Impurity effect of an $S = 1/2$ two leg spin ladder antiferromagnet \([\text{Ph(NH}_3\text{)](18\text{-crown-6})[\text{Ni(dmit)}_2]}\)
studied by ESR

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Abstract. Organic magnet \([\text{Ph(NH}_3\text{)](18\text{-crown-6})[\text{Ni(dmit)}_2]}\) is a candidate for an $S = 1/2$ two leg spin ladder system [S. Nishihara, T. Akutagawa, T. Hasegawa, and T. Nakamura, Chem. Commun. (Cambridge) 2002, 408.]. In order to investigate the non magnetic impurity effect for this compound, we performed X-band ESR measurement of \([\text{Ph(NH}_3\text{)](18\text{-crown-6})[\text{Ni(dmit)}_2]}_1-\chi[\text{Au(dmit)}_2]_\chi\). Non magnetic impurity concentration were estimated to be \(\chi = 0.029\). ESR measurements have been performed from \(T = 4.5\) K to 273 K using the Bruker ESR spectrometer. At \(T = 4.5\) K, the fine structure ESR signals were observed. These signals suggest the existence of ferromagnetically coupled $S = 1/2$ dimers in the system.

1. Introduction
For the last several decades, low dimensional spin systems have been extensively investigated both theoretically and experimentally. After the establishment of the Haldane gap system [1], the studies of quantum spin systems are extended to the complicated spin systems, such as spin-Peierls system CuGeO$_3$ [2], $S = 1/2$ bond alternating chain systems F$_3$PNNN [3], and $S = 1/2$ spin ladder systems SrCu$_2$O$_3$ [4, 5]. We will concentrate on the novel quantum effect in the spin ladder system in this paper, that is, the impurity effect. When non magnetic ions are substituted for magnetic ions in a spin gap system, the singlet ground state is disturbed so that staggered moments are induced around the impurities. If the induced moments interact through effective exchange interactions, which are mediated by intermediate singlet spins, exotic ground states appear. If the effective exchange interactions are three dimensional (3D), 3D long range order can arise. Such an impurity induced antiferromagnetic ordering was also observed in some spin gap systems, Cu$_{1-x}$Zn$_x$GeO$_3$ [6], Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$ [7] and Pb(Ni$_{1-x}$Mg$_x$)$_2$V$_2$O$_8$ [8]. On the other hand, in the case of one dimensional effective exchange interactions, we can investigate the spin-spin correlation in detail by observing the edge state. For example, high field ESR measurement of the non magnetic impurity doped Haldane chain Y$_3$BaNi$_{1-x}$Mg$_x$O$_5$ provided the direct information about the spin correlation at low temperature [9].
We have investigated the non-magnetic impurity effect in the organic spin ladder system [Ph(NH$_3$)$_3$][[18]crown-6][Ni(dmit)$_2$] by using X-band ESR. [Ni(dmit)$_2$]$^-$ (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate), which has an $S = 1/2$ spin, is an excellent building block for molecular magnetic materials. Each pair of [Ni(dmit)$_2$]$^-$ molecules forms a dimer through face to face interaction, embedded between the adjacent [18]crown-6 molecules. The dimer is located on a pair of spools in neighboring columns, and it aligns along the (011) direction guided by the ditch of the supramolecular cations giving a dimer chain structures. Figure 1(a) shows the schematic diagram of the spin ladder system. Nishihara et al. have reported the magnetic susceptibility of this compound [10]. The magnetic susceptibility takes a maximum at 120 K, and tend to 0 emu/mol around 15 K. The obtained spin gap is $\Delta/k_B = 190$ K. They estimated the exchange interactions for the leg direction as $J/k_B = 20$ K and the rung direction as $J'/k_B = 200$ K. Nishihara et al. have also reported the magnetic susceptibility of [Ph(NH$_3$)$_3$][[18]crown-6][Ni(dmit)$_2$]$_{1-x}$[Au(dmit)$_2$]$_x$ for $x = 0.029$ [11]. It has a broad maximum around 120 K, which indicates the existence of the spin gap, and has a minimum around 30 K. With decreasing temperature below 30 K, the magnetic susceptibility increases rapidly ($\propto 1/T$). By doping the non magnetic ion, the antiferromagnetically coupled spin pairs (spin dimers) are partially destroyed, and the unpaired spin $S = 1/2$ will appear in this system as shown in Fig. 1(b). As the exchange interaction along the leg is weaker compared to that of the rung, the induced spin is relatively isolated. The Curie like behavior can be attributed to these approximately isolated spins. When the distance between unpaired spins is not long, the effective exchange interaction between the unpaired spins is expected as shown in Fig. 1(c). In the case of Sr(Cu$_{1-x}$Zn$_x$)$_2$O$_3$, it shows an antiferromagnetic long range order because the effective exchange interactions between inter ladders also exist [7]. However, in the case of [Ph(NH$_3$)$_3$][[18]crown-6][Ni(dmit)$_2$]$_{0.971}$[Au(dmit)$_2$]$_{0.029}$, it does not show the long range order, which indicates that the inter ladder exchange interactions are negligible in this system. Therefore, this is an appropriate system to study the spin-spin correlation in the spin ladder, similar to the doped Haldane system Y$_2$BNi$_{1-x}$Mg$_x$O$_5$ [9]. Electron spin resonance (ESR) measurement is a powerful method to obtain the information of the local environment of the magnetic sites in the solid. In this study we performed X-band ESR measurement in order to investigate the non magnetic impurity effect in [Ph(NH$_3$)$_3$][[18]crown-6][Ni(dmit)$_2$].

![Figure 1](image_url)

**Figure 1.** (a)Spin ladder. (b) Defect in the spin ladder. When the magnetic ion is substituted by the non magnetic ion, $S = 1/2$ spin appears. (c) Example of an effective exchange interaction between unpaired spins.

