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2007 J. Phys.: Condens. Matter 19 145232

(http://iopscience.iop.org/0953-8984/19/14/145232)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 145232 (7pp) doi:10.1088/0953-8984/19/14/145232

Coherent behaviour without magnetic order of the triangular lattice antiferromagnet $NiGa_2S_4$

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Received 11 November 2006
Published 23 March 2007
Online at stacks.iop.org/JPhysCM/19/145232

Abstract

We present experimental evidence for the unconventional coherent state in two dimensions, found in the geometrically frustrated antiferromagnet $NiGa_2S_4$ with a triangular Bravais lattice. Despite strong antiferromagnetic coupling, $S = 1$ spins only show nanoscale order at low temperatures. Thermodynamic measurements, however, indicate a gapless linearly dispersive mode and suggest coherence beyond the two-spin correlation length.

(Some figures in this article are in colour only in the electronic version)

Geometrically frustrated magnets have attracted interest for their novel magnetic phenomena [1]. An interesting subject for such magnets is whether the geometrical frustration can completely suppress conventional magnetic orders, and promote the formation of novel spin-disordered phases, such as spin liquid and glass without any apparent structural disorder.

The triangular lattice antiferromagnet is one of the simplest forms of geometrically frustrated magnets. With antiferromagnetic nearest neighbour interactions, it is the only geometrically frustrated 2D Bravais lattice, Ising spins have residual entropy [2], and classical spins have a Kosterlitz–Thouless type transition and non-collinear Néel order at $T = 0$ [3]. For quantum spin-1/2, a 2D superposition of singlet coverings in a resonating valence bond state was first explored for the triangular lattice [4]. While the theoretical consensus at present favours long-range non-collinear order at $T = 0$ on the triangular lattice [5–7], this has not been established experimentally [8]. Classical spin antiferromagnets with long-range order have been found [8], but spin-1/2 systems reported so far are structurally distorted and have no magnetic order [9–11].

We have recently found a layered chalcogenide $NiGa_2S_4$ as the first example of low spin ($S \leqslant 1$) quasi-two-dimensional magnets with an exact triangular lattice [12]. Here we review

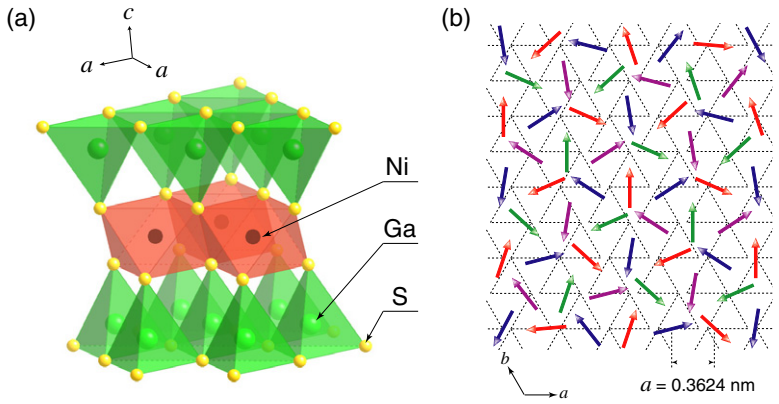

Figure 1. (a) Crystal structures of $NiGa_2S_4$. (b) Short-range correlated spin structure on the triangular Ni-lattice including the incommensurability observed by magnetic neutron diffraction. It approximates four independent 120° structures on the coloured sublattices with lattice parameters $2a$. The in-plane correlation length is 2.5(3) nm and the correlation time exceeds 0.3 ns. There are weak ferromagnetic correlations between nearest neighbour planes.

the low temperature magnetism of $NiGa_2S_4$, focusing on its unconventional coherent state in two dimensions. Despite strong antiferromagnetic (AF) interactions, $S = 1$ spins only show quasi-static order that is stunted at the nanoscale ($\xi = 2.5(3)$ nm). However, thermodynamic measurements indicate gapless linearly dispersive excitations and thus suggest the coherence beyond the two-spin correlation length. Remarkably, this coherent state emerges on cooling through the highly degenerate state, as signalled by an entropy plateau $\sim R/3 \ln 3$, and exhibits incommensurate spin correlations.

