

Unconventional spin freezing and fluctuations in the frustrated antiferromagnet NiGa₂S₄

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(Received 30 October 2008; published 5 December 2008)

Muon spin rotation (μ SR) experiments reveal unconventional spin freezing and dynamics in the two-dimensional (2D) triangular lattice antiferromagnet NiGa₂S₄. Long-lived disordered Ni-spin freezing (correlation time $\geq 10^{-6}$ s at 2 K) sets in below $T_f = 8.5 \pm 0.5$ K with a mean-field-like temperature dependence. The observed exponential temperature dependence of the muon spin relaxation above T_f is strong evidence for 2D critical spin fluctuations. Slow Ni-spin fluctuations coexist with quasistatic magnetism at low temperatures but are rapidly suppressed for fields ≥ 10 mT, in marked contrast with the field-independent specific heat. The μ SR and bulk susceptibility data indicate a well-defined 2D phase transition at T_f , below which NiGa₂S₄ is neither a conventional magnet nor a singlet spin liquid.

DOI: 10.1103/PhysRevB.78.220403

PACS number(s): 75.20.Hr, 75.40.Cx, 75.50.Ee, 76.75.+i

The layered chalcogenide NiGa₂S₄ is an example of a quasi-two-dimensional (2D) antiferromagnet (AFM) with a nearly perfect triangular lattice and is a candidate for a geometrically frustrated spin liquid.¹ Its crystal structure consists of triangular Ni planes well separated by GaS polyhedra, which assure the quasi-2D nature of the Ni magnetism. The Ni²⁺ $t_{2g}^6 e_g^2$ configuration is that of a $S=1$ Heisenberg magnet consistent with the nearly isotropic susceptibility. Neutron-scattering experiments^{1,2} revealed the development of quasistatic (correlation time $\tau_c \geq 3 \times 10^{-10}$ s) short-range incommensurate Ni-spin correlations below ~ 20 K, well below the paramagnetic Curie-Weiss temperature $|\theta_W| \approx 80$ K, with very weak correlations between Ni planes. The magnetic specific heat $C_M(T)$ exhibits a broad peak¹ at ~ 10 K, and the magnetic susceptibility shows a sharp kink at 8.5 K suggesting a transition at this temperature. Evidence for spin freezing below ~ 10 K was obtained from ⁶⁹Ga nuclear quadrupole resonance (NQR) experiments³ and substantiated by recent muon spin rotation (μ SR) data.⁴

In the temperature range 0.35–4 K $C_M(T) \propto T^2$, indicative of gapless linearly dispersive low-lying modes. Magnons in an ungapped 2D AFM would yield this result but would require long-range spin order, in apparent conflict with the neutron-scattering results. At all temperatures $C_M(T)$ is independent of applied magnetic field up to 7 T, as also observed in the 2D kagomé lattice AFM SrCr_{9p}Ga_{12-9p}O₁₉ (SCGO) (Ref. 5). This is certainly not expected for magnons or any other simple cooperative spin excitation and suggests the possibility of a singlet or singletlike spin liquid. A number of theoretical scenarios have been proposed for NiGa₂S₄ (Refs. 6 and 7), with magnetic properties that depend sensitively on details of the assumed model as is common in frustrated systems. It is important, therefore, to characterize the properties of this compound as fully as possible.

This Rapid Communication reports a detailed longitudinal-field μ SR (LF- μ SR) (Ref. 8) study of NiGa₂S₄, using the local nature of the muon spin probe to provide

unique information on the static and dynamic properties of Ni spins at low temperatures. Although preliminary μ SR results⁹ seemed to be inconsistent with spin freezing, the present data and those of Ref. 4 give clear evidence for a disordered quasistatic¹⁰ Ni-spin configuration. We find a lower bound on τ_c more than 3 orders of magnitude longer than the neutron-scattering value. This spin freezing sets in abruptly and exhibits disordered mean-field-like behavior below a freezing temperature $T_f \approx 8.5$ K. A kink is observed in the bulk susceptibility at the same temperature; together these results suggest a well-defined 2D phase transition. Dynamic muon spin relaxation is spatially inhomogeneous at all temperatures, exhibits an exponential temperature dependence for $T > T_f$ as expected for 2D Heisenberg critical fluctuations, and remains strong down to ~ 2 K for small applied fields. Our most unexpected finding is a significant suppression of this low-temperature relaxation by fields ~ 10 mT, which is difficult to reconcile with the field independence of the specific heat.

