Multi-frequency ESR in the Haldane magnet
NDMAP below 1 K

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Abstract. The $S=1$ quasi-one dimensional Heisenberg antiferromagnet Ni(C₅H₁₄N₂)₂N₃(PF₆),
abbreviated as NDMAP, has been studied by electron spin resonance (ESR) in a magnetic field
exceeding the critical field ($H_c$) above which this compound shows a long range order (LRO)
at sufficiently low temperatures. Our recently developed ESR apparatus with a dilution re-
frigerator is utilized to study the spin excitations of NDMAP above $H_c$ for $H||c$, because this
compound exhibits the LRO below about 1 K. The spin excitation modes above $H_c$ observed
below 1 K do not show any difference from those at 1.5 K and the lowest excitation mode
observed at 30 mK in the inelastic neutron experiments above $H_c$ was not observed at about
200 mK in this study. Accordingly, the result suggests that the lowest excitation mode is very
sensitive to temperature.

1. Introduction
Recently, considerable attention has been paid to the field-induced phenomena of quantum
spin-gap systems such as the $S=1/2$ weakly-coupled antiferromagnetic dimer, the $S=1/2$ or 1
bond-alternating one dimensional (1D) antiferromagnets, the $S=1/2$ two-leg antiferromagnetic
spin ladder and the $S=1$ Heisenberg antiferromagnet (HAF). The ground state of these spin
gap systems is a singlet and the first excited state is a triplet at zero field. One of the triplet
state goes down by applying magnetic fields and the energy gap closes at a certain magnetic
field ($H_c$) which corresponds to a quantum phase transition point at 0 K. In TlCuCl₃, one of
the $S=1/2$ weakly-coupled antiferromagnetic dimers, a long range order (LRO) observed above
$H_c$ is interpreted as a Bose Einstein condensation (BEC) of magnons [1]. The $S=1$ 1D HAF
with an axial symmetry in a magnetic field is expected to show a Tomonaga-Luttinger liquid
(TLL) behavior above $H_c$ [2]. Thus, the physics in the field-induced phase is one of the most
interesting topics in recent studies on quantum spin systems.

Ni(C₅H₁₄N₂)₂N₃(PF₆), abbreviated as NDMAP, is a model compound of the $S=1$ 1D HAF.
The Ni²⁺ ions are bridged by azido ions forming chains along the $c$ axis [3]. The Ni sites in
the chain are crystallographically equivalent, so that no staggered components of the magnetic
moments are retained. This compound exhibits the LRO above $H_c=4$ T below about 1 K
for $H||c$ [4]. The following parameters were obtained from a numerical fitting of the magnetic
Figure 1. Schematic drawing of the main part of the dilution refrigerator ESR system. The filled and open arrows show the flow direction of $^3$He and $^4$He gases, respectively. Each number shows the following component and meaning; 1. light pipes, 2. rotary pump for $^3$He circulation, 3. VTI insert, 4. $^3$He condenser, 5. still, 6. vacuum chamber, 7. sample position, 8. heat exchanger, 9. copper sample holder, 10. stainless steel block, 11. mixing chamber.

susceptibility data; $J/k_B=30.0$ K, $D/J=0.3$, $g_\parallel=2.10$, $g_\perp=2.17$ where $J$ is the nearest neighbor exchange constant along the chain, $D$ the single ion anisotropy constant, and $g_\parallel$ ($g_\perp$) the $g$ value parallel (perpendicular) to the chain [4]. The spin excitations above $H_c$ were observed by inelastic neutron scattering (INS) and electron spin resonance (ESR) measurements [5, 6]. The ESR data for $H\parallel c$ were taken at slightly higher temperatures than the LRO one. Three spin excitation modes were observed in the INS experiment at 30 mK, but the lowest excitation mode for $H\parallel c$ was not observed in the previous ESR experiments [6, 7]. Therefore, in order to confirm the lowest spin excitation mode by ESR, we performed ESR measurements on NDMAP below 1 K by utilizing a $^3$He-$^4$He dilution refrigerator.

2. Material and methods

Single crystals of NDMAP were synthesized according to the method reported by M. Monfort et al. [3]. The ESR system is composed of a vector network analyzer (MVNA-8-350, AB Millimeter, France), a 16 T superconducting magnet (Oxford Instruments, UK) and a dilution refrigerator (TAIYO NIPPON SANSO Corp., Japan) which covers the frequencies between 30 and 700 GHz, the magnetic fields up to 16 T and the temperatures from 0.2 K to 100 K. The schematic drawing of the main part of our ESR apparatus with the dilution refrigerator is shown in Fig. 1. The microwaves are introduced into a sample position (7) via light pipes (1). The $^3$He condenser (4) is cooled by pumping liquid $^4$He in the variable temperature insert (VTI) space (3). When the temperature of the $^3$He condenser reaches a few Kelvin, condensation of the mixed gas of $^3$He and $^4$He starts. The circulation of the $^3$He gas is controlled by a rotary pump (2) and a still heater (5). When the circulation of the $^3$He becomes stable, the condensed phase of the $^3$He appears in a mixing chamber (11) and then the lowest temperature is obtained in a few hours.

