Short-range magnetic ordering process for the triangular-lattice compound $NiGa_2S_4$: A positive muon spin rotation and relaxation study

A. Yaouanc,[1] P. Dalmas de Réotier,[1] Y. Chapuis,[1] C. Marin,[1] G. Lapertot,[1] A. Cervellino,[2,*] and A. Amato[3]
[1]*CEA/DSM/Institut Nanosciences et Cryogénie, 38054 Grenoble, France*
[2]*Laboratory for Neutron Scattering, ETH Zürich and Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland*
[3]*Laboratory for Muon-Spin Spectroscopy, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland*
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We report a study of the triangular-lattice Heisenberg magnet $NiGa_2S_4$ 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 $\simeq$7 ns; (ii) an unconventional stretched exponential relaxation function is found for $T_c<T<T_{\rm cross}$, where $T_{\rm cross}$=12.6 K, which is a signature of a multichannel relaxation for this temperature range; and (iii) above $T_{\rm cross}$, 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.

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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 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] $NiGa_2S_4$ 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 (μSR) 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 $T_c<T<T_{\rm cross}$, where $T_{\rm cross}$=12.6 K.

Polycrystalline powder of $NiGa_2S_4$ 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.

$NiGa_2S_4$ 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 $P\bar{3}m1$ 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 $T_\chi\simeq 8$ K.

Now, we report on our zero-field μSR data (see Refs. 6 and 7 for an introduction to the μSR techniques). A spectrum is expressed as $a_0 P_Z^{\rm exp}(t)$, where a_0 is an amplitude or asymmetry and $P_Z^{\rm exp}(t)$ 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 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 μSR oscillation is not a fingerprint of a long-range magnetic order.

The spectrum at 2.3 K has a steep slope for time $t<0.02$ μs. 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.[6] 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: $a_0 P_Z^{\rm exp}(t) = a_{\rm os} J_0(\gamma_\mu B_{\rm max} t)$

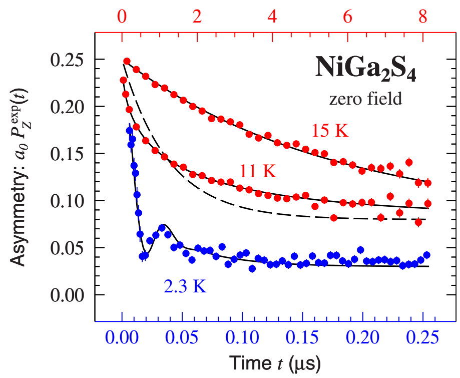

FIG. 1. (Color online) Three zero-field μSR spectra recorded for a powder sample of $NiGa_2S_4$ with the general purpose surface-muon instrument of the SμS facility at the Paul Scherrer Institute, Villigen, Switzerland. The spectra probe three distinct temperature regimes. At the bottom, we display a 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 ~30.

$\times\exp(-\gamma_\mu^2\Delta^2t^2/2)+a_{rel}\exp(-\lambda_Z t)+a_{bg}$. J_0 is the zeroth-order Bessel function of the first kind, B_{max} stands for the maximum of the spontaneous static local magnetic field distribution at the muon site, Δ^2 characterizes the broadening of the probed field distribution, and γ_μ is the muon gyromagnetic ratio (γ_μ=851.615 Mrad s^{-1} T^{-1}). The component of amplitude a_{rel} gauges the relaxation of the muons sensing a field parallel to their initial polarization. The associated spin-lattice relaxation rate is denoted by λ_Z. The asymmetry ratio of the first two components is $a_{os}/a_{rel}\simeq 1.6(2)$ to be compared to an expected value of 2. A weak texturation of the sample could explain this small deviation.

Figure 2 shows $B_{max}(T)$. The full line is a fit to the phenomenological function $B_{max}(T)=B_{max}(0)[1-(T/T_{stat})^b]^\beta$, with $b=2$ and $\beta=0.365$. We find $B_{max}(0)=222(20)$ mT and the temperature for which the spontaneous field vanishes, $T_{stat}=9.3(1)$ K. The magnitude B_{max} reflecting the ordered magnetic moment, the transition at T_{stat}, is consistent with a continuous transition. The field distribution is quite broadened, $\Delta/B_{max}\simeq 0.15$, 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:[10] $\tau_c \gtrsim 1/(\gamma_\mu B_{max})=5$ ns. Last but not least, λ_Z is far from being negligible. Its temperature dependence mimics $B_{max}(T)$ with a value of ~12 μs^{-1} at low temperature. Because of the finite λ_Z value, we can derive more than a bound for τ_c. From the relation $\lambda_Z=2\gamma_\mu^2\Delta^2\tau_c$,[6] we compute $\tau_c\simeq 7$ ns, since $\Delta=35(4)$ mT. This value and the previous bound are consistent. Therefore, the time scale of the magnetic correlations is $\tau_c\simeq 7$ ns at low temperature. The neutron scattering results,