Time-differential LF- μ SR measurements were carried out at the M20 beam line at TRIUMF, Vancouver, Canada, on a homogeneous and stoichiometric polycrystalline powder and a single crystal of NiGa₂S₄ (Ref. 1); the latter was grown using a chemical vapor transport method. Data were taken in a longitudinal field $\mu_0 H_L \geq 2$ mT ($\mathbf{H}_L \parallel [001]$) for the single crystal) to decouple the muon spins from nuclear dipolar fields¹¹ and to study the field dependence. Care was taken to minimize the spectrometer “dead time” between a muon stop and the earliest detection of the decay positron. This was necessary since the early-time relaxation in NiGa₂S₄ is very rapid; it was not observed in earlier μ SR experiments at the KEK pulsed muon facility³ due to the relatively long dead time inherent in pulsed μ SR.

Figure 1 shows representative LF- μ SR asymmetry decay data⁸ in polycrystalline NiGa₂S₄. The asymmetry $A(t)$ is proportional to the muon spin polarization $P(t)$. In agreement with previous results,⁴ the early-time data at low temperatures exhibit strongly damped oscillations, indicative of a

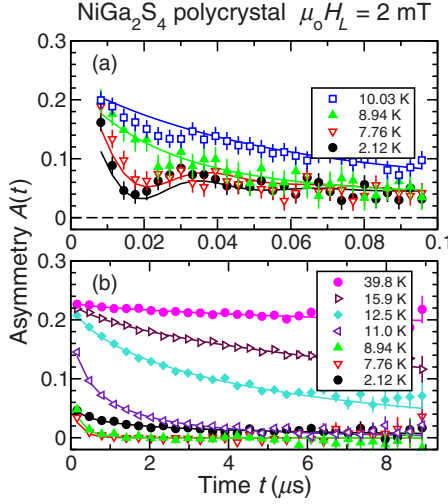


FIG. 1. (Color online) Representative (a) early- and (b) late-time LF- μ SR asymmetry data in polycrystalline NiGa₂S₄; applied longitudinal field $\mu_0 H_L = 2$ mT. Curves: fits to Eqs. (1)–(3).

quasistatic component $\langle \mathbf{B}_{\text{loc}} \rangle$ of the local field at the muon site. The oscillations are rapidly damped [Fig. 1(a)] due to inhomogeneity in $\langle \mathbf{B}_{\text{loc}} \rangle$, leaving a second signal that relaxes slowly [Fig. 1(b)]. This slow signal is due to the muon spin component parallel to $\langle \mathbf{B}_{\text{loc}} \rangle$ (Kubo-Toyabe behavior), and its relaxation is due to the fluctuating component $\delta \mathbf{B}_{\text{loc}}(t) = \mathbf{B}_{\text{loc}}(t) - \langle \mathbf{B}_{\text{loc}} \rangle$ (Ref. 11).

It should be noted that this two-component Kubo-Toyabe structure arises when the statistical properties of \mathbf{B}_{loc} [inhomogeneity in $\langle \mathbf{B}_{\text{loc}} \rangle$, fluctuation statistics associated with $\delta \mathbf{B}_{\text{loc}}(t)$] are the same at all muon sites, i.e., when the system is macroscopically homogeneous. Thus the two components should not be associated with separate volume fractions of a multiphase sample and are not by themselves evidence for multiple phases in NiGa₂S₄. We discuss below independent evidence for inhomogeneous spin dynamics obtained from the form of the slow-signal relaxation.

The oscillations and Kubo-Toyabe behavior are strong evidence for a quasistatic Ni-spin configuration in NiGa₂S₄. As $T_f = 8.5 \pm 0.5$ K is approached from below, the oscillation frequency decreases rapidly and the two-component behavior is lost. For $T > T_f$ there is only a single signal component, with a rapidly increasing rate as $T \rightarrow T_f$ as expected from critical slowing of Ni-spin fluctuations.

