ESR studies of quantum spin systems using the pulsed magnetic field

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Abstract. Studies of novel quantum effects in quantum spin systems by high field ESR will be reviewed. High field ESR measurements of the Haldane system Y$_2$BaNiO$_5$ doped with non-magnetic ion Mg$^{2+}$ have been performed. We have succeeded in resolving the ESR of finite Haldane chains using the high resolution feature of our high field ESR, and the direct information about the spin correlation in the Haldane chain at low temperature is obtained for the first time.

1. Introduction

Since the proposal of Haldane conjecture [1], novel quantum effects in quantum spin systems have attracted much attention. After the establishment of the Haldane gap system, which will be described later, the studies of quantum spin systems are extended to the modified chain systems, such as spin-Peierls system CuGeO$_3$ [2], S=1 bond alternating chain systems [3], and spin ladder systems SrCu$_2$O$_2$(S=1/2) [4] and BIPTENO (S=1) [5]. Furthermore, recent theories show that the magnetization plateau [6] and the field induced magnetic order [7] are considered as novel quantum effects in quantum spin systems. The magnetization plateaus are observed in many quantum spin systems, such as BIPTENO [5], the spin dimer system NH$_4$CuCl$_3$ [8], the Shastry and Sutherland model substance SrCu$_2$(BO$_3$)$_3$ [9] and the diamond chain compound azurite (Cu$_2$(CO$_3$)$_2$(OH)$_2$) [10]. Nikuni et al. also showed that the field induced magnetic order in the spin gap system TiCuCl$_3$, near the critical field can be considered as the Bose-Einstein condensation of dilute magnons [7]. And we can say that the studies of novel quantum effects in quantum spin systems are still expanding. However, we will concentrate on the novel quantum effect in the Haldane system in this paper, that is, the impurity effect.
In 1983 Haldane conjectured that a one dimensional (1D) antiferromagnetic (AFM) system with integer spin will have an energy gap between the ground state and the first excited state while a 1D AFM system with half-integer spin does not [1]. This conjecture was rather surprising to the community at that time because it was considered that the spin number would not affect qualitatively the des Cloizeaux and Pearson spin-wave spectrum without a gap known for S=1/2 1D AFM chain [11]. Therefore, the intensive studies of the S=1 Heisenberg 1D AFM system, which is called as a Haldane system, were performed theoretically and experimentally. The existence of the energy gap, which is nowadays called as a Haldane gap, is verified by the magnetization [12, 13], high field ESR [14] and neutron measurements [15] in the model substance NENP. On the other hand, an important concept named Valence Bond Solid (VBS) picture emerged through the theoretical study [16]. In this picture, the S=1 states are described as two S=1/2 states, and the ground state corresponds to a VBS state where each S=1/2 forms a singlet with the nearest neighbor belonging to the adjacent site (Figure 1).

Figure 1. (a) VBS state in S=1 1D AFM chain. (b) When the magnetic ion is substituted by the non-magnetic ion, two effective S=1/2 spins appear on both side of the non-magnetic ion. (c) Effective interaction between the effective S=1/2 spins through the finite Haldane chain. The right hand side shows the energy structures for odd and even chains where the ground states of the odd and even chains are the triplet and the singlet, respectively.
1 (a)). Therefore, if the S=1 1D AFM chain is broken by the non-magnetic ion, two effective S=1/2 spins are created on both sides of the non-magnetic ion as shown in Figure 1 (b). The existence of such effective S=1/2 spins was verified experimentally by ESR measurements on NENP containing magnetic or non-magnetic impurities [17-19]. Here, very low concentration of impurities can be substituted in case of NENP.

Although we showed the effective S=1/2 spin on the edge of the broken chain schematically in Figure 1 (b), the spin polarization distributes up to about 6 sites from the edge of the broken chain in reality. This is because the spin correlation, which decays exponentially in the Haldane chain, is known theoretically to extend up to about 6 sites [20]. Such distribution of spin polarization was observed by NMR down to 60 K, and the spin correlation length was estimated [21]. However such estimation was not possible below 60 K because of the broadening of NMR signal.

