendicular to the *c* axis. Within these, the Nd^{3+} form a distorted kagomé lattice, which is topologically equivalent to the ideal kagomé when only the shortest atom bridging interactions are considered. We emphasize that this Nd net is fully occupied and that large size single crystals can be grown.

Powders of Nd-langasite were prepared by solid state reactions of stoichiometric amounts of high purity oxides at 1420 °C in air whereas single crystals were grown from sintered powders by the floating zone method using a mirror furnace from the ''Cyberstar'' company. Single-crystal magnetization measurements confirmed that a geo-

metric frustration does materialize in this compound and revealed a strong magnetocrystalline anisotropy associated with crystal field effects on the ground multiplet of the $4f^3$ Nd^{3+} ions (total angular momentum $J = 9/2$) [18]. A quantitative analysis of the magnetic susceptibility χ at high temperatures T yielded a Curie-Weiss temperature $\theta = -52$ K accounting for antiferromagnetic interactions between the Nd moments and quadrupolar crystal field parameters indicating that these moments are coplanar rotators in the kagomé planes [18]. A change in the magnetocrystalline anisotropy occurs around 33 K due to the higher order terms of the crystal electric field, the c axis, perpendicular to the kagomé planes, becoming the magnetization axis at low temperature [18]. No phase transition towards a long-range magnetic order was detected down to 1.6 K, a temperature much smaller than the exchange coupling energy scale given by θ, neither in these magnetization measurements nor by elastic neutron scattering on powders, clearly suggesting that a spin-liquid phase could be stabilized in the compound [18].

Inelastic neutron scattering measurements were performed at the high flux reactor of the Institut Laue-Langevin to probe the low temperature dynamical magnetic correlation. Experiments with powders on the IN5 time of flight spectrometer informed essentially about the low levels of the energy spectrum of the Nd^{3+} ions as split by the crystal electric field. An additional much weaker signal was also detected around 1 meV [19].

In this Letter, we report on the results from an inelastic neutron scattering experiment on a large single-crystal, 40 mm long and 5 mm in diameter, performed on the cold neutron three-axis spectrometer IN14 to probe the weak magnetic signal around 1 meV and its distribution in the reciprocal space. The single crystal was mounted in a cryostat with the [100] and [010] axes in the horizontal scattering plane. Its temperature was maintained at 2 K. The neutron wavelength was selected from a vertically curved graphite monochromator PG(002). We used a fixed final energy of 4.66 meV with energy resolution around 165 μeV. In the following, the wave vectors Q are expressed via their coordinates $(\xi, \zeta, 0)$ in reciprocal lattice units (r.l.u.) or via their modulus $|Q|/|a^*| = \sqrt{(\xi + 1/2\zeta)^2 + 3/4\zeta^2}$ with $|a^*| = 0.899$ Å^{-1}.

Scans in neutron energy transfer (E scans) at different positions along the [100] and [2$\bar{1}$0] directions are shown in Fig. 1. At $Q = (1.5\,0\,0)$ (along [100]), a small signal is visible around 0.9 meV. At $Q = (1.3\ -0.65\,0)$ (along [2$\bar{1}$0]) a small signal is also present at a slightly smaller energy and mixed with the tail of the incoherent peak. Along each direction, the intensity of the signal decreases at larger Q values, as expected for magnetic excitations, which are multiplied by the square of the magnetic form factor [20]. Phonon excitations would have shown a rise of intensity with Q^2. A half width at half maximum (HWHM) $\Gamma = 0.47$ meV is deduced from the fit of the energy response at $Q = (1.5\,0\,0)$, with a Lorentzian times the detailed balance factor, which corresponds to a lifetime $\tau = 1.4 \times 10^{-12}$ s for the spin correlations.