For $T < T_f$ the asymmetry data were fit to the form

$$A(t) = A_r P_r(t) + A_s P_s(t), \quad P_r(0) = P_s(0) = 1, \quad (1)$$

where the first and second terms represent the rapid and slow components, respectively (“ $T < T_f$ fits”). The total asymmetry $A = A_r + A_s$ at $t = 0$ was assumed independent of temperature and applied field. A damped Bessel function

$$P_r(t) = \exp(-\lambda_r t) J_0(\omega_\mu t), \quad (2)$$

indicative of an incommensurate spin structure,¹² was found to fit the early-time data better than other candidates such as a damped sinusoid $\exp(-\lambda_r t) \cos(\omega_\mu t)$ or simple Kubo-Toyabe functions.^{11,13} The spectrometer dead time of ~ 8 ns

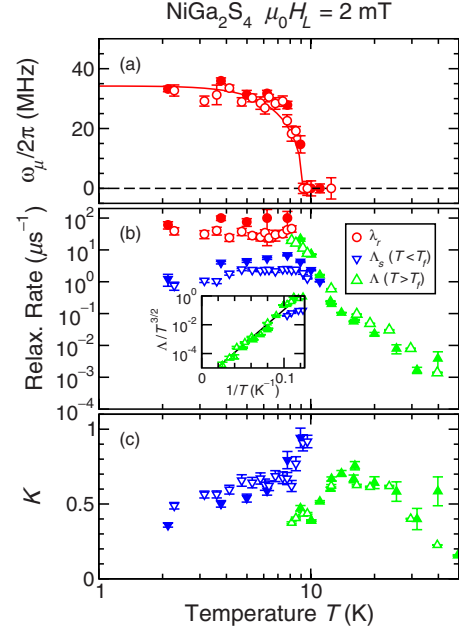


FIG. 2. (Color online) Temperature dependencies of fit parameters in NiGa₂S₄; $\mu_0 H_L = 2$ mT. Filled symbols: polycrystalline sample. Open symbols: single-crystal sample $\mathbf{H}_L \parallel [001]$. Circles: (a) oscillation frequency $\omega_\mu/2\pi$; (b) static relaxation rate λ_r . Inverted triangles: $T < T_f$ fits (see text); (b) dynamic rate Λ_s and (c) stretching power K . Upright triangles: $T > T_f$ fits; (b) Λ and (c) K . Inset to (b): $T > T_f$ and $\Lambda/T^{3/2}$ vs $1/T$. Line: $\Lambda/T^{3/2} \propto \exp(T^*/T)$ (Ref. 17), $T^* = 114(7)$ K.

makes the choice of fit function uncertain, but the fit value of the oscillation frequency ω_μ does not depend strongly on this choice. For the Bessel-function fit $\omega_\mu/2\pi = 34 \pm 2$ MHz, $\langle B_{\text{loc}} \rangle = \omega_\mu / \gamma_\mu = 251 \pm 15$ mT, where γ_μ is the muon gyromagnetic ratio. This value is qualitatively consistent with Ni dipolar fields at candidate muon stopping sites in the GaS layers. The ratio $\lambda_r / \omega_\mu \approx 0.2$ is a measure of the relative spread in $\langle B_{\text{loc}} \rangle$ due to disorder.

The late-time asymmetry data below T_f and the entire asymmetry function above T_f ($A_r = 0$; “ $T > T_f$ fits”) could be well fit with the “stretched-exponential” relaxation function,

$$P(t) [= P_s(t) \text{ for } T < T_f] = \exp[-(\Lambda t)^K], \quad K < 1, \quad (3)$$

often used¹⁴ to model an inhomogeneous distribution $p(W)$ of exponential rates W .¹⁵ The relaxation time $1/\Lambda$ gives the time scale of the relaxation and the power K controls its shape: broader distributions of relaxation rates are modeled by smaller values of K . For all fits K was found to be significantly smaller than 1, indicating that the spin fluctuations are inhomogeneous over the entire temperature range.¹⁶ At low temperatures and low fields the amplitude A_s of the slowly relaxing component is approximately $A/3$, as expected from quasistatic LF- μ SR relaxation in a powder sample.¹¹