The synthesis of polycrystalline samples for $NiGa_2S_4$ is described in the literature [12]. Single crystals were grown by chemical-vapour transport using iodine [13]. Powder x-ray diffraction measurements for single crystals and polycrystalline samples at room temperature confirmed single phases and the same crystal structures as previously reported [14]. Our powder neutron diffraction measurements in the temperature range between 1.5 and 300 K confirmed that $NiGa_2S_4$ retains the trigonal crystal structure down to 1.5 K with $P\overline{3}m1$ symmetry. We measured the d.c. susceptibility χ down to 1.8 K with a SQUID magnetometer. Specific heat, C_P, was measured by a thermal relaxation method down to 0.35 K under fields up to 7 T. In order to estimate the lattice part of the specific heat, $C_{\rm L}$, we measured C_P of the isostructural nonmagnetic analogue $ZnIn_2S_4$ and obtained the thermal variation of the Debye temperature $\theta_{\rm D}(T)$ using the Debye equation [27]. $\theta_{\rm D}(T)$ of $NiGa_2S_4$ was then estimated by multiplying a scaling factor according to $\theta_{\rm D} \propto M_0^{-1/2} V_0^{-1/3}$, where M_0 and V_0 are molar mass and volume, respectively. Finally, $C_{\rm L}$ was estimated by converting the scaled $\theta_{\rm D}(T)$ data into specific heat. The magnetic part, $C_{\rm M}$, was estimated as the difference between the total specific heat, C_P, and the lattice estimation $C_{\rm L}$.

$NiGa_2S_4$ is a layered chalcogenide Mott insulator with a stacked triangular lattice of Ni atomic moments [15]. As shown in figure 1(a) [14], the structure is highly two-dimensional, and can be described in terms of slabs consisting of two GaS layers and one NiS_2 layer, stacked along the c-axis and separated from each other by a van der Waals gap. The central NiS_2 layer is isostructural with the CoO_2 layer in superconducting $Na_xCoO_2{\cdot}yH_2O$ [16]. Magnetism is associated with Ni^{2+} with electronic configuration $t_{2g}^6 e_g^2$ and spin $S = 1$. The unit cell contains

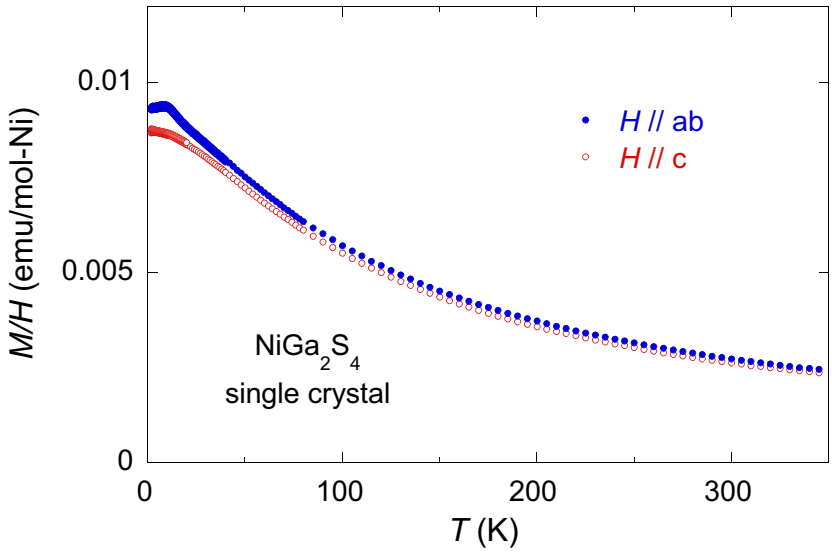

Figure 2. Temperature dependence of the susceptibility $\chi \equiv M/H$ of single crystalline $NiGa_2S_4$ measured under a field of 7 T along the ab-plane (closed circles) and c-axis (open circles).

a single Ni^{2+} atom so the intra- and inter-plane Ni separations are simply given by the lattice parameters $a = 0.3624$ nm and $c = 1.1999$ nm.