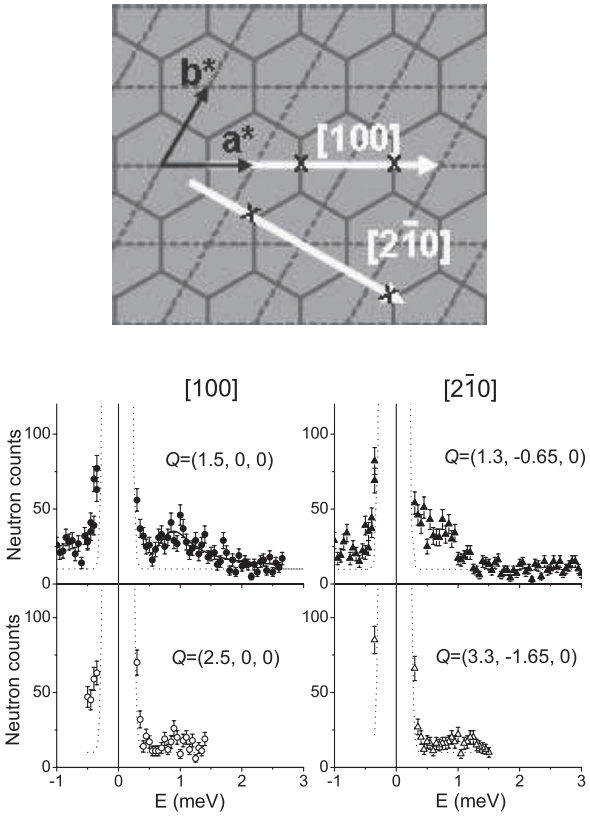

FIG. 1. Top: Intersection of the Brillouin zones with the (a^*, b^*) scattering plane (dark gray lines). The white arrows indicate the Q scans performed in both the [100] and [2$\bar{1}$0] directions. Bottom: E scans at 2 K for two different Q positions in each direction (crosses in the top panel). The thin lines are Gaussian fits of the incoherent peak. The thick line is a Lorentzian fit (see text).

Scans in neutron wave vector transfer (Q scans), along the [100] and [2$\bar{1}$0] directions, at the 0.5, 0.675, 0.85, and 1 meV energy transfers, show a weak, gradual, and global evolution (cf. Fig. 2). The signal is minimum around $|Q|/|a^*| = 2$, between a broad maximum and (in most scans) a second weaker maximum. The first maximum is also observed in the intermediate direction [4$\bar{1}$0] at the same Q value than in the other two directions, confirming the peculiar ring shape of this signal [19]. Its amplitude decreases and its position shifts from $|Q|/|a^*| = 1$ to 1.5 with increasing energy. This indicates a significant dispersion with Q of the magnetic scattering in the 0.5–1 meV range. The position and amplitude of a second maximum, when present, also vary with energy. The lines in Fig. 2 show the results of fits to two Lorentzians of same width, multiplied by the square of the Nd^{3+} magnetic form factor [21]. The fitted HWHM $\kappa \approx 0.49$ Å^{-1} corresponds to a correlation length $\lambda \approx 2$ Å, smaller than the distance between the nearest neighbors Nd^{3+} ions (4.2 Å).

