EPR measurements of a two-dimensional spin frustrated system, BIPNNBNO with $S=1$ and $S=1/2$

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Abstract. An organic triradical, BIPNNBNO [=3,5-bis(N-tert-butylaminoxyl)-4'-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)biphenyl] includes an antiferromagnetic spin pair of $S=1$ and $S=1/2$ within a molecule. In the crystals, ferrimagnetic chains are formed, accompanied by the antiferromagnetic interactions between the nearest and the next nearest neighbouring chains. These interactions induce frustrated spin structure in two-dimension. X-band and submillimeter EPR measurements of BIPNNBNO single crystals were performed. The change of the $g$-factor and linewidth was observed corresponding to the susceptibility and magnetization behaviour.

1. Introduction

There has been considerable interest in the study of low-dimensional quantum spin systems with spin frustration. Organic radicals consisting only of light elements are suitable to study such peculiar spin states. We have recently synthesized an organic triradical, BIPNNBNO [=3,5-bis(N-tert-butylaminoxyl)-4'- (1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)biphenyl], which includes three radical moieties of $S=1/2$, two of which are ferromagnetically coupled each other to form an $S=1$ species.[1] As is shown in Fig. 1(a) and (b), a BIPNNBNO molecule is regarded as a spin pair of $S=1/2$ and $S=1$ coupled antiferromagnetically to each other. The BIPNNBNO crystals belong to an orthorhombic system, $Pbcn$, $a=9.0126(7)$, $b=17.578(1)$, $c=33.924(3)$Å, $V=5374.3(6)$Å$^3$, $Z=8$. Along the $b$-axis, molecules align themselves side by side with the intermolecular contacts between the $S=1$ and $S=1/2$ units. The intra- and intermolecular antiferromagnetic couplings between $S=1$ and $S=1/2$ give a ferrimagnetic chain along the $b$-axis. The significant feature of this material is in the interchain interactions. Due to the large dihedral angle between the $S=1$ and $S=1/2$ radical planes, generated are contacts between not only the nearest neighboring chains but also the next nearest neighboring ones. Between the nearest and the next nearest neighboring chains, antiferromagnetic couplings between the $S=1/2$ units and between the $S=1$ units exist, respectively. Schematic illustration of the crystal structure is shown in Fig. 1(c). The system is two-dimensional (2D) and the spin frustration is induced.
Figure 1. (a) Molecular structure of BIPNNBNO and magnetic interaction scheme. (b) Extreme limit of the model (b) when $J_A > |J_{AB}|$. (c) Magnetic model of BIPNNBNO crystals. A BIPNNBNO molecule is represented by the formula of (b). Open and closed circles correspond to $S=1/2$ and $S=1$, respectively. Bold, thin and broken lines represent the exchange path of the interactions within a molecule, between the nearest neighbouring chains, and between the next nearest neighbouring chains, respectively.

In the measurements of the static magnetic susceptibility ($\chi_p$), a broad peak appears at around 15 K accompanied by a second peak at 4.3 K. A double peak structure in $\chi_p$ has been reported for other frustrated spin system such as a Kagome lattice [2] and a diamond chain [3]. The value of $\chi_p$ goes to zero as $T \to 0$. The singlet ground state of this material is proved by the magnetization measurement in pulsed high magnetic field up to 40 T. The finite magnetization is not observed below 4.5 T, above which it begins to grow. Magnetization takes $1 \mu_B/\text{f.u.}$ (1/3-magnetization plateau) in the field region of 6.5-23 T, and reaches full saturation of $3 \mu_B/\text{f.u.}$ above 29 T. It should be noted that a very narrow magnetization plateau of 2/3 appears at 26 T. This may be related to the spin frustration in this material.

In this paper, we describe the EPR measurements of this material. Two-dimensional nature appears in the angular dependence of the linewidth. The temperature dependence of $g$-factor shows an anomaly at 4 K. The field dependence of $g$-factor is similar to that of magnetization: the slope is changed at the field region corresponding to the 1/3- and 2/3-magnetization plateaux.

2. Experimental

BIPNNBNO was synthesized through 3,5-bis[N-tert-butyl-N-(tert-butyldimethylsiloxy)amino]-4'-formyl biphenyl by Negishi coupling. Following the conventional procedure [4,5] of 8 steps, BIPNNBNO was obtained as dark green solids. Single crystals were grown by slow diffusion of hexane to the concentrated solution of CH$_2$Cl$_2$-Et$_2$O at -10 °C.