3. Results

In order to confirm the spin excitations in the LRO phase for $H\parallel c$, we performed ESR measurements in two frequency regions. One is below about 100 GHz and the other is around 350 GHz. Figures 2 and 3 show the frequency dependence of ESR spectra at 0.2-0.3 K for $H\parallel c$. The temperature of the sample space slightly fluctuated in each measurement because of heating by eddy current caused by the field sweep. The observed signals are marked by some characters (a-f). Some signals show a dominant dispersion component because of the transmission measurement, but we determine the resonance fields by the vector detection of our network analyzer. These resonance fields and the previous experimental results of the INS at 30 mK [5] and the ESR at 1.5 K [6] were plotted on a frequency-field diagram as shown in
Figure 2. Frequency dependence of ESR spectra at 0.2-0.3 K for $H \parallel c$ in the low frequency region.

Figure 3. Frequency dependence of ESR spectra at 0.2-0.3 K for $H \parallel c$ in the high frequency region.

Figure 4. Frequency versus magnetic field diagram of the resonance fields at 0.2-0.3 K for $H \parallel c$. Filled symbols represent the results of this experiment. Open squares and circles are the data from the INS at 30 mK [5] and the ESR measurements at 1.5 K [6], respectively. Solid lines represent the results of a PFT calculation [8].

Fig. 4. The solid lines are the calculated excitation modes by a phenomenological field theory (PFT) [8]. The experimental data in the vicinity of $H_c$ are well explained by this calculation.

The modes d and e above $H_c \approx 4$ T correspond to the spin excitations in the LRO phase and do not show any differences from the previous reported ones at 1.5 K. The lowest mode above $H_c$ observed in the INS at 30 mK, however, was not observed in this experiment at about 0.2 K. The mode d below $H_c$, which connects smoothly to that above $H_c$, was observed in this experiment. The mode a is identical to the previous one at 1.5 K.

The origin of the modes a, b and c below about 100 GHz might be the paramagnetic impurity or the sample defects. If these correspond to the transitions within the excited triplet states, the ESR signal should become weak with decreasing temperature. On the other hand, if the signals come from paramagnetic impurities, the signal intensity does not change much in the sufficiently low temperature region compared to the frequency. The temperature dependence of ESR spectra at about 50 GHz between 0.2 and 1.0 K did not show any change of the signal intensity. This result suggests that the latter interpretation is preferable to the former one. The mode f must be the same as the mode a. The mode d below $H_c$ seems to arise from the transition between the lowest and the highest excited triplet branches. As mentioned above, the signal intensity of this mode becomes small with decreasing temperature but it was still observed at 0.2 K.
4. Discussions
In this section, we discuss the spin excitations above $H_c$. According to Kolezhuk and Mikeska, three excitation modes, $g\mu_B H(1-S_z)$ where $S_z=\pm 1.0$ and $\mu_B$ is the Bohr magneton, are expected above $H_c$ in the spin-gap systems [9]. The two higher-lying modes with a slope of $g$ and $2g$ have an energy gap and the lowest mode has no gap. In NDMAP, however, the lowest mode has a gap above $H_c$ because of its planar anisotropy. The experimental results above $H_c$ are well explained by this interpretation and the modes $d$ and $e$ correspond to the modes with the slope of $g$ and $2g$, respectively.

We did not observe any difference in the spin excitations around 350 GHz for $H||c$ between 0.2 K and 1.5 K. As described in Ref. [6], a finite amplitude of the $q=\pi$ component of magnons is important for ESR observation but not for phase coherence in the LRO. The $q=\pi$ components of magnons become finite at $H=H_c$ by closing the energy gap at $q=\pi$. In fact, the spin excitation modes for $H||a$ above $H_c$ do not have any anomaly at $H_{LRO}=9$ T which is the boundary field between the disordered and the LRO phases at 1.5 K [6]. This result suggests that the phase coherence of magnons does not affect the spin excitation modes in the vicinity of $H_c$. The same interpretation could be applied to the spin excitations for $H||c$. At slightly higher temperatures than the boundary temperature of the LRO phase, a short-range order must be developed enough to make the $q=\pi$ component of magnons above $H_c$, resulting in observing ESR signals for $H||c$. Accordingly, we did not observe any difference between the spin excitations at 0.2 K and 1.5 K.

On the contrary, the lowest spin excitation is different from the higher-lying two spin excitations. A thermal fluctuation effect must be the reason why the lowest spin excitation was not observed above $H_c$. The same issue was reported in Ref. [5] and the lowest mode was not observed for $H||a$ at 2 K but was observed at 30 mK. The lowest excited energy level above $H_c$ for $H||c$ is much lower than that for $H||a$. Thus, the thermal fluctuations must affect the lowest spin excitation and cause the damping of ESR signals at about 200 mK.

In summary, we have studied the spin excitations for $H||c$ below 1 K by using our ESR apparatus with a dilution refrigerator. The spin excitations between 0.2 K and 1.5 K are similar to each other but the lowest spin excitation reported in the INS experiment at 30 mK was not observed in our ESR experiment at about 200 mK. The result suggests that thermal fluctuations probably affect the observation of the lowest spin excitation.

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