Coherent Behavior and Nonmagnetic Impurity Effects of the Spin Disordered State in NiGa$_2$S$_4$

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Nonmagnetic impurity effects of the spin disordered state in the triangular antiferromagnet NiGa$_2$S$_4$ was studied through magnetic and thermal measurements for Ni$_{1-x}$Zn$_x$Ga$_2$S$_4$ (0.0 $\leq$ $x$ $\leq$ 0.3). Only 1 % substitution is enough to strongly suppress the coherence observed in the spin disordered state. However, the suppression is not complete and the robust feature of the $T^2$ dependent specific heat and its scaling behavior with the Weiss temperature indicate the existence of a coherent Nambu-Goldstone mode. Absence of either conventional magnetic order or bulk spin freezing suggests a novel symmetry breaking of the ground state.

KEYWORDS: triangular lattice, NiGa$_2$S$_4$, spin disordered state, Nambu-Goldstone mode

Geometrically frustrated magnets have attracted interest because of the possible emergence of novel magnetic phases at low temperatures by suppressing conventional magnetic order. Among such magnets, one of the simplest and most fundamental structures is the two-dimensional (2D) triangular lattice that has a single magnetic ion per unit cell. The 2D triangular lattice antiferromagnets (AFMs) have long attracted interest since a quantum spin disordered state was theoretically proposed more than three decades ago. While it is believed that the triangular AFM with nearest-neighbor coupling exhibits the so-called 120° order, recent theories suggest that the exchange interaction beyond nearest-neighbor such as longer range and multiple-spin exchange interactions may lead to a quantum disordered state. For experiment, only a few quasi-2D triangular AFMs with low spin, i.e. $S = 1$, have been reported, such as a solid $^3$He thin film and an organic material with a distorted triangular lattice.

Recently, a new quasi-2D $S = 1$ triangular AFM NiGa$_2$S$_4$ has been discovered as the first example of a bulk low-spin AFM with an exact triangular lattice. Interestingly, despite antiferromagnetic (AF) coupling of $\sim$ 80 K, neither long-range order nor bulk spin freezing has been detected down to 0.35 K. Instead, magnetic, thermal and neutron diffraction measurements indicate the formation of a gapless spin disordered state below about 10 K. The quadratic temperature dependence of the specific heat, as well as the temperature independent specific heat, as well as the temperature independent of the magnetic and thermal measurements for the Zn substituted insulating materials Ni$_{1-x}$Zn$_x$Ga$_2$S$_4$. Only 1 % is enough to substantially suppress the coherence of the spin disordered state in NiGa$_2$S$_4$. However, the Zn substitution never completely suppresses the coherence, but induces a “defect” component of weakly coupled $S = 1$ spin up to a few percent, which freezes at low temperatures. The robust feature of the quadratic temperature dependence of the magnetic specific heat, and its scaling with the Weiss temperature indicate the existence of the Nambu-Goldstone mode of a gapless linearly dispersive type. Absence of either conventional magnetic order or bulk spin freezing suggests a novel symmetry breaking of the ground state.

The polycrystalline samples of Ni$_{1-x}$Zn$_x$Ga$_2$S$_4$ are synthesized by annealing of Ni, Zn, Ga and S elements in evacuated silica tube at 850 $\sim$ 900 °C. In order to obtain a homogeneous mixture of Ni and Zn, we first ground the same molar amount of Ni and Zn powder, and repeated the dilutions by adding equal molar amount of Ni powder each time until we obtain an appropriate Zn concentration. Powder x-ray diffraction analysis at room temperature on our polycrystalline samples indicates single phases with the same trigonal structure as NiGa$_2$S$_4$ up to $x = 0.3$. Our preliminary neutron diffraction measurements for $x = 0.0, 0.1, 0.25$ confirmed both the trigonal structure with P$\bar{3}$m1 symmetry and the substitution of Zn at the Ni site at the same concentration as the nominal one within an error of $1 \%$. For $x \geq 0.4$, two phases coexistence of the trigonal and tetragonal phases is found because of a phase transition to the tetragonal phase of ZnGa$_2$S$_4$. In this letter, we focus on the physical properties of the trigonal phase region (0 $\leq$ $x$ $\leq$ 0.3).