If we can substitute high concentration of non-magnetic ions with Ni ions in Haldane system, we can obtain finite Haldane chains with various chain lengths. Then two effective S=1/2 spins on the both end of the finite chain are expected to have correlation as shown in Figure 1 (c) if the finite chain is short enough while these effective S=1/2 spins can be considered as free spins if the chain length is very long. Such coupled two effective S=1/2 spins will have different energy structure depending on the chain length. If we can separate such energy structure depending on the chain length by the experiment, we will be able to obtain the information about the spin correlation in the Haldane chain.

In this paper, we will show that such experiment is possible by our high field ESR. We employed Y$_2$BaNiO$_5$ for our measurement because high concentration of non-magnetic ions can be substituted. Y$_2$BaNiO$_5$ is a well known model substance for the Haldane system. It has an orthorhombic structure with lattice parameters a=3.76, b=5.76 and c=11.32 Å, and the 1D Ni$^{2+}$ (S=1) chains run along the a axis [22]. The magnetic susceptibility and the inelastic neutron measurements revealed that the intrachain AFM exchange interaction J, the Haldane gap and the single-ion anisotropy parameters were about 280 K, about 100 K, |D|=0.039J and |E|=0.0127J, respectively [23-27]. The existence of the effective S=1/2 states in Y$_2$BaNiO$_5$, by the impurity substitution were shown by specific heat and ESR measurements [28-31]. However, the convincing experimental results, which show the existence of the interaction between the effective S=1/2 spins on the edges through the finite Haldane chain, were not obtained due to the low concentration of impurity ions or the low frequency ESR. Our high field ESR measurement results on Y$_2$BaNi$_{0.96}$Mg$_{0.04}$O$_5$ will clearly show the existence of such interaction which will be discussed in the following sections [32].

2. Effective Hamiltonian and Experimental

The effective interaction between the effective S=1/2 spins produces a ferromagnetic dimer and an antiferromagnetic dimer for odd N and even N as shown in Figure 1 (c), where N is the chain length. The low energy effective Hamiltonian

$$H_{\text{eff}} = E_0(N) + [J\alpha(N) + D\beta(N)]\langle 0|0 \rangle$$

$$+ D\gamma(N)S_z^2 + E\gamma(N)(S_x^2 - S_y^2) - \mu_B \sum_{\mu\nu} B^{\mu\nu} g^{\mu\nu} S^\nu$$

(1)

is introduced by Batista et al., where $E_0(N)$, $\alpha(N)$, $\beta(N)$ and $\gamma(N)$ are functions of N, x, y and z correspond to the b, c and a axes, S is the spin operator for the dimer, $|0\rangle$ is the singlet state, and $g^{\mu\nu}$ is the gyromagnetic tensor [31]. Their calculated results by the density-matrix renormalization group (DMRG) technique are consistent with the specific heat or the inelastic neutron result [30, 31]. However, the inelastic neutron result can not resolve the N dependence directly. Their calculation also showed that the main peak and characteristic secondary peaks were expected in ESR spectra but the previous K-band (24 GHz) ESR measurement was not convincing at all because of the low frequency [30]. Therefore, high frequency high field ESR measurements are required.
High field ESR measurements of $Y_2BaNi_{0.96}Mg_{0.04}O_5$ have been performed in the temperature range from 4.2 to 80 K using the pulsed magnetic field up to 15 T. The frequency region from 40 to 420 GHz is covered by Gunn Oscillators and backward traveling oscillators (BWO). The details of our experimental setups can be found in Refs. [33-35]. The single crystal samples used in this study were grown by the traveling-solvent floating-zone method [36]. The size of the single crystal is about 3x4x5 mm$^3$.

