Multi-frequency ESR studies on a Haldane magnet in a field-induced phase at ultra-low temperatures

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Abstract. We report the results of multi-frequency electron spin resonance (ESR) measurements on single crystals of Ni(C₅H₁₄N₂)₂N₃(PF₆) which is regarded as the one-dimensional Heisenberg antiferromagnet with spin one, namely the Haldane magnet, at very low temperatures down to about 100 mK. We observed the lowest resonance branch below about 500 mK for the field along the chain direction (H∥c), which was observed previously only in an inelastic neutron scattering experiment at 30 mK. We compare the resonance branch with that calculated by a phenomenological field theory, and discuss the field dependence and the temperature sensitivity of this ESR branch.

1. Introduction
Peculiar features near a quantum phase transition (QPT), which is caused by changing a physical parameter such as pressure and magnetic field at zero Kelvin, have attracted a number of condensed matter physicists. A lot of unusual physical phenomena near the QPT have been reported in strongly correlated electron systems.

In the vicinity of a field-induced QPT in quantum spin-gap systems e.g. the one-dimensional Heisenberg antiferromagnet with spin (S) one, namely the Haldane magnet, the S=1 one-dimensional bond-alternating antiferromagnet, and the S=1/2 weakly-coupled antiferromagnetic dimer, intriguing phenomena such as a Bose-Einstein condensation of magnons [1] and a Tomonaga-Luttinger liquid behavior [2] have been observed. Spin excitations near the QPT field and in the field-induced phase have been studied extensively by electron spin resonance (ESR) techniques. To investigate the spin excitations near the QPT field at ultra-low temperatures, we have developed an ESR apparatus by utilizing a compact dilution refrigerator [3].

Ni(C₅H₁₄N₂)₂N₃(PF₆), abbreviated as NDMAP, is a model compound of the Haldane magnet. Ni²⁺ (S=1) ions are bridged by azido groups and form chains along the c axis [4]. This compound exhibits the long-range order (LRO) at low temperatures above a critical field (Hc) corresponding to the QPT field for all the field directions [5]. For H∥c, the LRO appears above Hc~4 T below TN~1 K. At Hc, one of the triplet excited state intersects the singlet ground state and the energy gap named the Haldane gap closes. The following values of the parameters were

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obtained from a numerical fitting of the magnetic 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 uniaxial single ion anisotropy constant, and \( g_\parallel \) (\( g_\perp \)) the \( g \) value parallel (perpendicular) to the chain [5]. NDMAP has an easy-planar anisotropy (\( D > 0 \)) and a small in-plane anisotropy (\( E \neq 0 \)). For \( H \parallel c \), the compound has a nearly axial symmetry and thus the lowest excitation gap above \( H_c \) is caused by this small \( E \).

The spin excitations above \( H_c \) in NDMAP were observed by ESR and inelastic neutron scattering (INS) measurements [6, 7]. Three excitation modes were observed in the INS experiment at 30 mK [7], but the lowest excitation mode for \( H \parallel c \) was not observed in the ESR experiment at 1.5 K which is higher than \( T_N \) [6]. Therefore, we tried to observe ESR signals from the lowest excitation branch above \( H_c \) by using our ultra-low temperature ESR apparatus mentioned above, but failed to observe them unfortunately in the previous study [8]. In the present study, we have succeeded in observing ESR signals from the lowest excitation branch above \( H_c \) by improving our ultra-low temperature ESR apparatus.

2. Materials and method

Single crystals of NDMAP were synthesized according to the procedure described in Ref. [4]. Our multi-frequency ESR system consists of a vector network analyzer MVNA and extensions (AB Millimetre, France), a 16 T superconducting magnet (Oxford Instruments, UK) and a dilution refrigerator (TAIYO NIPPON SANSO, Japan) which covers the frequencies between 30 GHz and 700 GHz almost continuously, the magnetic fields up to 16 T and the temperatures down to about 0.1 K. The details of this ESR system are described in Ref. [3]. Our improvements of the ESR apparatus in this study are as follows; We insert six thermal radiation cut filters named Fluorogold made of polytetrafluoroethylene (brand name:Teflon) containing a glass fiber into the light pipe of our cryostat, and make one united Cu-Be block with a sample holder which was previously composed of a Cu block with a sample holder and a stainless steel taper block close to a mixing chamber. The details of these improvements will be reported elsewhere.