DC magnetization $M$ was measured between 1.8 and 350 K under magnetic fields up to 7 T using a SQUID magnetometer. The specific heat $C_P$ was measured by thermal relaxation method down to 0.35 K. In order to estimate the lattice contribution, $C_L$, we measured $C_P$ of the isostructural nonmagnetic analogue ZnIn$_2$S$_4$ and get the thermal variation of Debye temperature $\theta_D (T)$ using Debye equation. $\theta_D (T) \propto M_0^{-1/2} \nu_0^{-1/3}$, where $M_0$ and $\nu_0$ are molar mass and volume, respectively. $C_L$ is thus estimated by con-
under 0.01 T (Fig. 1(a)) and 7 T (Fig. 1(b)), one notices the susceptibility becomes significantly field dependent. This suggests that the defect spins are more weakly coupled than the bulk spins with $\theta_W = 80$ K, and can be fully polarized under 7 T. In order to confirm this, the difference between $B = 0.01$ T and 7 T are fitted by $\chi_0 + yC_{S=1}/(T - \theta)$. The inset shows its fitting result, $y$ vs. $x$.

The Zn substitution increases the difference between FC and ZFC data at 1.8 K, $\Delta\chi (T = 1.8 K)$, linearly with the Zn concentration $x$ (inset of Fig. 1(a)). Under 7 T, no hysteresis between FC and ZFC data was observed down to 1.8 K (Fig. 1(b)).

Above 150 K, the susceptibility data for all concentration follow the Curie-Weiss law: $\chi(T) = C/(T - \theta_W)$. The effective moment $p_{\text{eff}}$ per Ni ion estimated from the Curie constant $C$ is close to the value expected for $S = 1$ (2.83 $\mu_B$). This confirms that Zn substitutes Ni by the same amount as the nominal concentration. The Weiss temperature $\theta_W$ is found negative and AF. As in the insets of Fig. 1(a) and 1(b), the absolute values of both $T_1$ and $\theta_W$ show a drastic change at $x \sim 0$, indicating the strong sensitivity of the bulk disordered state of NiGa$_2$S$_4$ to the impurity. Further substitution systematically decreases both $T_1$ and $|\theta_W|$ in a similar fashion.

In order to estimate the amount of Ni spins affected by the Zn substitution, we performed a two-component analysis on the magnetization results. Here, the two components are the bulk spins most likely forming the spin disordered state similar to NiGa$_2$S$_4$, and “defect spins” induced by the Zn substitution. Comparing the results under 0.01 T (Fig. 1(a)) and 7 T (Fig. 1(b)), one notices that the low-T susceptibility becomes significantly field dependent with $x$, while NiGa$_2$S$_4$ exhibits nearly field-independent susceptibility. This suggests that the defect spins are the bulk spins most likely forming the spin components are the bulk spins and the defect spins. We also performed the two-component analysis on the magnetization $M(B)$. For the pure NiGa$_2$S$_4$, the field dependence data ($0 \leq B \leq 7$ T) exhibit a linear increase at 1.8 K. However, non-linear Brillouin function type component appears and increases with the Zn substitution (Fig. 2(b)) because of the weakly coupled defect spins. In order to estimate the amount of the defect spins, we performed the fitting using the following equation in the range of $0 \leq B \leq 7$ T,

$$M(B, x) = \frac{dM}{dB}\bigg|_{B=7T} B + zg\mu_B S B_S \left(\frac{g\mu_B S B}{k_B T}\right). \quad (1)$$

Here, we assume that the susceptibility for bulk spins is insensitive to field as in the pure NiGa$_2$S$_4$ and is given by $\frac{dM}{dB}$ at 7 T where the defect spins are polarized. $B_S$ in the second term represents the Brillouin function for $S = 1$ defect spins. The eq. (1) fits the experimental results well as shown in Fig 2 (b). The fraction of the defect spins, $z$, increases linearly with $x$. The above two types of the analyses consistently give the same order of the defect spin concentration that are proportional to $x$. This indicates that the nonmagnetic impurity substitution induces $S = 1$ weakly coupled defect spins that most likely comes from Ni spins adjacent to Zn ions. Only a few percent of Ni site appears to induce the defect spins. Given the low temperature hysteresis $\Delta\chi(T = 1.8 K) \propto x$, these results indicate that it is not the bulk spins but the defect spins that freeze.
The absence of bulk spin freezing as well as spin order was confirmed by specific heat measurements under \( B = 0 \) T (Fig. 3(a)). The \( T \) dependence of the specific heat divided by \( T \), \( C_P/T \), shows only broad anomalies, indicating that conventional AF order is still suppressed in Ni\(_{1-x}\)Zn\(_x\)Ga\(_2\)S\(_4\) and that the interacting spin remain disordered in the low-\( T \)-limit. In order to probe the magnetic density of excited states, the \( T \) dependence of the magnetic part of the specific heat \( C_M(\theta_W) \) was estimated by subtracting the lattice part \( C_L(\theta_W) \) from \( C_P(T) \) (Fig. 3(b)). All \( x \neq 0 \) compounds have a double-peak structure, similar to NiGa\(_2\)S\(_4\) (\( x = 0 \)). One is the broader peak centered around \( T \sim \theta_W \), and the other is the prominent rounded peak at the temperature close to \( T_f \).