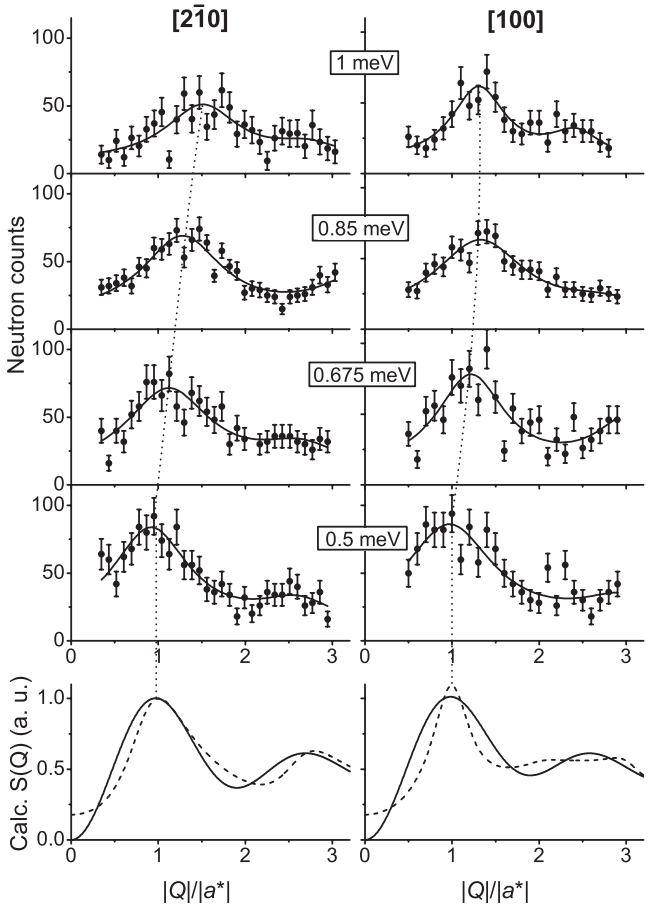

FIG. 2. Q scans at 2 K at several energy transfers, along the [100] and [2$\bar{1}$0] directions. The dotted lines indicate the position of the first maximum. The solid lines following the measured Q distributions (circles) are Lorentzian fits (see text). At bottom, static scattering, calculated using first neighbors magnetic correlations only (solid line), and in a model involving further neighbors correlations (dashed line), are plotted for the same directions for comparison (see text).

An interpretation of these results can be proposed from the comparison of the measured magnetic signal with calculated neutron static scattering intensities using different models of antiferromagnetically interacting classical spins on the distorted kagomé lattice formed by the Nd^{3+} ions. In all cases, the calculated Fourier-transformed spin correlation functions have been multiplied by the square of the Nd^{3+} magnetic form factor [21]. The simplest model is obtained considering correlations between first neighboring spins only and spin configurations minimizing the energy on each triangle of the structure. These are given as having the sum of three spins equal to zero for Heisenberg or XY spins and two spins in one state and the third spin in the opposite state for the Ising spins. Surprisingly, the resulting Q distribution of magnetic intensity does not depend on the spin degrees of freedom. This validates the interpretation of the experiment with this model albeit the low temperature anisotropy of the compound is not quantitatively determined at present. It is shown in Fig. 3 where it is compared to the same calculation on the nondistorted kagomé lattice. The magnetic intensity distribution in the scattering plane is more isotropic in the distorted case, consistently with the experimental data. A second model, describing an algebraic spin liquid at $T = 0$, was derived using classical isotropic infinite-component spin vectors following the method of Ref. [22]. The Q distribution of magnetic intensity was calculated at a finite temperature damping the dipolarlike long-range spin-spin correlation by an exponentially decaying term, hence smoothing the sharp features of the $T = 0$ K calculation. The main features of the measured Q distribution are reproduced by both models: a first broad maximum localized about $|Q|/|a^*| = 1$ from the origin and a second one, less well defined, around $|Q|/|a^*| = 2.6$. As expected from a static calculation, the best agreement between the measured and calculated Q distributions is obtained at the lowest energy, 0.5 meV, at least concerning the position of the first maximum which essentially reflects the first neighbors antiferromagnetic correlations (cf. Fig. 2).

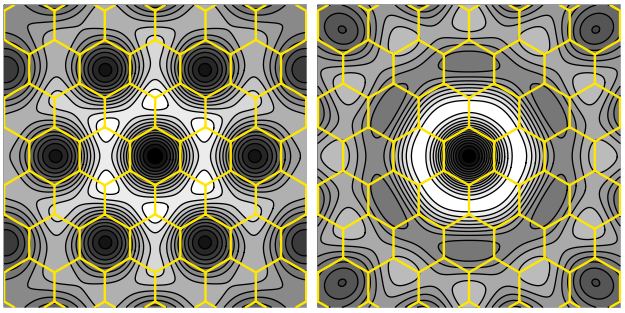

FIG. 3 (color online). Calculated static scattering map for the antiferromagnetic kagomé lattice (left) and for the distorted Nd-langasite kagomé lattice (right) using first-neighbor spin correlations (see text). The brightness increases with intensity.