The temperature dependence of the susceptibility $\chi(T) \equiv M(T)/H$ for the ab-plane component is presented in figure 2. The applied field, B, was 7 T, a field at which the magnetization, M, remains proportional to B. No difference was found between field cooled and zero field cooled data for both components. Susceptibility data above 150 K follows the Curie–Weiss law: $\chi(T) = C/(T - \theta_W)$ with a Curie constant, C, corresponding to an effective moment of 2.87(3) μ_B for the ab-plane component, and 2.82(3) μ_B for the c-axis component, both of which are consistent with the theoretical value 2.83 μ_B for spin-1. This almost isotropic value of the effective moment indicates that the spin-1 of Ni^{2+} is of Heisenberg type. The Weiss temperatures are also isotropic: $\theta_W = -77(2)$ K (ab-plane) and $-79(2)$ K (c-axis), indicating strong AF interactions. However, no sharp magnetic anomaly or field hysteresis is observed down to 1.8 K. Instead a finite susceptibility after showing a rounded maximum at $T \approx 10$ K on cooling for the ab-plane component indicates development of short-range correlations still with gapless excitations. Evidence of a phase transition is also absent in specific heat data, $C_P(T)$, measured under both $B = 0$ and 7 T between $T = 175$ and 0.35 K (not shown). This indicates that there is no conventional AF order.

The T dependence of the magnetic part of the specific heat $C_M(T)$ is shown in figure 3, which has an unusual two-peak structure: (I) a broad peak centred around $T = |\theta_W|$ below which the susceptibility is suppressed compared to the Curie–Weiss law. (II) A prominent rounded maximum at $T_{peak} \approx 10$ K where $\chi(T)$ also shows a broad maximum (figure 2). The entropy, S_M, obtained through integration of C_M/T (figure 3) correspondingly has a plateau at $S \approx \frac{1}{3} R \ln 3$ prior to high T saturation for $S \approx R \ln 3$. This indicates high degeneracy of low temperature states due to magnetic frustration and is similar to predictions for the spin-1/2 antiferromagnet on the Kagomé lattice of corner-sharing triangles [17].

The specific heat exhibits a power law behaviour at low temperatures (figure 3). The fitting to the expression, $C_M = AT^\alpha$, yields $\alpha = 2.001(5)$ for the temperature region between 0.35

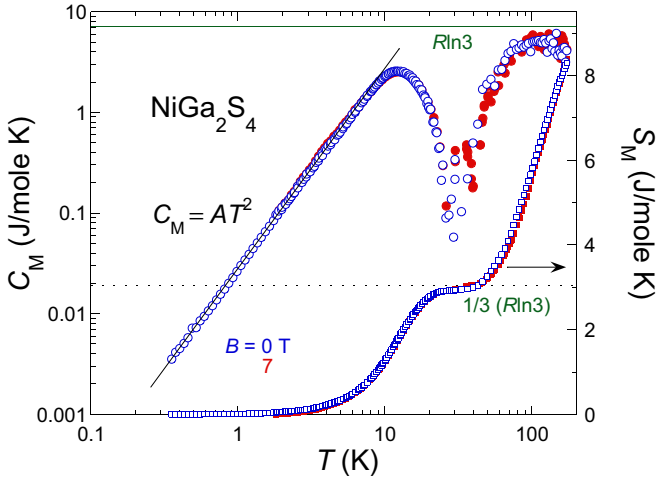

Figure 3. Magnetic part of the specific heat C_M (left axis) and the entropy S_M (right axis) of polycrystalline $NiGa_2S_4$ at 0 T (open symbol) and at 7 T (closed symbol) versus temperature. C_M and T are in a logarithmic scale. The horizontal line indicates $S = R \ln 3$ and $1/3(R \ln 3)$.

to 4.0 K. Thus, C_M follows a T^2-dependence through one decade of temperature, indicating gapless linearly dispersive modes in two-dimensions [1]. If the low-T peak was associated with AF ordering of *individual* spins, it would be suppressed under a field of $k_B T_{peak}/g\mu_B \sim 7$ T. Instead the specific heat is insensitive to field and both C_M and S_M for 7 T collapse on top of those for zero field. This indicates that the low-T peak reflects short-range correlations among composite degrees of freedom that do not couple to a uniform field [20]. It follows that the linearly dispersive waves implied by $C \propto T^2$ are collective modes of moment-free spin clusters. Likewise, the specific heat peak at high $T \sim |\theta_W|$ and the reduction in the susceptibility below that temperature are attributable to the formation of incoherent moment-free spin clusters. Similar thermodynamic properties have been reported for the Kagomé related antiferromagnets, $SrCr_{9p}Ga_{12-9p}O_{19}$ and deuteronium jarosite [18–20].

