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High-field electron spin resonance in the two-dimensional triangular-lattice antiferromagnet $NiGa_2S_4$

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We report experimental results of high-field electron spin resonance (ESR) measurements in magnetic fields up to about 53 T on the quasi-two-dimensional triangular-lattice antiferromagnet $NiGa_2S_4$. From the temperature evolution of the ESR absorption linewidth, we find three distinct temperature regions: those (i) above 23 K, (ii) between 23 K and 8.5 K, and (iii) below 8.5 K. The linewidth is affected by the dynamics of Z_2 vortices below 23 K and one of the conventional spiral resonance modes explains well the frequency dependence of the ESR resonance fields far below 8.5 K. Furthermore, we found an anomaly in the magnetization curve around one third of the saturation magnetization for $H \perp c$, corresponding to softening of another resonance mode. These results suggest the occurrence of a Z_2 vortex-induced topological transition at 8.5 K.

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Two-dimensional (2D) geometrically frustrated systems have attracted considerable interest over the last three decades because they are expected to have a ground state like a spin liquid. Among them, the 2D triangular-lattice antiferromagnet (TLAFM) has been studied extensively, both theoretically and experimentally. Since a spin-liquid state was theoretically suggested in 1973 in the $S=1/2$ Heisenberg TLAFM,[1] a lot of attention has been paid to the TLAFM until today. Recent theories, however, propose an ordered ground state with a 120° spin structure in the $S=1/2$ TLAFM with only nearest-neighbor exchange interactions[2] and a spin liquid in the $S=1/2$ TLAFM with distant neighbor and multiple-spin-exchange interactions.[3,4] Experimentally, there are only few samples which are highly 2D and show no long-range order (LRO) down to extremely low temperatures.[5] Therefore, it is difficult to clarify what kind of state is actually realized as the ground state of such a strongly frustrated system, and ideal compounds having highly 2D character and isotropic interactions are strongly desired to investigate their ground state. Recently, a quasi-2D $S=1$ TLAFM $NiGa_2S_4$ has attracted substantial interest as a candidate for the spin-liquid state.[6] This compound contains slabs consisting of two GaS layers and one NiS_2 layer, which are stacked along the c axis, and each slab is separated by a van der Waals gap, resulting in highly 2D character. In the NiS_2 layer, Ni^{2+} ($3d^8$, $S=1$) ions form an exact triangular lattice. Despite the fact that strong AF interactions are suggested by the large Weiss temperature $\theta_w \simeq -80$ K, there is no LRO down to 0.08 K,[7] and some noteworthy characteristics have been observed.[6] Neutron-diffraction measurements have clarified that AF correlation with a wave vector $\boldsymbol{q}=(0.158,0.158,0)$ extends to only about 2.5 nm (about seven lattice spacings) even at 1.5 K, which corresponds to a short-range order (SRO) with about 57° spiral spin structure. The magnetic susceptibility at 0.01 T exhibits a weak peak at about 8.5 K (T^*) and a finite value at the low-T limit, indicating the existence of gapless excitations. The magnetic specific heat shows broad peaks at about 10 and 80 K and T^2 dependence with no field dependence up to 7 T below 10 K. The T^2-dependent specific heat indicates the existence of the k-linear excitation similar to the Nambu-Goldstone mode associated with breaking of continuous symmetry. The T^2-dependent specific heat has also been reported for some 2D frustrated-spin systems. These curious experimental results have stimulated further theoretical and experimental studies on this compound in recent years.[7–14] In some theoretical works, bilinear-biquadratic exchange interactions were considered to account for such peculiar experimental results.[8–10] Very recent NMR, nuclear quadrupole resonance (NQR), and μSR measurements evidenced the occurrence of a state where the spins have a megahertz scale dynamics through a weak freezing below about 10 K.[7]

In this paper, we report the results of electron spin resonance (ESR) measurements in high magnetic fields up to about 53 T on single crystals of $NiGa_2S_4$ to clarify the spin dynamics in more detail. We have found that the dynamics of Z_2 vortices affects the temperature dependence of the ESR absorption linewidth, and the frequency dependence of the ESR resonance fields at 1.3 K below T^* is well explained by conventional spin-wave theory. These results suggest the occurrence of a Z_2 vortex-induced topological transition.