Figure 2 gives the temperature dependencies of the parameters from fits to data from both single-crystal and polycrystalline samples. For the two samples $\omega_\mu(T)$ and K reproduce well. With increasing temperature ω_μ decreases and vanishes at $T_f = 8.5 \pm 0.5$ K, in agreement with the kink in

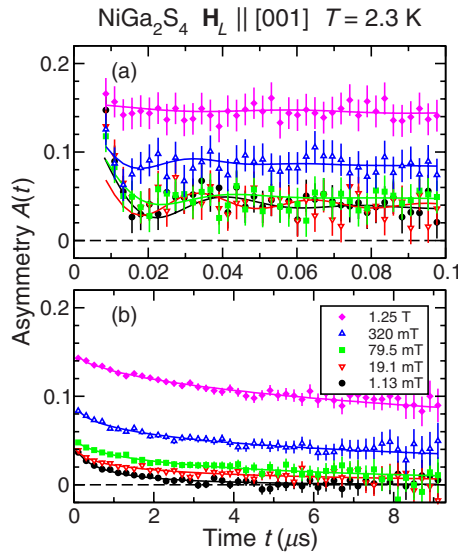


FIG. 3. (Color online) Representative (a) early- and (b) late-time LF- μ SR asymmetry plots in single-crystal NiGa_2S_4 at $T=2.3$ K and applied longitudinal fields $\mathbf{H}_L \parallel [001]$.

the bulk susceptibility.¹ A mean-field temperature dependence [Brillouin function for $S=1$; curve in Fig. 2(a)] describes the data to within experimental uncertainty.

The dynamic relaxation rates in the polycrystalline sample are higher below T_f and lower above T_f than in the single crystal but follow the same trends [Fig. 2(b)]. As T approaches T_f from above Λ increases strongly, suggestive of critical slowing down of paramagnetic-state spin fluctuations. The data can be fit to $\Lambda/T^{3/2} \propto \exp(T^*/T)$ [inset of Fig. 2(b)] with $T^*=114(7)$ K. This form is expected for critical fluctuations of Heisenberg spins on a 2D lattice¹⁷ with $T^*=2\pi\rho_s$, where for $S=1$ the spin-wave stiffness $\rho_s \approx J$. From $\theta_W = zJS(S+1)/3$ with $z=6$ Ni nearest neighbors, we estimate $T^*=2\pi\rho_s \approx 125$ K, in good agreement with the measured value. The differences in Λ and K for $T < T_f$ and $T > T_f$ fits near T_f [Figs. 2(b) and 2(c)] probably reflect a distribution of freezing temperatures.

With decreasing temperature below T_f Λ_s decreases slightly, but for both samples remains $\geq 1 \mu\text{s}^{-1}$ down to $2.1 \text{ K} \approx T_f/4$. This strong relaxation is consistent with the loss of ^{69}Ga NQR signal in the same temperature range.³ Somewhat similar relaxation behavior has been observed in the triangular AFM NaCrO_2 (Ref. 18) with, however, no indication of critical slowing down above $T_f \approx 40$ K.

LF- μ SR asymmetry data from the single-crystal sample at 2.3 K are shown in Fig. 3 for $\mu_0 H_L$ in the range 1.13 mT–1.25 T. The rapid early-time relaxation is decoupled (the late-time amplitude increases) for $\mu_0 H_L \geq \langle B_{\text{loc}} \rangle$. This decoupling is independent evidence for a distribution of quasistatic fields¹¹ and is in contrast to the “undecouplable Gaussian” relaxation observed in μ SR experiments on SCGO (Ref. 19). Figure 4 shows the field dependencies of Λ_s and K at 2.1 K (polycrystal) and 2.3 K (single crystal). The stretching power $K \approx 0.4$ is more or less independent of field. It can be seen that Λ_s is strongly suppressed by applied field $\mu_0 H_L \geq 10$ mT $\ll \langle B_{\text{loc}} \rangle$. This suppression is not due to an effect of H_L on the muon Zeeman splitting¹⁴ because the resultant