Significantly, \( C_M/T \) for all \( x \) shows a \( T \) linear dependence at \( T \rightarrow 0 \). This is in sharp contrast with \( T \) independent \( C_M/T \) due to the local nature of spin fluctuations in canonical spin glasses. This indicates absence of spin glass state in the bulk, but the coherent propagation of a gapless and linearly dispersive mode in two dimensions.

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-\( T \) asymptotic form

\[
\frac{C_M(T)}{R} = \frac{C_0}{T} + 3\sqrt{3} \zeta(3) \left( \frac{aK_B}{hD} \right)^2 \theta_W, \tag{2}
\]

for \( hD/L_0k_B \ll T \ll \theta_W \), where \( C_0 = -\left( \sqrt{3\pi/2} / aL_0 \right)^2R \) and \( \zeta(3) = 1.202^{9,12} \) Here \( a \) is the lattice constant, and \( D \) the spin stiffness constant.

For NiGa\(_2\)S\(_4\), \( C_M \) shows quadratic \( T \) dependence with \( C_0 = 0.0(2) \) mJ/mole K and this indicates infinitely long \( L_0 \) with the lower bound \( \approx 130 \) nm, which is far beyond the two-spin correlation length \( \xi \sim 2.5 \) nm determined by the neutron scattering.\(^9\) With the substitution of Zn, however, \( L_0 \) sharply decreases at \( x \sim 0 \) (inset of Fig. 4). This shows the coherence of the pure NiGa\(_2\)S\(_4\) is fragile and can be easily suppressed by a few percent impurity. On the other hand, the spin stiffness constant shows the continuous decrease with \( x \) (inset of Fig. 4). For ordinary AFMs that order at \( T \sim \theta_W \), the stiffness constant \( D_0 \) can be estimated by the relation: \( D_0^2 = (3\sqrt{3} \zeta(3)/4\pi)(aK_B/\theta_W/h)^2/\ln(2S+1) \).\(^9,12\) The observed \( D \) is between 0.65 and 0.85 km/sec, nearly three times smaller than the expected \( D_0 = 2.3 \) - 3.0 km/sec. This softening comes from the magnetic frustration, and indicates the spectral weight downshift. Further evidence for the downshift is found in the magnetic entropy \( S \) (inset of Fig. 3(b)), obtained by integration of \( C_M/T \). The observed intermediate temperature plateau of \( S \) prior to high-\( T \) saturation at \( ~\rangle R \ln 3 \) amounts to \( 1/4 \sim 1/3 \) of \( R \ln 3 \), indicating the highly degenerate low-\( T \) states.

Interestingly, the observed systematic change of the specific heat and susceptibility as a function of \( x \) roughly scales with the Weiss temperature. When the system is dominated by the single scale \( \theta_W \), the molar entropy should take the form \( S = f(T/\theta_W) \). Indeed, \( S \) presented in the inset of Fig. 3(b) shows such a scaling as a function of \( T/\theta_W \), except one for NiGa\(_2\)S\(_4\). Then, the specific heat should be given by \( T/\theta_W \) times a scaling function of \( T/\theta_W \). In order to check this, we plot \( C_M(\theta_W)/T \) vs. \( T/\theta_W \) in Fig. 4(a). Surprisingly, all the curves except the one for the pure NiGa\(_2\)S\(_4\) overlaps on top of each other. Moreover, including NiGa\(_2\)S\(_4\), the peak temperature of \( C_M(\theta_W)/T \) and the initial slope as a function of \( T/\theta_W \) are constant, indicating that the peak temperature is proportional to \( \theta_W \), and \( T^2 \) constant of \( C_M \) is proportional to \( \theta_W^{-2} \). In order to further check this, \( (C_M - C_0)/\theta_W^2/T^2 \) is plotted against \( \ln(T/\theta_W) \) in Fig. 4(b). All the results including the one for NiGa\(_2\)S\(_4\) (with \( C_0 = 0.0(2) \) mJ/mole K) starts to have the same constant value below the temperature of \( T/\theta_W \sim 0.04 \). While the lower \( T \) limit to define \( C_0, hD/L_0k_B \) corre-
sponds to $T/|\theta_W| = 0.015(4)$ for the Zn substituted samples, the eq. (2) roughly describes $C_M$ down to the lowest $T$ given by $T/|\theta_W| \sim 0.004$, much lower than the limit. On the other hand, the scaling behavior in the susceptibility is not so clear as in the specific heat results probably because the susceptibility is more sensitive to defect spins at low temperatures. However, we note the three important characteristic temperatures that scale with $|\theta_W|$.