3. Results and discussion

Figure 2 shows the typical ESR spectrum observed at 210 GHz and 4.2 K for B//c. A strong main absorption line at around $g=2.2$ and many secondary peaks are observed as suggested by Batista et al. [31]. From the frequency-field dependence, which will be discussed later, the main absorption line crosses the origin and it can be considered as free S=1/2 spins in the very long finite chain. On the other hand, the secondary peaks correspond to the signal from the finite chains N=1, 3, 5, ... from the following analyses. Here the N=1 signal corresponds to the signal from a Ni$^{2+}$ ion sandwiched by two Mg$^{2+}$ ions. The secondary peaks approach the main peak as N increases because the effective interaction becomes weak as N increases. Only the odd chain is visible at 4.2 K because the even chain has a singlet ground state due to the effective antiferromagnetic interaction as shown in Figure 1 (c). The signal from the even chain is observed when the temperature is increased above 4.2 K.

Figure 3 shows the frequency-field diagrams at 4.2 K for B//a, B//b and B//c. The main peaks (solid circles) cross the origin and the obtained $g$-values $g_{aa}$, $g_{bb}$ and $g_{cc}$ are 2.25, 2.18 and 2.16, respectively. Many secondary peaks (open circles) are observed and they show anisotropic frequency-field dependence for B//a, B//b and B//c. As shown by solid lines in Fig. 3, we can interpret all data by effective Hamiltonian (1) considering the effective interaction between S=1/2 edge spins through the finite Haldane chains. As the excited state is a singlet in the case of N=odd chains (Figure 1 (c)), we have to consider only the effective S=1 spin Hamiltonian with the single ion anisotropy $D\gamma(N)$ and $E\gamma(N)$, which corresponds to the second line in equation (1). Allowed ESR transitions among the triplet states are considered. The bold solid lines in Figure 3 are calculated by $D=-8.97$ K and $E=-2.98$ K, which are consistent with the known values for non-doped $Y_2BaNiO_5$. Other secondary peaks can be
Figure 3. Frequency-field diagrams of Y$_2$BaNi$_{0.96}$Mg$_{0.04}$O$_5$ obtained at 4.2 K for (a) B//a, (b) B//b and (c) B//c. Solid and open circles correspond to main and secondary peaks, respectively.

interpreted completely as shown by solid lines in Figure 3 by only one scaling factor $\gamma$(N) where $\gamma$(1)=1. From the analyses, N dependence of $\gamma$(N) is obtained up to N=27 as shown in Figure 4. Obtained $\gamma$(N) contains the information about the spin correlation in the Haldane chain and it can be compared with the DMRG calculated result by Batista et al. [31]. $\gamma$(N) obtained experimentally is qualitatively consistent with that obtained by the DMRG calculation. However, although the
calculation assumes $E=0$, the $\gamma(N)$ obtained experimentally is slightly larger above $N=5$. This may suggest that the spin correlation length is longer than 6 as expected by the theory. Further theoretical consideration of our result is required.

Finally we would like to comment on the intensity distribution of secondary peaks in Figure 2. The ESR intensity of the secondary peak is proportional to the probability to have chain length $N$, that is $x^2(1-x)^N$ where $x=0.04$. Figure 5 shows the experimental results (solid circles) and the calculated results (solid line). The experimental results show that the shorter finite chains have stronger intensity than expected. Although the transition probability and the contribution from the Boltzman distribution should be also considered, this may suggest that Mg$^{2+}$ ions are not homogeneously distributed but tend to distribute close together.
4. Summary
We have succeeded in observing the ESR signals of finite Haldane chain separately in Y$_2$BNi$_{0.96}$Mg$_{0.04}$O$_5$. This became possible due to the high spectral resolution of high frequency high field ESR. From the analyses of obtained frequency-field relations, we are able to obtain the N dependence of single ion anisotropy parameters $D_\gamma(N)$ and $E_\gamma(N)$, where $\gamma(N)$ gives the direct information about the spin correlation in the Haldane system. As the experimental result suggests longer correlation length than that in previous theories, further theoretical consideration is required.

Acknowledgements
The authors are grateful to Prof. M. Kaburagi for fruitful discussion. This work was partly supported by Grant-in-Aid for Scientific Research on Priority Areas “High Field Spin Science in 100T” (No. 451) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan and Grant-in-Aid for Scientific Research (B) 16340106 from the Japan Society for the Promotion of Science (JSPS).

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