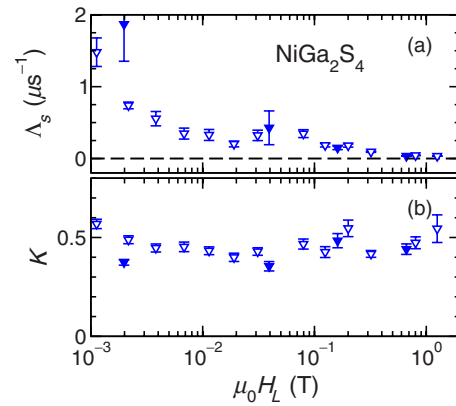


FIG. 4. (Color online) Dependencies of (a) slow relaxation rate Λ_s and (b) stretching power K [Eq. (3)] on applied longitudinal field H_L in NiGa_2S_4 . Filled symbols: polycrystalline sample, $T=2.1$ K. Open symbols: single-crystal sample, $T=2.3$ K and $H_L \parallel [001]$.

muon field $\mu_0 \mathbf{H}_L + \langle \mathbf{B}_{\text{loc}} \rangle$ is still approximately $\langle \mathbf{B}_{\text{loc}} \rangle$. Thus H_L must affect the Ni-spin-fluctuation spectrum directly. This contrasts sharply with the field-independent specific heat, which is unaffected to within a few percent by a field of 7 T.

We conclude that NiGa_2S_4 , which should be a good example of a 2D triangular Heisenberg $S=1$ magnet, is neither a “conventional” AFM, for which spin freezing would be accompanied by a decrease in the muon relaxation at low temperatures, nor a singlet spin liquid, for which there would be no spin freezing. The LF- μ SR data are consistent with a well-defined 2D phase transition at $T_f \approx 8.5$ K leading to a disordered AFM ground state, as found from previous ^{69}Ga NQR and μ SR studies.^{3,4} This is in contrast to SCGO, which exhibits a field-independent specific heat⁵ but no spin freezing.¹⁹ The low-temperature relaxation rate Λ_s gives a lower bound on the frozen-spin correlation time τ_c of $1/\Lambda_s \sim 10^{-6}$ s at 2 K, more than 3 orders of magnitude longer than the lower bound from neutron scattering and 7 orders of magnitude longer than the inverse exchange frequency. Thus the Ni spins are very viscous indeed, if not completely frozen. The transition at T_f is unlikely to be due either to three-dimensional (3D) coupling or to Ni-spin anisotropy, both of which are weak;¹ a topological transition associated with vortex binding⁷ is one candidate mechanism. NiGa_2S_4 is chemically and structurally well ordered, raising the question of why the μ SR and ^{69}Ga NQR relaxation³ is spatially inhomogeneous.

The persistent muon spin relaxation at low temperatures [Fig. 2(b)] is evidence for significant Ni-spin-fluctuation noise power at low frequencies. This is often observed in frustrated magnets without spin freezing²⁰ but less frequently in spin-frozen states.^{18,21,22} It indicates a high density of spin excitations that coexists with spin freezing at low temperatures.²³ A mean-field-like order parameter is also rare in 2D frustrated antiferromagnets²⁴ and to our knowledge has never been seen together with persistent low-temperature dynamics.

Easily the most remarkable result of this work is the contrast between the suppression of the low-temperature muon spin relaxation by $H_L \geq 10$ mT [Fig. 4(a)] and the negligible magnetic-field dependence of the specific heat up to fields

more than 2 orders of magnitude greater.¹ There is no fundamental paradox here, since the entropy of a spin system is not explicitly dependent on the time scale of the fluctuations. But it is hard to understand how strong muon spin relaxation, usually associated with most or all of the spin excitation degrees of freedom of a system, could change so drastically with field without the slightest signature in the entropy. Reconciling the LF- μ SR and specific-heat results is clearly an important task for theory.

We are grateful for technical assistance from the TRIUMF Centre for Molecular and Materials Science, where these ex-

periments were carried out. We wish to thank H. Kawamura, Y. Maeno, and R. R. P. Singh for useful discussions and K. Onuma for help with the experiments. This work was supported by the U.S. NSF under Grants No. 0422674 (Riverside) and No. 0604015 (Los Angeles), by Grants-in-Aid for Scientific Research from JSPS, and by a Grant-in-Aid for Scientific Research on Priority Areas under Grant No. 19052003 (Tokyo).

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