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 relaxation technique. 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 $\tau=7$ ns; (ii) an unconventional stretched exponential relaxation function is found for $T_c<T<T_{cross}$ where $T_{cross}=12.6$ K, which is a signature of a multichannel relaxation for this temperature range; and (iii) above $T_{cross}$, 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 glass or spin liquid even without crystalline disorder. The simplest example of geometrical frustration, stacked two-dimensional triangular lattices with a single magnetic ion per unit cell, has been studied intensively.$^2$ NiGa$_2$S$_4$ is a rare example of such a two-dimensional antiferromagnet which does not exhibit a long-range magnetic order at low temperature and which is characterized by gapless excitations.$^3,4$ These physical properties lead naturally to the assumption that its ground state is a spin liquid. Here, we report muon spin rotation and relaxation ($\mu$SR) measurements which show that a spontaneous static magnetic field appears below $T_c=9.2(2)$ K where an appreciable spin dynamics is measured. In addition, we find the spin dynamics to be unconventional in the temperature range $T_c<T<T_{cross}$, where $T_{cross}=12.6$ K.

Polycrystalline powder of NiGa$_2$S$_4$ has been obtained from a solid-vapor reaction using a stoichiometric mixture of pure elements. The synthesis took place in an evacuated silica ampoule. A slow heat treatment over several days up to 1000 °C has been performed with respect to the high sulfur vapor pressure.$^5$ After a final grinding, the powder was treated for a week at 1000 °C.

NiGa$_2$S$_4$ is a chalcogenide magnetic insulator with the Ni$^{2+}$ magnetic ions (spin $S=1$) sitting on a regular triangular lattice. The interactions are of the Heisenberg type, referring to the isotropic Curie constant.$^4$ The crystal structure consists of two GaS 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 $P3m1$ 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 of 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 et al.$^3$ As these authors reported, we also find that the susceptibility recorded under a field of 0.01 T displays a weak kink at $T_\chi=8$ K.

Now, we report on our zero-field $\mu$SR data (see Refs. 6 and 7 for an introduction to the $\mu$SR techniques). A spectrum is expressed as $a_0P^\alpha_Z(t)$, where $a_0$ is an amplitude or asymmetry and $P^\alpha_Z(t)$ 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 nanoscale 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. Our observation is also technically interesting. It shows that, contrary to common wisdom, the detection 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.$^9$ This translates in time space to a Bessel function rather than cosine oscillations.$^5$ Our observation is not surprising since it has been established by neutron 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: $a_0P^\alpha_Z(t)=a_0\exp(\gamma_\mu B_{\text{max}}t)$.
FIG. 1. (Color online) Three zero-field $\mu$SR spectra recorded for a powder sample of NiGa$_2$S$_4$ with the general purpose surface-muon instrument of the S$\mu$S facility at the Paul Scherrer Institute, Villigen, Switzerland. The spectra probe three distinct temperature regimes. At the bottom, we display a spectrum recorded deep into the short-range ordered state. The solid line is the result of a fit to a function given in the main text. The spectrum in the middle has been taken at 11 K where the fit relaxation function is a stretched exponential (full line). For reference, the dashed line displays the best fit to an exponential relaxation. Such an exponential function is observed at 15 K (top spectrum). For clarity, the two high-temperature spectra are shifted up by 0.05 relative to the third one. Their time scale is given by the top horizontal axis, while the scale for the low-temperature spectrum is at the bottom horizontal axis; the range spanned by these two time scales differs by a factor $\sim 30$.

$\exp(-\gamma_0^2 \Delta^2 t^2/2) + a_{\text{rel}} \exp(-\lambda_{\text{rel}} t) + a_{\text{bg}}$, $J_0$ 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 probe field distribution, and $\gamma_0$ is the muon gyromagnetic ratio ($\gamma_0=851.615$ Mrad s$^{-1}$ K$^{-1}$). 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 by $\lambda_{\text{rel}}$. The asymmetry ratio of the first two components is $a_{\text{rel}}/a_{\text{bg}}=1.67(2)$ to be compared to an expected value of 2. A weak texturation of the sample could explain this small deviation.

Figure 2 shows $B_{\text{max}}(T)$. The full line is a fit to the phenomenological function $B_{\text{max}}(T)=B_{\text{max}}(0)[1-(T/T_{\text{stat}})^{\beta}]^\delta$, with $b=2$ and $\beta=0.365$. We find $B_{\text{max}}(0)=222(20)$ mT and the temperature for which the spontaneous field vanishes, $T_{\text{stat}}=9.3(1)$ K. The magnitude $B_{\text{max}}$ reflecting the ordered magnetic moment, the transition at $T_{\text{stat}}$ is consistent with a continuous transition. The field distribution is quite broadened, $\Delta/B_{\text{max}}=0.15$, in accord with our observation of only two oscillations. The detection of these oscillations provides a bound for the time scale of the magnetic correlations,

$$\tau_z \simeq 1/(\gamma_0 B_{\text{max}}) = 5 \text{ ns}.$$  

Last but not least, $\lambda_{\text{rel}}$ is far from being negligible. Its temperature dependence mimics $B_{\text{max}}(T)$ with a value of $\sim 12 \mu\text{s}^{-1}$ at low temperature. Because of the finite $\lambda_{\text{rel}}$ value, we can derive more than a bound for $\tau_z$. From the relation $\lambda_{\text{rel}}=2\gamma_0^2 \Delta \tau_z$, we compute $\tau_z=7 \text{ ns}$, since $\Delta=35(4)$ mT. This value and the previous bound are consistent. Therefore, the time scale of the magnetic correlations is $\tau_z=7 \text{ ns}$ at low temperature. The neutron scattering results, which set a lower bound of $\tau_{\text{min}}=0.3 \text{ ns}$ for this time, are fully consistent.

