Unconventional spin freezing and fluctuations in the frustrated antiferromagnet NiGa$_2$S$_4$

D E MacLaughlin$^1$, S Nakatsuji$^2$, Y Nambu$^2$, K Ishida$^3$, R H Heffner$^{4,5}$, Lei Shu$^{1,6}$ and O O Bernal$^7$

$^1$Department of Physics and Astronomy, University of California, Riverside, California 92521, U.S.A.
$^2$Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan
$^3$Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan
$^4$Advanced Science research Center, Japan Atomic Energy Agency, Tokai 319-1195, Japan
$^5$Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.
$^7$Department of Physics and Astronomy, California State University, Los Angeles, California 90032, U.S.A.

E-mail: macl@physics.ucr.edu

Abstract. Longitudinal-field muon spin rotation (LF-$\mu$SR) experiments in the two-dimensional geometrically-frustrated antiferromagnet NiGa$_2$S$_4$ reveal a number of features of spin freezing and dynamics in this system. Long-lived (correlation time $\gtrsim 10^{-6}$ s at 2 K) disordered Ni spin freezing sets in abruptly below $T_f = 8.5 \pm 0.5$ K. At low temperatures slow Ni spin fluctuations are found in low applied field $H_L$ that are rapidly suppressed for $H_L \gtrsim 0.04$ T. Activated muon spin relaxation above $T_f$ is strong evidence for 2D critical behaviour. The LF-$\mu$SR data indicate that NiGa$_2$S$_4$ is neither a conventional magnet nor a singlet spin liquid, and raise the question of how to reconcile the strongly field-dependent muon relaxation with the field-independent specific heat.

The layered chalcogenide NiGa$_2$S$_4$ is an example of a low-spin ($S \leq 1$) quasi-two-dimensional antiferromagnet with a nearly perfect triangular lattice [1]. The magnetic specific heat $C_M(T)$ exhibits a broad peak at $\sim 10$ K and the magnetic susceptibility shows a kink at 8.5 K, suggesting a phase transition at this temperature. Neutron scattering experiments [1, 2] revealed short-range incommensurate Ni spin correlations that set in well below the paramagnetic Curie-Weiss temperature $|\theta_W| \approx 80$ K. Evidence for spin freezing was obtained from $^{69}$Ga NQR experiments [3] and substantiated by recent muon spin rotation ($\mu$SR) data [4]. In the temperature range 0.35–4 K $C_M(T) \propto T^2$, and at all temperatures $C_M(T)$ is sensibly independent of applied magnetic field up to 7 T. This is certainly not expected for magnons or any other simple cooperative spin excitation, apparently suggesting the possibility of a singlet or singlet-like spin liquid.

A number of scenarios have been proposed to understand this behaviour [5–9]. As is common in frustrated systems, the ground state depends sensitively on details of the assumed model. It is important, therefore, to characterise the properties of this compound as fully as possible.

$^6$ Present address: Department of Physics and Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92093, U.S.A.
This paper is a preliminary report of a longitudinal-field \(\mu\)SR (LF-\(\mu\)SR) \[10\] study of \(\text{NiGa}_2\text{S}_4\), which uses the local-probe nature of the \(\mu\)SR technique to provide unique information on the static and dynamic behaviour of the Ni spins at low temperatures. The \(\mu\)SR data give clear evidence for a disordered quasistatic Ni spin configuration that sets in abruptly below a freezing temperature \(T_f \approx 8.5\) K, suggestive of a 2D phase transition. Dynamic muon spin relaxation, which is spatially inhomogeneous at all temperatures, exhibits 2D critical behaviour for \(T > T_f\), and at low temperatures is strong for small applied longitudinal fields \(H_L\), but is rapidly suppressed for \(H_L \gtrsim 0.04\) T. The latter result is the most unexpected finding of this study, since it is difficult to reconcile with the field-independent specific heat.

LF-\(\mu\)SR measurements were carried out at the M20 beam line at TRIUMF, Vancouver, Canada, on a powder sample of \(\text{NiGa}_2\text{S}_4\) prepared as described previously \[1\]. All data were taken with \(\mu_0 H_L \geq 2\) mT, to ‘decouple’ the muon spins from nuclear dipolar fields \[11\] and to study the field dependence. Figure 1 shows representative LF-\(\mu\)SR asymmetry decay data for \(\mu_0 H_L = 2\) mT at temperatures in the range 2–40 K. The asymmetry \(A(t)\) in decay positron count rates is proportional to the muon polarisation decay function \(P(t)\) \[10\]. In agreement with previous results \[4\], the early-time data at low temperatures exhibit oscillations indicative of a quasistatic local field \(\langle B_{loc} \rangle\) at the muon site. The oscillations are rapidly damped [Fig. 1 (top)], leaving a second signal that relaxes more slowly [Fig. 1 (bottom)]. This slow signal is due to the muon spin component parallel to \(\langle B_{loc} \rangle\) (two-component Kubo-Toyabe \[11\] behaviour), and is dynamic in origin. The oscillations and Kubo-Toyabe behaviour are strong evidence for a quasistatic Ni spin configuration. As \(T_f = 8.5 \pm 0.5\) K is approached from below the oscillation frequency decreases rapidly, and the two-component behaviour is lost. Above \(T_f\) there is only a single signal component with a rapidly-increasing rate as \(T_f\) is approached from above, as expected from critical slowing of Ni-spin fluctuations.