![Figure 1: Temperature dependence of the ESR spectra for \( H \parallel c \) at 32.6 GHz.](image1)

![Figure 2: Frequency dependence of the ESR spectra for \( H \parallel c \) at 100 mK.](image2)
3. Results

Figure 1 shows the temperature dependence of the ESR spectra for \(H \parallel c\) at 32.6 GHz and at temperatures between 100 mK and 600 mK. Two signals indicated by arrows are clearly seen below 500 mK above \(H_c\) and do not change their resonance fields upon heating, and disappear at about 600 mK. The frequency dependence of the ESR spectra for \(H \parallel c\) at 100 mK is displayed in Fig. 2. Two ESR signals observed at 29.7 GHz are shifted oppositely with increasing frequency and merge into one signal at about 35 GHz. Between 35 GHz and 50 GHz, no signal is observed in magnetic fields between \(H_c\) and 14 T. One of the signals observed at higher magnetic field than the other is very broad and hardly visible at 29.7 GHz.

These resonance fields are plotted on the frequency-field diagram by solid circles together with the previous ESR data taken at 1.5 K (open circles) and the INS data at 30 mK (open squares) as shown in Fig. 3. Our ESR data above \(H_c\) on the lowest energy branch lie at low frequencies compared to the INS data.

**Figure 3.** Frequency vs. magnetic field diagram of the resonance fields for \(H \parallel c\) at 100 mK together with the data of the ESR experiment at 1.5 K and the INS experiment at 30 mK. The solid and dotted lines are the calculated excitation modes by a phenomenological field theory (PFT) for \(H \parallel c\) and the paramagnetic resonance line with \(g=2.1\), respectively.

4. Discussion

We compare the numerical data calculated by a phenomenological field theory (PFT) with the experimental ones. The solid lines in Fig. 3 are the results of the PFT calculation which were identical with those in Refs. 8 and 9. The calculated data are close to the experimental ones near \(H_c\) and deviate from them well above \(H_c\). Our ESR data (solid circles) are close to the calculated ones in comparison with the INS data and behave similarly to the calculated ones. Both data have a round peak above \(H_c\), implying an instability of the field-induced LRO phase at high fields. The agreement between the experiment and the calculation is satisfactory in the field region near \(H_c\). It is, however, noted the difference between them becomes appreciable at higher field. This is reasonable because the PFT calculation is suitable in the field region near \(H_c\) [11].

As discussed in our previous paper, 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 system [10]. The ESR signals on the two higher-lying excitation modes with a slope of \(g\) and \(2g\) were observed in NDMAP both in the ESR experiment at 1.5 K and in the INS experiment at 30 mK, and are temperature-insensitive irrespective of LRO. On the other hand, the ESR signals on the lowest mode were not observed in the previous ESR experiment at 1.5 K, but they were observed in the present ESR experiment below 500 mK. This temperature sensitivity of the lowest-mode signals
may be caused by weakening the in-plane anisotropy by thermal fluctuation for the case of nearly axial symmetry ($H\parallel c$) or shortening the relaxation time abruptly by thermal fluctuation. The former case, however, probably causes the shift of the resonance fields due to the change of the excitation branches. Hence, the latter reason might be the origin of abrupt damping of the ESR signals on the lowest excitation branch, but the line width does not increase much with increasing temperature, resulting in no definitive cause of the signal dumping so far.

As suggested above, when we extrapolate the lowest branch to higher fields, the softening of the branch is expected to occur at about 15 T. This softening of the ESR branch is probably related to an anomaly observed in a specific heat experiment in magnetic fields up to 32 T [12]. The anomaly is interpreted as a spin-reorientation transition in the field-induced magnetic ordering phases caused by a peculiarity of the structure of NDMAP [11].

In summary, we performed ESR measurements on single crystals of NDMAP for $H\parallel c$ down to about 100 mK and observed ESR signals above $H_c$ corresponding to the signals on the lowest excitation mode, which were previously observed in the INS experiment at 30 mK. The experimental excitation mode was compared with that calculated by a phenomenological field theory (PFT) and satisfactory agreement between them was obtained. The temperature and the frequency dependences of the ESR signals are discussed.

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