We used magnetic neutron scattering to probe low-energy spin-correlations in $NiGa_2S_4$ [12]. The signal (not shown) is resolution limited in energy ($\delta E = 0.10$ meV), indicating spin correlations that persist on a timescale exceeding 0.3 ns. Absence of a difference signal in the $Q \to 0$ limit indicates a correlated state built from moment-free spin clusters. Classical spins on a triangular lattice with nearest neighbour AF interactions should develop Néel order at $T = 0$ in the so-called 120° structure with wavevector $\boldsymbol{q} = (\frac{1}{3}, \frac{1}{3}, 0)$. $NiGa_2S_4$ exhibits a peak at $Q_M = 0.57(1)$ Å^{-1} $\approx 2\pi/3a = 0.5779$ Å^{-1}, which is the length of $\boldsymbol{q} = (\frac{1}{6}, \frac{1}{6}, 0)$. By comparing the data to the spherical average of magnetic scattering from a quasi-2D magnet, we found that the AF correlation has the wavevector at a slightly incommensurate position $(\eta, \eta, 0)$ with $\eta = 0.158(1)$. Furthermore, the peak is not resolution limited, yielding the in-plane correlation length, $\xi = \kappa^{-1} = 2.5(3)$ nm. The corresponding time and site averaged spin is $|\langle S \rangle| = 0.75(8)$. This value is notably reduced from $S = 1$ for Ni^{2+} due to quantum fluctuations enhanced by frustration and low dimensionality. Ferromagnetic inter-plane correlations are limited to nearest neighbours as indicated by $\alpha = \langle \boldsymbol{S_0} \cdot \boldsymbol{S}_{\pm c} \rangle \langle \boldsymbol{S_0} \cdot \boldsymbol{S_0} \rangle^{-1} = 0.25(5)$.

The incommensurate short-range order inferred from the diffraction data is shown in figure 1(b). It has various possible explanations. If third neighbour AF interactions, J_3,

dominate, there should be 120° order on the four interpenetrating triangular lattices with side length $2a$ and magnetic Bragg peaks for $\boldsymbol{q} = (\frac{1}{6}, \frac{1}{6}, 0)$ and $(\frac{1}{3}, \frac{1}{3}, 0)$. At the mean field level, nearest neighbour couplings, J_1, eliminate one peak and drive the other slightly incommensurate, as in our diffraction data. From the value of $\eta = 0.158(1)$, mean field theory yields $J_1/J_3 = -0.2(1)$. Indeed, because the nearest neighbour Ni–S–Ni bond angle is near 90°, J_1 should be weak and potentially ferromagnetic. Alternatively, proximity of the NiS_2 layer to a metal–insulator transition may produce multiple spin exchange that stabilizes a larger unit cell.

While quenched disorder in general may play a role in stabilizing a magnetically disordered state, it seems unlikely that impurities alone define the correlation length $\xi = 2.5(3)$ nm. On the other hand, the coherence length for gapless excitations implied by $C \propto T^2$ and finite susceptibility at low temperatures can be estimated by a standard finite size analysis on a 2D linear dispersive mode [12, 21]. With a 2D gapless linearly dispersive mode with a coherent propagation limited up to a length scale L_0 at $T = 0$, the specific heat deviates from the low temperature asymptotic form as

$$\frac{C_{\mathrm{M}}(T)}{R} = \frac{C_0}{R} + \frac{3\sqrt{3}\zeta(3)}{2\pi}\left(\frac{ak_{\mathrm{B}}T}{\hbar D}\right)^2, \tag{1}$$