For \(T < T_f\) the asymmetry data were fit to the form

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

where the the first and second terms represent the rapid and slow components, respectively. At low temperatures and low applied fields the relative amplitude \(A_s/(A_r + A_s)\) of the slowly-relaxing component is approximately \(1/3\), as expected from low-field quasistatic relaxation in a powder sample \[11\]. A damped Bessel function

\[
P_s(t) = \exp(-\lambda_s t)J_0(\omega_s t),
\]

is the best fit function. For \(T < T_f\) the data were fit to the form

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

where the first and second terms represent the rapid and slow components, respectively. At low temperatures and low applied fields the relative amplitude \(A_s/(A_r + A_s)\) of the slowly-relaxing component is approximately \(1/3\), as expected from low-field quasistatic relaxation in a powder sample \[11\]. A damped Bessel function

\[
P_s(t) = \exp(-\lambda_s t)J_0(\omega_s t),
\]

is the best fit function.
indicative of an incommensurate spin structure [12], was found to fit the early-time data better than other candidates such as a damped sinusoid \(\exp(-\lambda t)\cos(\omega t)\) or simple Kubo-Toyabe functions [11, 13]. At low temperatures \(\omega_\mu/2\pi = 34 \pm 2\) MHz, \(\langle B_{\text{loc}} \rangle = \omega_\mu/\gamma_\mu = 251 \pm 15\) mT, where \(\gamma_\mu\) is the muon gyromagnetic ratio. This value is consistent with Ni-spin dipolar fields at candidate muon stopping sites in the GaS layers, assuming the Ni moment configuration found from neutron scattering [1]. The ratio \(\lambda_\mu/\omega_\mu \approx 0.2\) is a measure of the relative spread in \(\langle B_{\text{loc}} \rangle\) due to disorder. The late-time data [Fig. 1 (bottom)] could be well fit with the ‘stretched exponential’ relaxation function

\[
P_s(t) = \exp\left[-\left(\Lambda_s t\right)^K\right], \quad K \approx 0.5,
\]

often used to model an inhomogeneous distribution of exponential rates. The strong relaxation below \(T_s\) (\(\Lambda_s \gtrsim 1\) \(\mu s^{-1}\)) is consistent with the loss of \(^{69}\text{Ga}\) NQR signal in the same temperature range [3]. Above \(T_s\) the data could be fit with a single stretched exponential [second term of Eq. (1)], again with \(K\) significantly smaller than 1 [14].

Representative LF-\(\mu\)SR asymmetry data at 2.1 K are shown in Fig. 2 for \(\mu_0 H_L\) in the range 2 mT–2 T. Figure 2. (colour online) Representative early-time (top) and late-time (bottom) LF-\(\mu\)SR asymmetry plots in NiGa\(_2\)S\(_4\) at various applied longitudinal fields, \(T = 2.1\) K. Curves: fits to Eqs. (1–2).
or to Ni-spin anisotropy, both of which are shown to be weak by a number of experiments. A Kosterlitz-Thouless transition or a topological transition associated with vortex binding [8] are candidate mechanisms. NiGa$_2$S$_4$ is chemically and structurally ordered, and the inhomogeneous dynamic relaxation is not well understood; it may, however, be related to the disordered spin structure found from neutron scattering [1]. The strong low-temperature relaxation found in NiGa$_2$S$_4$ is often observed in frustrated magnets without spin freezing [17] but less frequently in spin-frozen states [18–20]. It indicates a high density of low-lying thermal excitations that are not spinless objects such as spin singlets [21].

The most unexpected feature of these results is the contrast between the negligible magnetic field dependence of the specific heat up to 7 T [1] and the suppression of the low-temperature muon spin relaxation by much smaller fields. This not fundamentally inconsistent, because the entropy of a spin system has no explicit dependence on the time scale of the fluctuations. But strong muon spin relaxation, usually associated with most or all of the spin excitation degrees of freedom of a system, would not normally be expected to change so drastically with field without the slightest signature in the entropy.