2. **Experiment**

Single crystals of [Ph(NH$_3$)$_3$][[18]crown-6][Ni(dmit)$_2$]$_{1-x}$[Au(dmit)$_2$]$_x$ were prepared from (n-Bu$_4$N)[Ni(dmit)$_2$], (n-Bu$_4$N)[Ni(dmit)$_2$], [18]crown-6 and [Ph(NH$_3$)$_3$](BF$_4$) in acetonitrile by diffusion method [11]. The non magnetic ion [Au(dmit)$_2$]$^-$ concentrations $x$ were estimated to be 0.029. The ESR measurements have been performed from 4.5 to 13 K using a Bruker ESR spectrometer EMX081 with a TE$_{103}$ rectangular cavity and Oxford He flow cryostat ESR900.
3. Results and Discussions
At 4.5 K, we have observed signal-A as shown in Fig. 2(a). The temperature dependence of the integrated intensity agrees well with the temperature dependence of the magnetic susceptibility of [Ph(NH$_3$)][(18|crwon-6)|Ni(dmit)$_2$|Au(dmit)$_2$]. Moreover, the linewidth above 30K is broader than that below 30 K. These results indicate that $S = 1/2$ antiferromagnetic spin dimers contribute mainly to the ESR absorption above 30 K and unpaired spins caused by the impurity doping contribute mainly to ESR absorption below 30 K. We measured the angular dependence of these absorption lines. In (2 1 1) plane, the $g$-value of the electron paramagnetic resonance (EPR) is determined by $g_1$, $g_2$, and angle $\theta$ between the direction of sample [0 1 1] and the direction of applied magnetic field: $g = \sqrt{g_1^2 \cos^2 \theta + g_2^2 \sin^2 \theta}$. From the angular dependence of signal A, we can obtain $g_1 = 1.96$ and $g_2 = 2.17$.

Figure 2(b) is the expanded spectrum data of (a). We observed the satellite signals B and C. Moreover we observed signal F around $971 \text{G}$[12]. The origin of these signals are not hyperfine splitting. The splitting of signals B and C from signal A is much larger than typical hyperfine splitting ($\sim 20 \text{(G)}$) [12], the origin of these signals are not hyperfine splitting.

In order to understand the origin of signals B and C, we measured the angular dependence of these signals. Figure 3 shows the angular dependence of the difference between resonance field of signal B(C) and signal A: $B_{B,C} - B_A$. If we assume $S = 1$ with the uniaxial anisotropy $D$, the angular dependence of the resonance fields can be described as, $B_{B,C} - B_A = \pm \frac{1}{2} \frac{D_{\beta \gamma}}{g_1 \mu_B} (3 \cos^2 \theta - 1)$, where $\mu_B$ is Bohr magneton, and $\theta$ is angle between the direction of sample and the direction of magnetic field in the plane [13]. By comparing this function to the experimental results, we can interpret the results very well as shown in Fig. 3 and $D_B/(g_1 \mu_B) = 503 \text{G}$ and $D_C/(g_1 \mu_B) = 350 \text{G}$ are obtained. These results indicate that this system has at least two kinds of $S = 1$ site with the uniaxial anisotropy. Signals B and C can be considered as transitions between $S_z = -1$ and $S_z = 0$, and between $S_z = 0$ and $S_z = -1$, where $S_z$ is $z$-component of spin quantum number of $S = 1$. By accepting this assumption, we can also interpret signal F. The Signal F is so called the “half field” resonance and corresponds to the transitions between $S_z = -1$ and $S_z = +1$ in the $S = 1$ system. This transition is usually forbidden. However, due to the mixing of wave functions at low field, $\Delta S_z = 2$ transition becomes the allowed transition.

However, as this spin system is consisted of $S = 1/2$, what is the origin of the spin $S = 1$. As described before, this spin system has unpaired spins due to the non magnetic doping, which are relatively isolated and are the origin of signal A. However, some unpaired $S = 1/2$ spins are very close to each other, and a coupling is expected for such unpaired spins through the singlet sites, similar to the case of nonmagnetic doped Haldane system [9]. Due to the antiferromagnetic correlation in the ladder, an effective ferromagnetic coupling is expected between two $S = 1/2$ spins with odd number singlet sites as shown in Fig. 3 (c). The coupling becomes weaker as the distance between two $S = 1/2$ spins becomes larger, and this effective ferromagnetic coupling induces the effective $S = 1$ with the effective coupling induces the effective anisotropy term $D S_z^2$. With this picture, we can interpret why we observed signals B and C coming from $S = 1$ states with different $D$ term.

4. Conclusion
We have performed X-band ESR measurement of the non magnetic molecular doped spin ladder system [Ph(NH$_3$)][(18|crwon-6)|Ni(dmit)$_2$|Au(dmit)$_2$]. We observed several ESR signal
Figure 2. ESR spectrum at 4.2K (a) and expanded spectrum (b).

Figure 3. Angular dependence of the resonance fields of signal B and signal C, subtracted by the resonance field of signal A.

(A, B, C, F). The angular dependence and temperature dependence of Signal B, C and F is attributed to $S = 1/2$ ferromagnetic dimers with different couplings, which are $S = 1$ effectively with different uniaxial anisotropy. From these results, we have found that the spin system consists of not only “singlet sites and isolated unpaired spins”, but also “effective ferromagnetic dimers.” Ferromagnetic dimers arisen from the effective ferromagnetic exchange interaction between unpaired spin caused by the non magnetic ion doping. Such effective ferromagnetic dimers are observed in the spin ladder system for the first time, and it is a clue to understand the spin correlation in the spin ladder.

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