Short-range magnetic ordering process for the triangular lattice compound NiGa$_2$S$_4$: a positive muon spin rotation and relaxation study

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We report a study of the triangular lattice Heisenberg magnet NiGa$_2$S$_4$ by the positive muon spin rotation and relaxation techniques. We unravel three temperature regimes: (i) below $T_c = 9.2 (2)$ K a spontaneous static magnetic field at the muon site is observed and the spin dynamics is appreciable: the time scale of the modes we probe is $\sim 7$ ns; (ii) an unconventional stretched exponential relaxation function is found for $T_c < T < T_{\text{cross}}$ where $T_{\text{cross}} = 12.6$ K, which is a signature of a multichannel relaxation for this temperature range; (iii) above $T_{\text{cross}}$, the relaxation is exponential as expected for a conventional compound. The transition at $T_c$ is of the continuous type. It occurs at a temperature slightly smaller than the temperature at which the specific heat displays a maximum at low temperature. This is reminiscent of the behavior expected for the Berezinskii-Kosterlitz-Thouless transition. We argue that these results reflect the presence of topological defects above $T_c$.

On cooling, in the same way as liquids, magnetic materials, usually crystallize to form long-range periodic arrays. However, magnetic materials with antiferromagnetically coupled spins located on triangular motifs exhibit geometrical magnetic frustration which may prevent the crystallization to occur [1]. Such materials are a fertile ground for the emergence of novel spin-disordered states such as spin liquid or spin glass even without crystalline ground state. Here we report muon spin rotation and relaxation measurements ($\mu$SR) which show a spontaneous internal field, vanishes at a temperature which is about half the temperature at which the neutron magnetic reflections disappear. This is further discussed below. Our observation is also technically interesting. It shows that, contrary to common wisdom, the detection

The crystal structure consists of two GaS$_2$ layers and a central NiS$_2$ layer stacked along the c-axis. A Rietveld refinement of a neutron powder diffraction pattern recorded at 50 K at the cold neutron powder diffractometer DMC of the SINQ facility at the Paul Scherrer Institute (Villigen, Switzerland) is consistent with the $P6_3$1m space group. The lattice parameters are $a = 0.3619$ nm and $c = 1.1967$ nm, in agreement with previous results [3]. The refinement is consistent with the nominal stoichiometry and no impurity phase is detected (detection limit: 1%).

Further characterizations of our sample have been done by zero-field specific heat and susceptibility measurements. The magnetic specific heat $C_m$ (divided by the temperature) is displayed in Fig. 2. It is in very reasonable agreement with the data of Nakatsuji and coworkers [3]. As these authors reported, we also find that the susceptibility recorded under a field of 0.01 T displays a weak kink at $T_\chi \sim 8$ K.

Now we report on our zero-field $\mu$SR data; see Refs. [6,7] for an introduction to the $\mu$SR techniques. A spectrum is expressed as $a_0P_{Z}^{\exp}(t)$ where $a_0$ is an amplitude or asymmetry and $P_{Z}^{\exp}(t)$ a polarization function. In Fig. 1 we display three spectra which probe the three temperature regimes that we have unveiled.

