High-frequency ESR study on a frustrated mixed spin system BIPNNBNO

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Abstract. High-frequency ESR measurements were made for single crystals of an organic triradical BIPNNBNO having $S = 1/2$ and $S = 1$ species within a molecule. [BIPNNBNO=3,5-bis(N-tert-butylaminoxyl)-4'(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)biphenyl] The temperature and field dependences of the linewidth and resonance field were studied. The dominant magnetic exchange coupling is discussed and the frustrated spin structure of this compound is suggested.

1. Introduction
There has been considerable interest in the study of low-dimensional quantum spin systems with spin frustration. Since organic radicals consisting of only light elements show very small spin-orbit coupling, they are regarded as ideal Heisenberg spin systems and are suitable to study quantum nature of spin systems. Recently we have developed a frustrated spin system by using an organic triradical BIPNNBNO, where BIPNNBNO = 3,5-bis(N-tert-butylaminoxyl)-4'-1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)biphenyl. Since two radical units of $S = 1/2$ ferromagnetically couple strongly to form an $S = 1$ species, BIPNNBNO is regarded as a mixed spin system with $S = 1$ and $S = 1/2$. The study of the mixed spin systems with two kinds of antiferromagnetically exchange coupled spins, in particular, the mixed spin systems with integer and half-integer spins is much attractive [1]. The ground state properties depend on the periodic arrangement of the different spins. For example, an alignment of elementary cells with spins 1, 1, 1/2, 1/2 in this order results in a singlet ground state with an excitation gap [2]. Properties of alternating-spin ladder were also theoretically studied and the quantum fluctuations play a crucial role in the nonmagnetic ground state [3]. We have developed some mixed spin systems using organic triradicals and different ground states were observed depending on the intermolecular networks. The crystals of PNNBNO, where PNNBNO = 2-[3',5'-bis(N-tert-butylaminoxyl)phenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1H imidazol-1-oxyl 3-oxide, has the intermolecular antiferromagnetic coupling between the $S = 1$ and $S = 1/2$ in three dimension and is the first example of organic ferrimagnets [4]. On the other hand, the crystals of PIMBNO and BIPNNBNO involve the intermolecular contacts between $S = 1$ units and/or the ones between $S = 1/2$ units, where PIMBNO = 2-[3',5'-bis(N-tert-butylaminoxyl)phenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1H imidazol-1-oxyl. Only BIPNNBNO shows the singlet ground state with an excitation gap, whereas
PIMBNO shows a gapless ground state [5]. The crystal structural analysis has revealed the complex spin network in BIPNNBNO crystals. The flexibility of the molecule gives BIPNNBNO competing magnetic exchange couplings, which induces frustrated spin structure.

The two dimensionality in BIPNNBNO crystals is confirmed by the angular dependence of the peak-to-peak linewidth of X-band (9.5 GHz) ESR spectra at room temperature [6]. However, the spin correlation by the magnetic exchange interaction is not clear yet. In an organic radical, the spin densities distribute on the whole molecule due to π–conjugation. Since the magnetic exchange is related to the overlap between the molecular orbitals, the treatment of an organic spin as a point dipole is not always good approximation. The largest exchange interaction does not always occur between spins with the shortest distance which show the largest magnetic dipole-dipole interaction. For example, the temperature dependence of the ESR g-factor in an organic spin-ladder compound BIP-TENO shows opposite tendency to the theory proposed to one-dimensional antiferromagnetic chain [7] and importance of the consideration of the spin density distribution within a molecule was pointed out [8]. The spin density distribution in organic molecules also makes it difficult to understand the spin correlation. For the elucidation of the magnetic exchange interaction, we have started to study the ESR measurements by using single crystals. In this paper, we report the temperature and frequency dependences of the linewidth and resonant field of BIPNNBNO crystals.