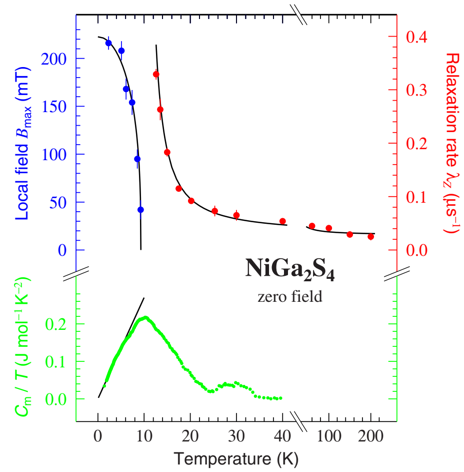

FIG. 2. (Color online) Upper panel: thermal dependence of two parameters extracted from μSR spectra. The maximum of the static local magnetic field at the muon site B_{max} for $T<T_{stat}$ is presented on the left-hand side. The relaxation rate λ_Z for $T>T_{cross}$ is displayed on the right-hand side of the same panel, 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.

which set a lower bound of $\tau_{min}=0.3$ ns for this time, are fully consistent.[3]

The spectrum in the middle of Fig. 1 has been recorded at a temperature above T_{stat} and in a regime where the relaxation is stretched exponential-like: $a_0P_Z^{exp}(t)=a_{rel}\times\exp[-(\lambda_Z t)^{\beta_\mu}]+a_{bg}$. This occurs in the range $T_{stat}<T<T_{cross}=12.6$ K for which three spectra have been recorded at 10, 11, and 11.6 K. We get consistently $\beta_\mu=0.56(3)$.

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 i.e., $\beta_\mu=1$. As seen in Fig. 2, λ_Z increases for decreasing temperature. This is the signature of the slowing down of the magnetic fluctuations. The relaxation rate is fitted to the formula $\lambda_Z=\lambda_0[T/(T-T_{dyn})]^2$, where $\lambda_0=0.028(3)$ μs^{-1} and $T_{dyn}=9.2(2)$ K. This formula is derived from the random phase approximation (RPA).[11] It is expected to be valid for $T>T_{stat}$ provided T is not too close to T_{stat} which is the case for $T>T_{cross}$. As expected, the characteristic temperature T_{dyn} introduced in this model is equal to T_{stat} within error bars: we henceforth replace T_{dyn} and T_{stat} with a unique parameter $T_c=9.2(2)$ K.

We now discuss the implications of our results for the physics of $NiGa_2S_4$. We note that C_m displays a rounded peak with a maximum at ~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 $GdNi_5$ (Ref. 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 μSR[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 $T_c < T < T_{cross}$ 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}.[3] Here, $\Delta I(T)$ 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_χ. 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 τ_{min}. B_{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 τ_{min}. dc 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 $NiGa_2S_4$. This could be a common property of geometrically frustrated magnets since it has already been encountered for $Tb_2Sn_2O_7$.[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 τ_{min}.

Previous thermodynamic and neutron results[3] and the present μSR measurements on $NiGa_2S_4$ demonstrate that this two-dimensional Heisenberg triangular-lattice antiferromagnet has unique low-temperature properties: (i) while its Curie–Weiss temperature is rather large, $\Theta_{CW} = -80(2)$ 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 $T_c = 9.2(2)$ 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 $NiGa_2S_4$ exhibits a conventional paramagnetic spin dynamics down to T_{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 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.[25–28] 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 $T_c < T < T_{cross}$. 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 $NiGa_2S_4$ 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_{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 $T_c < T < T_{cross}$ 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 $NiGa_2S_4$ 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 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 $NiGa_2S_4$, 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 $T = 0$ 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 $T \ll T_c$.[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.

*On leave from CNR, Istituto di Cristallografia (CNR-IC), 70126 Bari, Italy.

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[11] More specifically, through a combined used of the RPA approximation for the wave vector dependent susceptibility and the fluctuation dissipation and Kramers–Kronig theorems, an expression for the spin correlation function at zero frequency $\Lambda(\mathbf{q},\omega=0)$ is derived. λ_Z is proportional to a weighted sum over the Brillouin zone of $\Lambda(\mathbf{q},\omega=0)$. Assuming that $\lambda_Z(T)$ is mainly driven by the correlation at a given wave vector (the magnetic structure propagation vector), the result given in the main text is found. The detailed derivation will be published elsewhere.
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