At variance with Ref. [8], a strongly damped oscillation is observed at low temperature where nano-scale magnetic correlations have been detected by neutron diffraction [3]; see the spectrum at the bottom of Fig. 1. Remarkably, this oscillation which reflects the presence of a spontaneous internal field, vanishes at a temperature which is about half the temperature at which the neutron magnetic reflections disappear. This is further discussed below.
for a material of a zero-field $\mu$SR oscillation is not a fingerprint of a long-range magnetic order. The spectrum at 2.3 K has a steep slope for time $t < 0.02 \mu s$. Such a shape is typical for an incommensurately ordered magnet which shows a characteristic field distribution at the muon site [3]. This translates in time-space to a Bessel function rather than cosine oscillations [6]. Our observation is not surprising since it has been established by neutron diffraction diffraction that the magnetic structure is indeed incommensurate [3]. The spectrum is described by the sum of two components for the compound and a third component which accounts for the muons missing the sample and stopped in its surroundings: $a_0 F^\exp_Z(t) = a_{\text{cos}} J_0(\gamma_{\text{mu}} B_{\text{max}}) \exp(-\gamma_{\text{mu}} \Delta^2 t^2/2) + a_{\text{rel}} \exp(-\lambda_{Z} t) + a_{\text{bg}}$. $J_0$ is the zeroth-order Bessel function of the first kind, $B_{\text{max}}$ stands for the maximum of the spontaneous static local magnetic field distribution at the muon site, $\Delta^2$ characterizes the broadening of the probed field distribution and $\gamma_{\text{mu}}$ is the muon gyromagnetic ratio ($\gamma_{\text{mu}} = 851.615$ Mrad s$^{-1}$ T$^{-1}$). The component of amplitude $a_{\text{rel}}$ gauges the relaxation of the muons sensing a field parallel to their initial polarization. The associated spin-lattice relaxation rate is denoted $\lambda_{Z}$. The asymp-
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FIG. 2: (color online). Upper panel: thermal dependence of two parameters extracted from $\mu$SR spectra. On the left-hand side is presented the maximum of the static local magnetic field at the muon site, $B_{\text{max}}$, for $T < T_{\text{Stat}}$. On the right-hand side of the same panel is displayed the relaxation rate, $\lambda_2$, for $T > T_{\text{Cross}}$, i.e. when the relaxation function is exponential. The full lines are results of fits described in the main text. Lower panel: zero-field magnetic specific heat divided by the temperature, $C_m/T$, deduced from the measured specific heat using a dynamic adiabatic technique after subtraction of the lattice contribution. The full line is obtained for a linear dependence of $C_m/T$.

Measured in its paramagnetic state; see e.g. elemental Ni [13] or Fe [14] or the intermetallics GdNi$_2$ [15]. A stretched exponential relaxation has been observed for a wide variety of physical quantities in many different systems and research areas [16]. It arises from a continuous sum of exponential decays [17]. A square-root relaxation of the Nuclear Magnetic Resonance [18] and $\mu$SR [19] relaxation function is also observed for spatially disordered systems. It stems, e.g. for spin-glass materials, from the distributed nature of the coupling of the probe to its environment. Our sample is spatially homogeneous. We ascribe the stretched exponential relaxation for $T_c < T < T_{\text{Cross}}$ to a multichannel relaxation process.

Nakatsuji et al have presented the temperature dependence of the difference $\Delta I(T)$ between the elastic powder neutron scattering intensity recorded at $T$ and 50 K, for wave vector $q_c = 0.58$ Å$^{-1}$ [20]. $\Delta I(T)$ decreases smoothly up to $\sim$ 18 K where it becomes negligible. This temperature is quite different from $T_c$, where the muon spontaneous field vanishes, and from $T_{\text{Cross}}$. These differences are not surprising, given the different magnetic modes which are probed by the three techniques. The neutron intensity integrates the $q_c$-correlations for times longer than $\tau_{\text{min}}$. $B_{\text{max}}$ is built up from the sum of the dipole magnetic fields at the muon site due to a restricted $q$ range of the Ni$^{2+}$ magnetic moment Fourier components, and characterized by a time scale longer by an order of magnitude than $\tau_{\text{min}}$. d.c. susceptibility probes an even longer time scale. That $\Delta I(T)$ vanishes only at $\sim$ 18 K suggests a relatively large continuous spectrum of magnetic fluctuations in NiGa$_2$S$_4$. This could be a common property of geometrically frustrated magnets since it has already been encountered for Tb$_2$Sn$_2$O$_7$ [10, 20, 21]. Because of the notable reduction of the Ni$^{2+}$ ($S = 1$) magnetic moment as measured by neutron diffraction ($\sim 25\%$), the spectral weight must also extend to time scales smaller than $\tau_{\text{min}}$.