2. Experimental

BIPNNBNO was synthesized by following the conventional procedure [4,9] and crystallized to rhombus shaped dark green single crystals. The BIPNNBNO crystal belongs to an orthorhombic system, \( Pbcn \), \( a = 9.0126(7) \), \( b = 17.578(1) \), \( c = 33.924(3) \, \text{Å} \), \( V = 5374.3(6) \, \text{Å}^3 \), \( Z = 8 \) [5]. The rhombus plane corresponds to the crystallographic \( bc \) plane and the longer and shorter diagonal is parallel to the \( b- \) and \( c- \) axis, respectively. Submillimeter wave ESR measurements have been performed at frequencies of up to 716 GHz and in pulsed magnetic fields of up to 29 T, with the field direction parallel to the crystallographic axes. Three pieces of single crystals were used. An optical pumped far-infrared laser, backwarstravelling wave tubes and Gunn oscillators have been employed as radiation sources. We have employed a simple transmission method with Faraday configuration where the propagation vector of the incident radiation is aligned parallel to the external magnetic field [10]. The polarization of light is random in the plane normal to the propagation vector. An InSb is used as the detector. For the field calibration, DPPH or ruby was used.

3. Summary of the magnetic properties of BIPNNBNO

The crystal structure of BIPNNBNO is schematically shown in Figure 1 (a). Molecules are connected by three kinds of radical-radical contacts [5,6], which always yield antiferromagnetic interactions [4,11]. The two dimensional sheet is spread on the \( ab \)-plane. Along the \( a \)-axis, a ladder-like structure is formed by two kinds the radical-radical contacts, which will induce a frustrated spin structure. On the other hand, ferrimagnetic chains are formed along the \( b \)-axis.

The temperature dependence of the paramagnetic susceptibility (\( \chi_p \)) of BIPNNBNO crystals were compared with the one for isolated molecules diluted in diamagnetic polyvinylenechloride matrix [12]. Below 30 K, the \( \chi_p \) values of crystals become smaller than the ones of isolated molecules, reflecting the intermolecular antiferromagnetic interactions. The double-peak structure was observed at 4.2 and 15 K in the temperature dependence of \( \chi_p \) of BIPNNBNO crystals, which suggests the existence of at least two kinds of intermolecular antiferromagnetic interactions. The value of \( \chi_p \) of BIPNNBNO crystals decreases to zero as temperature decreases below 4.2 K, which suggests the singlet ground state of this material. The magnetization isotherm of BIPNNBNO measured at 0.4 K is shown in Figure 1(b) [5]. The finite magnetization is not observed below \( B_{c0} = 4.5 \, \text{T} \). Above \( B_{c0} \), magnetization increases rapidly and reaches \( 1 \mu_B/\text{f.u.} \), which corresponds to the value of 1/3 of the full saturation magnetization (\( 3 \mu_B/\text{f.u.} \)). Between \( B_{c1} = 6 \, \text{T} \) and \( B_{c2} = 23 \, \text{T} \), the magnetization takes a constant value of \( 1 \mu_B/\text{f.u.} \), which is called 1/3 magnetization plateau. Above \( B_{c2} \), it increases again and saturates to \( 3 \mu_B/\text{f.u.} \) at \( B_{\text{sat}} = 29 \, \text{T} \). A very narrow magnetization plateau of 2/3 is also appears around \( B_{c3} = 26 \, \text{T} \).
We categorize the magnetic field in three regions: gapped, gapless, and $1/3$ magnetization plateau regions are defined as the one below $B_{c0}$, between $B_{c0}$ and $B_{c1}$, and between $B_{c1}$ and $B_{c2}$, respectively.