The ESR measurements at frequencies up to 1.4 THz were conducted in pulsed magnetic fields up to about 53 T at temperatures between 1.3 K and about 90 K. The ESR measurements below 500 GHz in steady magnetic fields up to 14 T at 1.4 K were done by utilizing a superconducting magnet and a vector network analyzer. The single crystals used for the measurements were grown by chemical-vapor transport technique using iodine.[14]

Figures 1(a) and 1(b) show the temperature dependence of the ESR absorption spectra at 584.8 GHz in pulsed magnetic fields for $H \parallel c$ and for $H \perp c$. We observe a strong resonance signal indicated by the arrows whose linewidth is extremely broad and another weak signal indicated by the crosses. The weak resonance signal is considered to arise from paramagnetic resonances caused by imperfections in the lattices. The temperature dependences of the absorption linewidth and of the resonance field of the broad signal are plotted in Fig. 2

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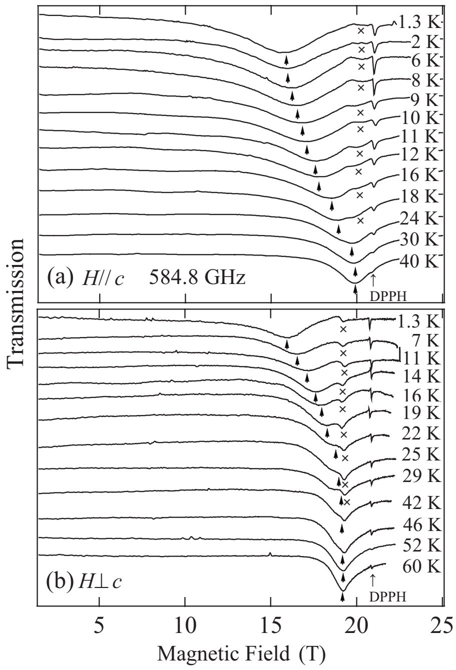

FIG. 1. Temperature dependence of ESR absorption spectra of $NiGa_2S_4$ at 584.8 GHz for (a) $H \parallel c$ and for (b) $H \perp c$. The arrows and crosses indicate the broad large signal and the weak one, respectively. The sharp signal at about 21 T is from an ESR standard sample of DPPH for correction of the magnetic field.

and its inset, respectively. Below about 30 K the broad ESR signal shifts with decreasing temperature toward lower fields for both directions. The absorption linewidth increases as the temperature is lowered from about 80–8.5 K, and a bending appears at 23 K at which the tendency of the linewidth to increase with decreasing temperature becomes more gradual. This behavior between 80 and 23 K is interpreted as the line broadening due to the development of the SRO as suggested by NQR measurements.[7] Thus, we separately examine the temperature ranges above 8.5 K, namely, above 23 K and between 23 and 8.5 K. First, the linewidth above 23 K is investigated in terms of the critical behavior in the 2D Heisenberg antiferromagnet (AFM). The common expression for the temperature dependence of the linewidth (full width at half maximum) associated with the AF LRO temperature T_N is

$$\Delta H_{1/2} \propto (T - T_N)^{-p}, \tag{1}$$

where p is a critical exponent which reflects the anisotropy and the dimensionality of the system. Based on Kawasaki's dynamic equations, the critical exponent of a 2D AFM is given by $p=(3-2\eta)\nu$, where ν is the critical exponent for the inverse correlation length and η is the critical exponent related to the static correlations.[15] In the case of a 2D Heisenberg AFM, p is evaluated to be about 2.5 from the experimentally obtained $\eta=0.2$ and $\nu=0.95$.[16] In $NiGa_2S_4$, one expects that the development of the SRO gives the same critical behavior as that of the 2D Heisenberg AFM. In addition, since there is no LRO down to 0.08 K,[7] T_N must be small enough to be approximated by zero. Thus, we fit Eq. (1) with $p=2.5$ and $T_N \simeq 0$ to the experimental linewidth below 80 K and we obtain a good agreement above 23 K. Below 23 K, the increase in the linewidth with decreasing temperature becomes gradual. This indicates that some effect disturbs the development of the SRO below 23 K. We take into account a topologically stable point defect which is the so-called Z_2 vortex, characterized by a two-valued topological quantum number suggested theoretically[17] for the Heisenberg TLAFM. Unlike a conventional vortex of spins in the *XY* model, it is a vortex of spin chiralities. The Z_2 vortices form bound pairs at low temperatures and begin to dissociate at a certain critical temperature T_V, causing a Kosterlitz-Thouless type of phase transition. Above T_V, the unbound free vortices are thermally excited, and the spin fluctuates through the passage of the vortices. Hence, unbound Z_2 vortices disturb the development of the SRO. The effect of a Z_2 vortex on the ESR linewidth has been discussed for Heisenberg TLAFMs, $HCrO_2$, and $LiCrO_2$.[18] According to the analysis used for these compounds, the ESR linewidth above T_V is expected to behave as