(1) Below 4 % of $|\theta_W|$, the susceptibility becomes constant, as indicated by the vanishing $T$ derivative, $d\chi/dT$ (Fig 4(c)). (2) The minimum of $d\chi/dT$ appears at nearly the same scaled temperature of $T/|\theta_W| \sim 0.2$ (Fig 4(c)). (3) $T_I$ scales with $|\theta_W|$, so the frustration parameter $f \equiv |\theta_W|/T_I$ keeps almost a constant value around 10, indicating the significant magnetic frustration even with the Zn substitution (inset of Fig. 1(b)).

Despite the above scaling behavior with the Zn substitution, only the pure NiGa$_2$S$_4$ exhibits the following two noticeable anomalies at the crossover temperature to the low-$T$ asymptotic behavior. (1) Not following a scaling function for the Zn substituted systems, only NiGa$_2$S$_4$ exhibits a broad kink in $(C_M - C_0)/|\theta_W|^2/T^2$ at $T_0 \simeq 13$ % of $|\theta_W|$ $\sim 10$ K, below which nearly $T^2$ dependence $C_M$ appears. (2) Only for NiGa$_2$S$_4$, $d\chi/dT$ crosses zero at the same characteristic temperature $T_0$, below which the nearly constant $\chi$ appears. Interestingly, this low temperature crossover behavior in the pure NiGa$_2$S$_4$ can be easily suppressed only by 1 % Zn, similar to the rapid loss of the coherence scale $L_0$.

The Zn substitution substantially but never completely suppresses $L_0$ and $T^2$ dependent specific heat. The observed robust scaling of the low temperature behavior, especially the $T^2$ form of the specific heat, strongly suggests the existence of the Nambu-Goldstone mode, which has a gapless and linearly dispersive character and a $T^2$ coefficient scaling with $|\theta_W|^{-2}$. 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 a unconventional long-range order without long-range two-spin correlation is a spin nematic phase. 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 $T = T_0$, spin fluctuations should show a critical slowing down, which may well lead to the freezing of impurity spins at $T_I$ close to $T_0$. 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. 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 $T_0$, resulting in the broad feature of the specific heat near $T_I$. Furthermore, the orthogonal spin nematic order with three sublattices has no geometrical frustration on the triangular lattice, 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 $T_I$. Slow dynamics associated with bound vortex-like defects may cause non-ergodicity below a KT type transition into a critical state with a finite $\xi$.

Other possibilities include the critical behavior toward an AF transition below $T = 0.35$ K. However, it is not yet clear whether such a low-$T$ AF order with geometrical frustration could be robust against nonmagnetic impurities of the concentration up to 30 %.

Finally, a quantum spin liquid phase is also an interesting candidate. For triangular AFMs, Imada et al. discuss a gapless spin liquid phase through the theoretical calculations based on the Hubbard model. However, it is not yet clear whether the formation of such a liquid state may lead to the $T^2$ dependence of the specific heat.

To conclude, the Zn substitution for Ni in NiGa$_2$S$_4$ leads to the abrupt loss of the coherence by the substitution less than 1 %. However, the loss is not complete and the robust low temperature behavior, i.e. the constant susceptibility, the $T^2$ dependent specific heat, and their scaling behavior with the Weiss temperature indicate the existence of Nambu-Goldstone mode of the gapless linearly dispersive type. The absence of either conventional magnetic order or bulk spin freezing suggests that the ground state has a novel symmetry breaking.

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