for $hD/L_0k_{\mathrm{B}} \ll T \ll |\theta_{\mathrm{W}}|$, where $C_0 = -(\sqrt{3}\pi/2)(a/L_0)^2R$ and $\zeta(3) = 1.202$ [12, 21]. Here a is the lattice constant, and D the spin stiffness constant. While the second term gives the ordinary quadratic term for a linear dispersive mode, the first term is a uniform negative shift due to a finite size gap. A least square fit to the data given by C_{M} versus T^2 yields an intercept less than the standard deviation, and places a lower limit of a length scale L_0 to be ∼200 nm. Notably, this is far greater than $\xi = 2.5(3)$ nm derived from diffraction, and indicates that the coherent mode appears as a bulk effect. This indicates that spins are not completely frozen, for in conventional spin glasses, propagating modes are generally not found owing to local fluctuations [22]. It appears that the constraints associated with moment-free clusters in this highly frustrated spin system emphasize collective modes over local modes.

In order to clarify the origin of the coherent behaviour, we studied the nonmagnetic impurity effects by substituting Zn for Ni in $NiGa_2S_4$ [23]. We synthesized polycrystalline samples of $Ni_{1-x}Zn_xGa_2S_4$ using the homogeneous mixture of Ni and Zn powders. Powder x-ray diffraction analysis at room temperature on our polycrystalline samples indicates single phases with the same trigonal structure as $NiGa_2S_4$ up to $x = 0.3$.

As show in figures 4(a) and (b), the temperature dependence of both the susceptibility and specific heat show the systematic change as a function of Zn concentration x(Zn), and exhibit no anomaly due to the long-range magnetic ordering for all concentrations up to $x = 0.3$. The Weiss temperature estimated by the Curie–Weiss fitting to the susceptibility at $T > 150$ K, becomes smaller with the substitution, and finally decreases by about 25% at $x = 0.3$ (inset of figure 4(a)). Thus, the low temperature susceptibility increases as a function of x and remain finite at the lowest temperature 1.8 K. Significantly, for all x(Zn) of this trigonal phase, C_{M}/T shows a T linear dependence at $T \to 0$ (inset of figure 4(b)). This indicates that the Zn substitution does not induce a canonical spin glass phase. On the other hand, L_0 estimated using equation (1) sharply decreases at $x \sim 0$ (inset of figure 4(c)). This shows the coherence of the pure $NiGa_2S_4$ is fragile and can be easily suppressed by a few per cent impurity.

Interestingly, the observed systematic change of the specific heat as a function of x roughly scales with the Weiss temperature. When the system is dominated by the single scale $|\theta_{\mathrm{W}}|$, the molar entropy should take the form $S = f(T/|\theta_{\mathrm{W}}|)$. Then, the specific heat should be given by $T/|\theta_{\mathrm{W}}|$ times a scaling function of $T/|\theta_{\mathrm{W}}|$. In order to check this, we plot $C_{\mathrm{M}}|\theta_{\mathrm{W}}|/T$ versus $T/|\theta_{\mathrm{W}}|$ in figure 4(c). Surprisingly, all the curves except the one for the pure $NiGa_2S_4$ overlaps