The measured Q distribution is consistent with a disorder phase with specific magnetic correlations, the degeneracy of which would result in apparent very short correlation lengths. Crudely enlightened by the models, its main features are the broad ring shape scattering about $|Q|/|a^*| = 1$, the scattering empty Brillouin zone around the origin, and the scattering minima in Brillouin zones around certain reciprocal lattice points (cf. Fig. 3). They can be indeed understood as expressing the coexistence of many configurations at the same energy with frustration constrained antiferromagnetic correlations. A similar interpretation was invoked for the $Y_{0.97}Sc_{0.03}Mn_2$ spin liquid, the short-range magnetic correlations of which would originate from 4-site collective spin singlets associated with the tetrahedral building unit of the pyrochlore lattice. Note also the similarity of the Q scans recorded in both Nd-langasite and $Y_{0.97}Sc_{0.03}Mn_2$ [15], which can be related to the fact that the kagomé lattice is obtained

through a cut perpendicular to the cube diagonal of the pyrochlore lattice. A basic difference is that no dispersion of the magnetic signal was observed in $Y_{0.97}Sc_{0.03}Mn_2$, owing to a much shorter lifetime of the spin correlations, $\approx 7 \times 10^{-14}$ s, so that the modes either have no time to propagate or are drowned within the soft modes of the ground manifold.

Spin waves can propagate in locally ordered regions if the system retains a sufficient temporal and spatial stiffness. In a disordered medium, the spin waves lifetime is reduced, not only through thermal fluctuations (τ_{th}) [23], but also through the time scale on which the medium fluctuates (autocorrelation time τ_a) [8], both of the order of $\hbar/k_BT$. The mixing of the excitations built on a degenerate ground state manifold further reduces their lifetime to approximately $\hbar/[Jk_BT]^{1/2}$ (see Ref. [8]). But at the temperature we are interested in, we have $\tau_{\text{th}} \sim \tau_a \sim 3.8 \times 10^{-12}$ s and a measured lifetime $\tau \sim 1.4 \times 10^{-12}$ s. In this regime, the reduction due to the degeneracy of the ground state is small and the dynamics may still be seen as conventional, e.g., the spin wave spectrum should be built as a superposition of all excitations developing over each magnetic configuration of the ground state manifold. As a consequence, the density of quasistatic excitations should be much larger than the one at finite energy because of the soft modes. Assuming a Lorentzian shape with a HWHM $\sim$0.2 meV (from τ_a) for their description, it is reasonable to state that these quasistatic excitations also contribute to the scattering function at finite energy transfer. This would explain why the Q dependence of the scattering is well accounted for by the calculated static scattering intensities, especially at the lowest energy transfer (0.5 meV). Quasistatic contributions from soft modes have a smaller weight at higher energies and propagating modes become dominant, as evidenced from the dispersion of the position of the first maximum in the Q distribution. Now, a spatial propagation is expected for excited modes with wavelength smaller than the local order correlation length. The one deduced from the Q dependence of the scattering ($\xi \sim 2$ Å) seems too short to produce the observed dispersion. This apparent contradiction can be lifted considering that the correlation length associated to each configuration of the ground state manifold would be large enough to allow propagation of excited modes, whereas the measured one reflects the distribution of close configurations. The conjugate observation of a very broad signal associated to a dispersion of its maximum could thus be a consequence of the high degeneracy of magnetic states in this frustrated compound.

In conclusion, signatures of a cooperative paramagnet were evidenced in $Nd_3Ga_5SiO_{14}$, in particular, a peculiar Q distribution of the magnetic correlations that would emerge from a highly degenerate manifold of configurations. Although the unusual dispersion of the magnetic correlations and the role of the single-ion magnetocrystalline anisotropy have to be further clarified, the compound provides us with the first measurements of the spatial and temporal magnetic correlations in a spin-liquid phase of a geometrically frustrated kagomé antiferromagnet.

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