$$\Delta H_{1/2} \propto \exp\left(\frac{E_V}{k_B T}\right), \tag{2}$$

where E_V is the activation energy of a free Z_2 vortex[18] and k_B is the Boltzmann constant. According to an estimation by a Monte Carlo simulation,[17] T_V and E_V are given by $T_V=0.31JS^2$ and $E_V=1.65JS^2$, where J is the nearest-neighbor exchange interaction, and thus the ratio E_V/T_V becomes constant. We take $T_V=8.5$ K from the anomaly of the magnetic susceptibility and then obtain $E_V=45.2$ K. Using this value, satisfactory agreement between experiment and calculation is attained between 8.5 and 23 K, as shown in Fig. 2. In a neutron-scattering experiment, it has been found that the cor-

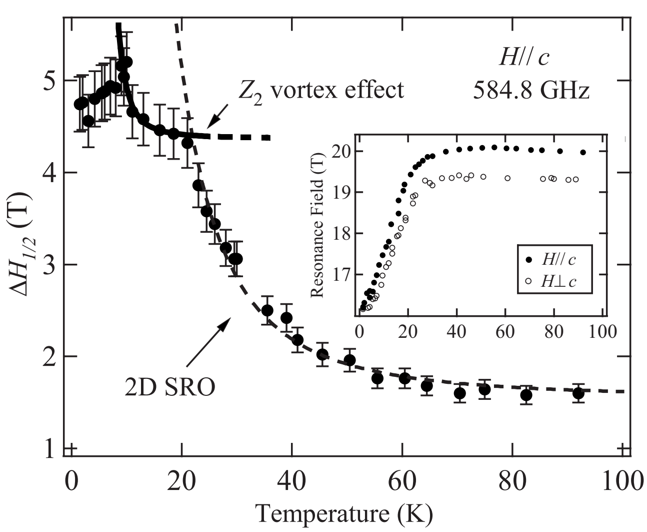

FIG. 2. Temperature dependence of full width at half maximum of the ESR linewidth in $NiGa_2S_4$ for $H \parallel c$ at 584.8 GHz. Solid and broken lines indicate calculated linewidths caused by the dynamics of Z_2 vortices and the development of 2D SRO, respectively. The inset shows the temperature dependence of the resonance field of the large ESR signal in $NiGa_2S_4$ at 584.8 GHz. Open and closed circles represent the resonance fields for $H \parallel c$ and $H \perp c$, respectively.