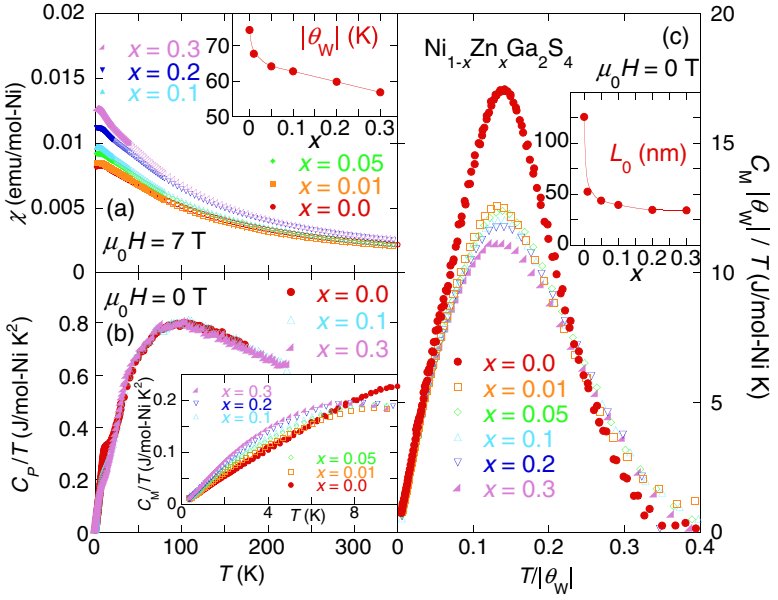

Figure 4. (a) Temperature dependence of the susceptibility. The inset shows the x(Zn) dependence of the Weiss temperature. (b) Temperature dependence of the specific heat divided by temperature $C_{\rm P}/T$. The inset shows the magnetic part of the specific heat divided by temperature $C_{\rm M}/T$ at $T < 10$ K. (c) $T/|\theta_{\rm W}|$ dependence of $C_{\rm M}|\theta_{\rm W}|/T$. The inset shows the x dependence of the coherent scale L_0.

on top of each other. Moreover, including $NiGa_2S_4$, the peak temperature of $C_{\rm M}|\theta_{\rm W}|/T$ and the initial slope as a function of $T/|\theta_{\rm W}|$ are constant, indicating that the peak temperature $T_{\rm peak}$ is proportional to $|\theta_{\rm W}|$, and T^2 constant of $C_{\rm M}$ is proportional to $|\theta_{\rm W}|^{-2}$.

In general, while the neutron diffraction only probes the two-body correlation length, the bulk coherence found by thermodynamic measurements may come from all possible spin configurations. Thus, our observations suggest the existence of the coherence beyond the two-spin correlation length. The observed robust scaling of the low temperature T^2 form of the specific heat in the Zn substituted system strongly suggests the existence of the Nambu–Goldstone mode, which has a gapless and linearly dispersive character and a T^2 coefficient scaling with $|\theta_{\rm W}|^{-2}$ [21]. Generally, a Nambu–Goldstone mode appears with a broken symmetry in comparison with its high-T phase. Therefore, in our case, the absence of the evidence for conventional long-range order in thermodynamics and neutron results points to a novel magnetic order in two dimensions.

One candidate for such an unconventional long-range order without long-range two-spin correlation is a spin nematic phase [24]. This phase may be classified as a spin liquid because the static site average of spin is zero, while its magnetic quadrupole correlation is long-ranged. If the transition occurs at $T = T_{\rm peak}$, spin fluctuations should show a critical slowing down, which may well lead to the freezing of impurity spins at $T_{\rm f}$ close to $T_{\rm peak}$. Recently, the mean-field type calculations by Tsunetsugu and Arikawa have shown that a spin nematic order can be indeed stable on a 2D triangular lattice, and generates a Nambu–Goldstone mode of the gapless linearly dispersive type [25]. In our case, the strong two-dimensionality of the spin interactions may suppress the three-dimensional character of the order and instead promote a rapid development of the correlation at a crossover temperature $T_{\rm peak}$, resulting in the broad feature of the specific heat near $T_{\rm f}$. Furthermore, the orthogonal spin nematic order with three

sublattices has no geometrical frustration on the triangular lattice [25], and may be robust against the substitution of a sizable amount of nonmagnetic impurities.

Another candidate is a Kosterlitz–Thouless (KT) type phase driven by two-valued vortices with the transition around T_f [3]. Slow dynamics associated with bound vortex like defects may cause non-ergodicity below a KT type transition into a critical state with a finite ξ. A recent theory that treats the low T region below the KT type transition predicts the T^2 dependent specific heat and the nearly constant susceptibility, which are consistent with our observations [26].

Our results establish that $NiGa_2S_4$ exhibits a new type of two-dimensional coherent behaviour of magnets, which is characterized by coherent modes through nanoscale quasi-static order, as well as a finite-T entropy plateau. The origin of the coherent behaviour and its response to various kinds of perturbations are interesting subjects for future research.

Acknowledgments

We are grateful for the fruitful discussions with H Tsunetsugu, H Kawamura, S Fujimoto, K Ishida, R Macaluso, J Chan and R Moessner. This work was supported in part by Grants-in-Aid for Scientific Research from JSPS and for the 21st Century COE 'Center for Diversity and Universality in Physics' from MEXT of Japan, and by the Inamori Foundation. Work at JHU was supported by the US Department of Energy.

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