The spectrum in the middle of Fig. 1 has been recorded at a temperature above $T_{\text{stat}}$ and in a regime where the relaxation is stretched exponential-like: $a_0\exp(-\lambda_{\text{rel}} t)\exp(-\lambda_{\text{stat}} t)$. This occurs in the range $T_{\text{stat}}<T<T_{\text{cross}}=12.6$ K for which three spectra have been recorded at 10, 11, and 11.6 K. We get consistently $\beta_{\text{rel}}=0.56(3)$.

The third spectrum in Fig. 1 corresponds to the case where the sample is magnetically homogeneous and the magnetic fluctuations are fast enough to give rise to an exponential relaxation function $\tau_z=1$. As seen in Fig. 2, $\lambda_{\text{rel}}$ increases for decreasing temperature. This is the signature of the slowing down of the magnetic fluctuations. The relaxation rate is fitted to the formula $\lambda_{\text{rel}}=\lambda_{\text{dyn}}[T/\tau_{\text{stat}}]$, where $\lambda_{\text{Dyn}}=0.028(3) \mu\text{s}^{-1}$ and $T_{\text{Dyn}}=9.2(2)$ K. This formula is derived from the random phase approximation (RPA).

It is expected to be valid for $T>T_{\text{stat}}$ provided $T$ is not too close to $T_{\text{stat}}$ which is the case for $T>T_{\text{cross}}$. As expected, the characteristic temperature $T_{\text{Dyn}}$ introduced in this model is equal to $T_{\text{stat}}$ within error bars: we henceforth replace $T_{\text{Dyn}}$ and $T_{\text{stat}}$ with a unique parameter $T_r=9.2(2)$ K.

We now discuss the implications of our results for the physics of NiGa$_2$S$_4$. We note that $C_m$ displays a rounded peak with a maximum at $\sim 13$ K, i.e., just above $T_c$. Such a behavior is reminiscent of the Berezinskii–Kosterlitz–Thouless transition temperature relevant for a planar XY magnet (see Fig. 9.4.3 of Ref. 12). This is a key result from our study.

The relaxation function from a magnetically homogeneous sample is expected to be exponential when measured...
in its paramagnetic state [see, e.g., elemental Ni (Ref. 13) or Fe (Ref. 14) or the intermetallics GdNi₅ (Ref. 15)]. A stretched exponential relaxation has been observed for a wide variety of physical quantities in many different systems and research areas.²⁶ It arises from a continuous sum of exponential decays.¹⁷ A square-root relaxation of the nuclear magnetic resonance and μSR 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 \( T = 50 \text{ K} \) for wave vector \( q \approx 0.58 \text{ Å}^{-1} \). Here, \( \Delta I(T) \) decreases smoothly up to \( T_c \approx 18 \text{ K} \) 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 \( q \) 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 Ni²⁺ magnetic moment Fourier components, and characterized by a time scale longer by an order of magnitude than \( \tau_{\text{min}} \). dc susceptibility probes an even longer time scale. That \( \Delta I(T) \) vanishes only at \( T_c \approx 18 \text{ K} \) suggests a relatively large continuous spectrum of magnetic fluctuations in NiGa₂S₄. This could be a common property of geometrically frustrated magnets since it has already been encountered for Tb₂S₉O₁₇.²⁰,²¹ Because of the notable reduction of the Ni²⁺ \( (S=1) \) magnetic moment as measured by neutron diffraction (\( \approx 25\% \)), the spectral weight must also extend to time scales smaller than \( \tau_{\text{min}} \).

Previous thermodynamic and neutron results³ and the present μSR measurements on NiGa₂S₄ demonstrate that this two-dimensional Heisenberg triangular-lattice antiferromagnet has unique low-temperature properties: (i) while its Curie–Weiss temperature is rather large, \( \Theta_{\text{CW}} = -80(2) \text{ K} \), it does not display a long-range magnetic ordering; only an incommensurate short-range order with a nanoscale correlation length and a spontaneous static interstitial magnetic field below \( T_{\text{c}} = 9.2(2) \text{ K} \); (ii) its ground state is highly degenerate; and (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 NiGa₂S₄ 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 with 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 Ni²⁺ 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.²⁵–²⁸ 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 NiGa₂S₄ to topological defects inherent to the Heisenberg triangular two-dimensional systems, the so-called \( Z_2 \) vortices.²⁹,³⁰ Gapless excitation modes and a nearly constant susceptibility are predicted.³¹ Based on the Monte Carlo simulations, a phase transition was suggested.²⁹ However, because of spin-wave interactions, the correlation length is finite.³¹–³⁴ 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 the 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 NiGa₂S₄ first behaves as a conventional magnetic compound ordering at \( T_c = 9.2(2) \text{ K} \). This behavior is, however, observed only down to 12.6 K (i.e., \( \approx 3.4 \text{ K} \) above \( T_c \)). Below this temperature, the μSR 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 NiGa₂S₄, it is necessary to examine the wave vector 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 \( T = 0 \text{ K} \) are possible for the triangular lattice as it seems to be the case for the kagomé structure.³⁵ This would provide an explanation for the observed persistent spin dynamics for \( T < T_c \).³⁶

A related report including μSR data recorded on this material is also available.³⁷ We note that the time range available at the μSR facility used to record these data does not allow the authors to evidence the spontaneous muon spin precession that we have observed.
More specifically, through a combined use of the RPA approximation for the wave vector dependent susceptibility and the fluctuation dissipation and Kramers–Kronig theorems, an expression for the wave vector dependent susceptibility and the magnetic propagation vector is derived. The detailed derivation will be published elsewhere.