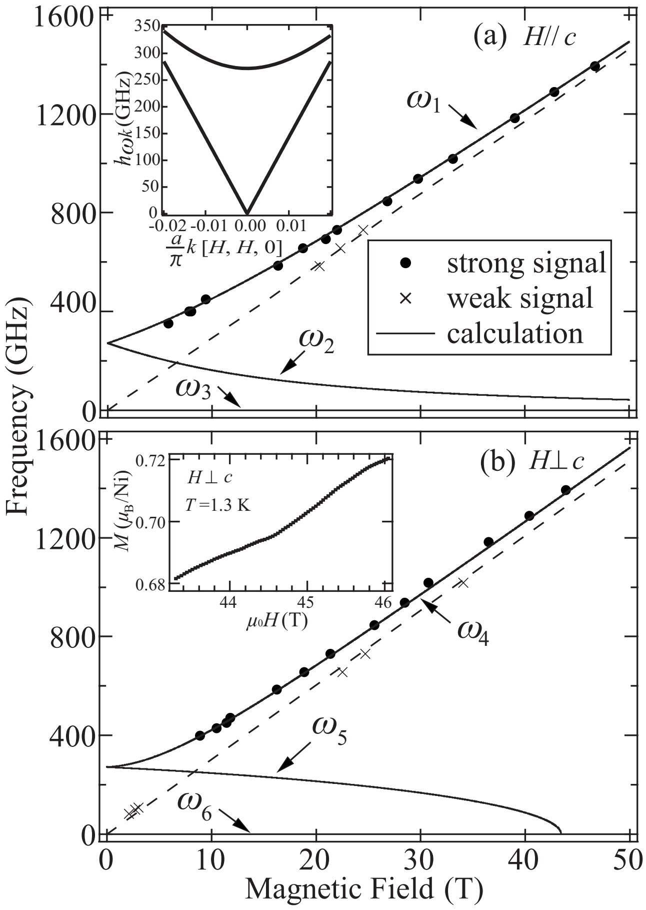

FIG. 3. Frequency-field diagram of $NiGa_2S_4$ at 1.3 K in pulsed magnetic fields and at 1.4 K in steady magnetic fields for (a) $H \parallel c$ and (b) $H \perp c$. Closed circles and crosses denote strong and weak signals, respectively. Solid and broken lines represent calculated resonance modes and the paramagnetic-resonance line, respectively. The insets in (a) and (b) show the calculated spin-wave dispersion relation near $k=0$ at $H=0$ T, where a is the lattice parameter and the magnetization curve for $H \perp c$ at 1.3 K near the softening field around 44 T, respectively.

relation length in the triangular plane grows up to be about three lattice units at 23 K.[19] This result indicates that a correlation length of about three lattice units is needed to observe the Z_2 vortex effect. The temperature-dependent shift of the resonance field below about 30 K in the inset of Fig. 2 is also thought to be caused by growing up of the correlation length which is about two lattice units at 30 K.[19] Below about 10 K, the linewidth shows a gradual decrease as the temperature is lowered and even at the lowest temperature, it remains a large value. On the basis of NQR measurements, Takeya *et al.*[7] suggested that a gradual spin freezing occurs between 10 and 2 K and that inhomogeneous internal fields appear below 2 K. This considerably large ESR linewidth at the lowest temperature must reflect a distribution of internal fields. Accordingly, the temperature dependence of the ESR linewidth is consistent with the NQR results.