Previous thermodynamic and neutron results [3] and the present $\mu$SR measurements on NiGa$_2$S$_4$ demonstrate that this two-dimensional Heisenberg triangular lattice antiferromagnet has unique low-temperature properties: (i) while its Curie-Weiss temperature is rather large, $\Theta_{\text{CW}} = -80(2)$ K, it does not display a long-range magnetic ordering, but only an incommensurate short-range order with a nano-scale correlation length and a spontaneous static interstitial magnetic field below $T_c = 9.2(2)$ K; (ii) its ground state is highly degenerate; (iii) there is a slowing down of magnetic fluctuations as the compound is cooled down through $T_c$ rather than a spin-freezing as observed for canonical spin glasses. In fact, we have found that NiGa$_2$S$_4$ exhibits a conventional paramagnetic spin dynamics down to $T_{\text{Cross}}$, where an effective multichannel relaxation process sets in down to $T_c$. A finite spin dynamics is detected below $T_c$.

Before discussing theoretical proposals for the ground state of an exact triangular lattice of isotropic spins in light of the experimental results, we note that different techniques show that the exchange interaction between third neighbors is strong [22, 23]. This result provides a clue for the existence of strong frustration, in agreement with experimental data [3].

A hidden order parameter associated to an ordered nematic phase can be proposed for this system [24], on the ground of the large coherent length inferred from an analysis of the specific heat data [3]. In this case there are no long-range two-spin correlations and only the quadrupole moments of the Ni$^{2+}$ ions order in a long-range manner. This phase is classified as a spin liquid. It can be stable on a two-dimensional triangular lattice and massless excitations are present [25, 26, 27, 28]. However, at least for the model available, strong biquadratic interactions are required.

A second possibility for the ground state relies on the presence of residual defects in the system, the effect of which is enhanced by frustration. This picture would naturally explain the stretched exponential muon relaxation function for $T_c < T < T_{\text{Cross}}$. However, the substitution...
of only 1% of Zn for Ni dramatically affects the specific heat [4]. Hence, the amount of residual defects is probably small. In addition, we are not aware of a model calculation which would explain the limited correlation length and the persistence of relatively fast fluctuation modes below $T_c$.

A third candidate model attributes the unique properties of NiGa$_2$S$_4$ to topological defects inherent to Heisenberg triangular two-dimensional systems, the so-called $Z_2$-vortices [28, 30]. Gapless excitation modes and a nearly constant susceptibility are predicted [31]. Based on Monte Carlo simulations, a phase transition was suggested [29]. However, because of spin-wave interactions, the correlation length is finite [31, 32, 33, 34]. It is therefore tempting to attribute the transition at $T_c$ to the dissociation of the $Z_2$-vortices and $T_{\text{cross}}$ to the crossover temperature where the spin dynamics starts to be driven by usual Heisenberg spin fluctuations. Remarkably, the $Z_2$-vortices manifest themselves in the temperature vicinity where $C_m$ has a rounded peak. The multichannel relaxation for $T_c < T < T_{\text{cross}}$ reflects the magnetic disorder induced by the unbinding of $Z_2$-vortices.

In conclusion, we have found that, on cooling, the frustrated two dimensional triangular lattice compound NiGa$_2$S$_4$ first behaves as a conventional magnetic compound ordering at $T_c = 9.2(2)$ K. This behavior is however observed only down to 12.6 K (i.e. $\sim 3.4$ K above $T_c$). Below this temperature the $\mu$SR relaxation is stretched exponential-like. This result is interpreted as the signature of an intrinsic property of the triangular system such as the $Z_2$-vortices. The dynamics is never frozen, even far below $T_c$. Finally, the transition at $T_c$ from the short range ordered to the paramagnetic phase is of the continuous type and occurs at a temperature just below that of the specific heat bump, reminding the Berezinskii-Kosterlitz-Thouless transition.

For a further insight into the properties of NiGa$_2$S$_4$, it is necessary to examine the wavevector dependence of the fluctuating magnetic modes below $T_c$. On the theoretical front, an interesting result would be to determine whether modes with a temperature dependent gap vanishing at $T = 0$ K are possible for the triangular lattice as it seems to be the case for the kagomé structure [33]. This could provide an explanation for the observed persistent spin dynamics for $T < T_c$ [30].

Note added. A related report including $\mu$SR data recorded on this material is also available [37]. We note that the time range available at the $\mu$SR facility used to record these data does not allow the authors to evidence the spontaneous muon spin precession that we have observed.

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