X-band (9.5 GHz) EPR measurements were done using a Bruker ESP300E spectrometer. Submillimeter wave EPR measurements were performed using a pulsed magnetic fields up to 29 T and far-infrared (FIR) radiation between 95-762 GHz. An optical pumped FIR laser and Gunn oscillators were employed as radiation sources. For the field calibration, DPPH or ruby was used.

3. Results and Discussion

3.1. X-band EPR measurements

Angular dependences of X-band EPR $g$-factor and peak-to-peak linewidth ($\Delta H_{pp}$) were measured at room temperature. The principal values of $g$-factor were determined to $g_a = 2.0066, g_b = 2.0068, g_c = 2.0051$, which reflect the orientation of radical moieties in the crystal. Figure 2 shows angular dependences of $\Delta H_{pp}$. The largest linewidth was observed for the field direction perpendicular to the $ab$
plane, \( i.e. H \parallel c \). As the magnetic field is tilted from the \( c \)-axis from \( \theta = 0 \) to 90°, the linewidth decreases and passes a shallow minimum and increases again. The observed behaviour is characteristic of 2D magnetic systems.[6] The angular dependence is fitted by the formula,

\[
\Delta H = A(3 \cos^2 \theta - 1) + B \sin \theta \cos^2 \theta + C \sin^2 \theta ,
\]

instead of

\[
\Delta H = A(1 + \cos^2 \theta) + B .
\]

![Figure 2. Angular dependence of the EPR peak-to-peak linewidth \((\Delta H_{pp})\) at room temperature for the \(a, b,\) and \(c\)-rotations. Solid curves are the calculation using eq.(1).](image)

The lineshape is almost Lorentzian at any field direction. In an ideal 2D system, a non-Lorenzian lineshape is expected when \( \Delta H_{pp} \) is not minimum. However, the deviation from Lorentzian in known to be less pronounced than in 1D cases and nearly Lorentzian lineshapes are usually observed even in 2D systems.[6-8]

The temperature dependences of the \( g \)-factor and \( \Delta H_{pp} \) were also measured with the field direction parallel to \( a, b, \) and \( c \). The increase of \( \Delta H_{pp} \) below 20 K was observed at any field direction. In the susceptibility measurements, the difference appears below 30 K between the crystals and diluted systems. The increase of \( \Delta H_{pp} \) below 20 K is reflecting the spin-spin correlation due to the intramolecular and/or intermolecular antiferromagnetic interactions. The rapid increase of \( \Delta H_{pp} \), below 4 K is remarkable for \( H \parallel a, c \). The value of \( g \)-factor decreased for \( H \parallel a \), and increased for \( H \parallel b, c \), as decreasing temperature. Moreover, the temperature dependence of \( g \)-factor shows a bend at 4 K where the susceptibility value takes a maximum. Below this temperature, the change of the spin-spin correlation is suspected.

3.2. Submillimeter EPR measurements

The temperature dependences of EPR signals were measured below 50 K at 95, 135, 190 GHz with the field direction parallel to the crystallographic axis. The similar tendency of the \( g \)-shift was observed to the X-band results: the negative \( g \)-shift was observed for \( H \parallel a \), whereas the positive \( g \)-shift for \( H \parallel b, c \). Below 20 K, the broadening of the EPR signal was observed at any field direction. When \( H \parallel a \), the
rapid increase of the full widths of the half maxima ($\Delta H_{1/2}$) of signals was remarkable. This is the same tendency as the X-band results.

The frequency dependence was measured at 0.5K with the frequency range of 95-762 GHz for $H // a$. Non-linear frequency dependence of the $g$-factor was observed. The plot of the $g$-factor vs. the resonance field shows the same field dependence as the magnetization. The slope of the $g$-factor against the field changes at 5-20 T and 26-27 T, which corresponds to the 1/3- and 2/3-magnetization plateau, respectively. The existence of the 2/3-plateau is proved by the field dependent behavior of the $g$-factor.

4. Summary
X-band and submillimeter EPR measurements were performed for BIPNNBNO single crystals. The two-dimensional nature appears in the angular dependence of the linewidth at room temperature. The EPR linewidth gradually increases below 20 K and rapidly increases below 4 K. Non-linear field dependence of the $g$-factor was observed at 0.5K. The change of the $g$-factor is in accordance with the magnetization value. The existence of the 2/3-magnetization plateau is supported. Precise measurements to determine the energy diagram is now in progress.

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