Next, we discuss the frequency dependence of the resonance field of the strong ESR signal at the lowest temperature. Figures 3(a) and 3(b) show the resonance fields at various frequencies obtained from the ESR absorption spectra at 1.3 K in pulsed magnetic fields and at 1.4 K in steady magnetic fields for $H \parallel c$ and for $H \perp c$, respectively. The broken line in each figure represents a paramagnetic-resonance line with g factor measured at about 90 K. As mentioned before, the weak signal probably comes from isolated Ni ions due to the imperfection of the lattices and gives rise to the paramagnetic-resonance line. The ESR modes of the strong signal have a zero-field gap and approach the paramagnetic-resonance modes with increasing field for both field directions. These ESR modes are reminiscent of the spiral spin resonance mode observed in TLAFM with easy-plane anisotropy.[20] It is known that even in the disordered phase, some low-dimensional magnets exhibit resonance modes expected in the LRO phase in the temperature region where the SRO well develops.[21] Therefore, we analyze the experimental results in terms of spiral spin resonances. Conventional mean-field approximation theory gives that the exchange constants are required to be $J_1/J_3=-0.2$ and $J_2=0$, with $J_1<0$ (ferromagnetic) and $J_3>0$ (antiferromagnetic), to realize the 57° spiral spin structure indicated by the neutron-diffraction measurements. The J_i $(i=1,2,3)$ represent the first-, second-, and third-neighbor exchange interactions, respectively. The existence of considerably strong third-neighbor exchange interaction is also suggested in Ref. 12. Since J_3 is large enough compared to the others, we consider $J_1=0$ for simplicity. From conventional spin-wave theory, three kinds of excitation modes are extracted for the spiral magnet. In the case of a Heisenberg system with no anisotropy, these modes are degenerate and gapless at zero field. However, when the system has easy-plane anisotropy ($D>0$), two modes have a gap whereas one mode remains gapless. These two excitations with gap are expected to be observed in the ESR experiment. The resonance modes with 120° spiral spin structure for $H \parallel c$ and $H \perp c$ have been derived by conventional spin-wave theory[22] and molecular-field approximation,[23] respectively. The calculated three resonance modes, namely, two gapped and one gapless modes, are presented in Fig. 3. The agreement between experiment and calculation is good for the following parameter values: $J_3/k_B=21$ K, $D/k_B=0.9$ K, $g_{\parallel}=2.09$, and $g_{\perp}=2.15$. The zero-field energy gap is evaluated to be about 13 K. From the obtained J_3, we estimate the Weiss temperature to be -84 K, which is nearly equal to the value obtained from the magnetic susceptibility.[6] We did not observe the resonance modes, $\hbar\omega_2$ and $\hbar\omega_5$, which gradually lower with increasing field. These modes have a weak field dependence and are expected to show a much broader resonance linewidth than the upper ones. Hence, these resonance modes were hardly observed. According to Ref. 23, the magnetic field at which the $\hbar\omega_5$ becomes zero corresponds to the field at which the collinear spin configuration is reached, in which the spins on the two sublattices are parallel and those on one sublattice are antiparallel to the applied magnetic field in the basal plane. In accordance with the calculation in Ref 23, we observed an anomaly in the magnetization curve for $H \perp c$ around 44 T, as shown in the inset of Fig. 3(b), the magnitude of which is about one third of the saturation magnetization ($2.15\mu_B$/Ni), while no anomaly is observed in the magnetization curve for $H \parallel c$.

The above analysis suggests that spin-wave-like excitation modes develop at low temperatures in $NiGa_2S_4$. Importantly, the lowest gapless mode derived in our analysis has k-linear dispersion at $k \sim 0$, as shown in the inset of Fig. 3(a). This mode remains gapless even in finite magnetic fields. Furthermore, the spin-wave velocity v_s, which corresponds to the slope of the k-linear dispersion, is almost constant in fields sufficiently low compared with the saturation field, which is evaluated to be about 130 T. Actually, $v_s = 948$ m/s at 7 T, calculated for $H \| c$ with the parameters determined from the ESR measurements, is almost the same as $v_s = 949$ m/s at 0 T. In addition, it is considered that the gapped mode does not affect the specific heat below 10 K because of the energy gap evaluated to be about 13 K. These features can qualitatively explain the field-independent specific heat with T^2 dependence. From the magnon with k-linear dispersion on the 2D triangular lattice, we obtain the specific heat in the low-temperature region as $C = [3\zeta(3)/\pi] N_A k_B^3 (T/v_s)^2$, where N_A is the Avogadro number and $\zeta(3) = 1.202$. The calculated result, however, is somewhat smaller than the experimental one. For a quantitative agreement with the experimental specific heat, the value of v_s is required to be nearly three times smaller than that expected from our ESR analysis. On the basis of conventional spin-wave theory, a well-defined sharp energy dispersion is expected. On the other hand, the distribution of the internal field in $NiGa_2S_4$ likely gives a broad energy structure of the excitation modes, which were implied from the considerably large ESR linewidth. This broadening of the energy spectrum may cause a specific heat larger than that expected from spin-wave theory. For direct observation of the energy dispersion, a detailed inelastic-neutron-scattering experiment is desired.

Finally, we discuss the possibility of the Z_2 vortex scenario in Ref. 10. If the Z_2 vortex-induced topological transition with small biquadratic exchange interaction occurs at T_v, the low-temperature phase is dominated by spin-wave excitations, and the spin-correlation length remains finite.[10] In our observation, below $T_v \simeq 8.5$ K, the experimental results suggest spin-wave-like excitations. In addition, the Z_2 vortices effect can be found in the temperature dependence of the ESR absorption linewidth. Consequently, the unconventional properties of $NiGa_2S_4$ in the low-temperature region strongly suggest such a vortex-induced topological transition.

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