In summary, our results show that NiGa$_2$S$_4$ is neither a ‘conventional’ magnet (where spin freezing would be accompanied by a decrease of the muon relaxation at low temperatures) nor a $T=0$ singlet spin liquid (where there would be no spin freezing). Reconciling the LF-µSR and specific-heat results is clearly an important task for theory.

Acknowledgments
We are grateful for technical assistance from the TRIUMF Centre for Molecular and Materials Science, where these experiments were carried out. We thank H. Kawamura, Y. Maeno, and R. Singh for useful discussions, and K. Onuma for experimental help. This work was supported by the U.S. NSF, Grants 0422674 (Riverside) and 0604015 (Los Angeles), by Grants-in-Aid for Scientific Research from JSPS, and by a Grant-in-Aid for Scientific Research on Priority Areas (19052003) (Tokyo).

[1] Nakatsuij S, Nambu Y, Tonomura H, Sakai O, Jonas S, Broholm C, Tsumetsugu H, Qiu Y and Maeno Y 2005 Science 309 1697–1700
[2] Nakatsuij S, Nambu Y, Onuma K, Jonas S, Broholm C and Maeno Y 2007 J. Phys.: Condens. Matter 19 14532–1–7
[3] Takeya H, Ishida K, Kitagawa K, Ibara Y, Onuma K, Maeno Y, Nambu Y, Nakatsuji S, MacLaughlin D E, Koda A and Kadono R 2008 Phys. Rev. B 77 054429–1–13
[4] Yaouanc A, Dalmas de Réotier P, Chapuis Y, Marin C, Lapertot G, Cervellino A and Amato A 2008 Phys. Rev. B 77 092403–1–4
[5] Lauchli A, Mila F and Penc K 2006 Phys. Rev. Lett. 97 087205–1–4
[6] Bhattacharjee S, Shenoy V B and Senthil T 2006 Phys. Rev. B 74 092406–1–4
[7] Tsunetsugu H and Arikawa M 2006 J. Phys. Soc. Jpn. 75 083701–1–4
[8] Kawamura H and Yamamoto A 2007 J. Phys. Soc. Jpn. 76 073704–1–4
[9] Podolsky D and Kim Y B Halpern-Saslow modes as the origin of the low temperature anomaly in NiGa$_2$S$_4$ arXiv:0805.3347
[10] Brewer J H 1994 Encyclopedia of Applied Physics vol 11 ed Trigg G L (New York: VCH Publishers) p 23
[11] Hayano R S, Uemura Y J, Imazato J, Nishida N, Yamazaki T and Kubo R 1979 Phys. Rev. B 20 850–9
[12] Le L P, Keren A, Luke G M, Sternlieb B J, Wu W D, Uemura Y J, Brewer J H, Riseman T M, Upasani R V, Chiang L Y, Kang W, Chaikin P M, Csiba T and Grüner G 1993 Phys. Rev. B 48 7284–7296
[13] Uemura Y J, Yamazaki T, Harshman D R, Senba M and Ansaldo E J 1985 Phys. Rev. B 31 546–563
[14] Reference [4] reported exponential rather than stretched-exponential muon relaxation in zero field above ~10 K. This difference may be due to nuclear dipolar fields, which contribute in zero field (cf. Ref. [3]) but are decoupled in our LF-$\mu$SR experiments.
[15] Uemura Y J, Keren A, Kojima K, Le L P, Luke G M, Wu W D, Ajiro Y, Asano T, Kuriyama Y, Mekaza M, Kikuchi H and Kakurii K 1994 Phys. Rev. Lett. 73 3306–9
[16] Keren A, Mendels P, Campbell I A and Lord J 1996 Phys. Rev. Lett. 77 1386–9
[17] Mendels P, Olariu A, Bert F, Bono D, Limot L, Collin G, Ueland B, Schiffer P, Cava R J, Blanchard N, Duc F and Trombe J C 2007 J. Phys.: Condens. Matter 19 145224–1–9
[18] Olariu A, Mendels P, Bert F, Ueland B G, Schiffer P, Berger R F and Cava R J 2006 Phys. Rev. Lett. 97 167203–1–4
[19] Bert F, Mendels P, Bono D, Olariu A, Ladieu F, Trombe J C, Duc F, Baines C, Amato A and Hillier A 2006 Physica B 374-375 134–7
[20] Yaouanc A, Dalmas de Réotier P, Glazkov V, Marin C, Bonville P, Hodges J A, Gubbens P C M, Sakarya S and Baines C 2005 Phys. Rev. Lett. 95 047203–1–4
[21] Ramirez A P, Hessen B and Winklemann M 2000 Phys. Rev. Lett. 84 2957–2960