4. Results and discussions

4.1. X-band ESR

Figure 2 shows the temperature dependence of the X-band ESR $g$-factors and peak-to-peak linewidth ($\Delta B_{pp}$) when the magnetic field is applied parallel to the orthogonal crystallographic axes ($B \parallel a$, $b$, $c$). The small anisotropy of the principal values of $g$-factors at room temperature ($g_a = 2.0066$, $g_b = 2.0068$, $g_c = 2.0051$) means that this compound is an almost ideal Heisenberg spin system. The temperature dependence of $\Delta B_{pp}$ shows a broad maximum at about 100 K. The temperature dependence of $\chi_p$ of crystalline states above 30 K is identical with the one of isolated molecules and the $\chi_p T$ value of isolated molecules starts to decrease below 100 K. Thus, the broad maximum in $\Delta B_{pp}$ at about 100 K is related to the spin-spin correlation between $S = 1$ and $S = 1/2$ within a molecule. Below 20 K, where $\chi_p$ takes a broad maximum, the broadening of $\Delta B_{pp}$ is remarkable at any field direction. It is related to the spin-spin correlation due to the intermolecular antiferromagnetic interactions. In one and two dimensional antiferromagnets, broadening of the linewidth due to the short range order was reported [13,14]. The $g$-factor shows positive and negative shift upon cooling for $B \parallel b$, $c$ and $B \parallel a$, respectively. The $a$-axis is perpendicular to the thin rhombus plane and the largest demagnetizing field
is expected along this direction. By using the approximation of ellipsoid [15], the contribution of the demagnetizing field is estimated to be at most 50% of the observed g-shift. Thus the observed g-shift is intrinsic to the spin network of this material. The observed g-shift does not agree with the reports on the one and two dimensional antiferromagnets [7,16], probably due to the spin density distribution [8].

4.2. High-frequency ESR

4.2.1. Temperature dependence of linewidth

In the high-frequency ESR measurements, a single absorption signal was observed in the whole frequency and temperature range. Figure 3 shows the temperature dependences of the full width at the half maximum ($\Delta B_{1/2}$) measured at 190, 357, 716 GHz. The measurements at 95 and 135 GHz were also made but the data were not shown. The signal became broad as increasing frequency. The value of $\Delta B_{1/2}$ for $B \parallel b$ is smaller than the ones for other two field directions. As decreasing temperatures, the value of $\Delta B_{1/2}$ gradually increases below 20 K similarly to the X-band result. The $\Delta B_{1/2}$ below 10 K behaves differently depending on the field region. In the gapped (95 GHz) and plateau region (357, 716 GHz), the value of $\Delta B_{1/2}$ approaches a maximum below about 10 K, whereas in gapless region (135 and 190 GHz), the monotonous increase with decreasing temperature was observed.

At 190 GHz corresponding to the end of the gapless region, the rapid increase of $\Delta B_{1/2}$ was remarkable below 4 K for $B \parallel a, b$. For $B \parallel c$, only the subtle change of $\Delta B_{1/2}$ was observed, which is probably due to the considerably small magnetic correlation along this direction.

4.2.2. Temperature dependence of the shift of resonant fields

Figure 4 shows the temperature dependences of the shift of the resonant field ($B_{\text{res}}$) for $B \parallel a, b, c$. The plotted symbols represent the difference of the resonance field from that at 50 K, $\Delta B_{\text{res}} = B_{\text{res}}(T) - B_{\text{res}}(50 \text{ K})$. The positive and negative shift was observed for $B \parallel b, c$ and $B \parallel a$, respectively. At 95 GHz in the gapped region, the maximum shift was observed at 4 K in any field directions, which is the
same tendency observed at X-band. At 716 GHz in the 2/3 plateau region, no shift was observed for \( B//a \), which suggests the saturated magnetic behaviour. The behaviour in gapless (135, 190 GHz) and 1/3-plateau (357 GHz) region depends on the field direction. For \( B//a \), monotonous shift was observed. The maximum shift was observed at 190 GHz in the end of the gapless region. The shift in the 1/3 magnetization plateau region is moderate as compared with that in the gapless region. For \( B//b \), similarly to \( B//a \), the largest shift was observed at 190 GHz. In the gapless region, the value of \( B_{\text{res}} \) was almost constant. At 357 GHz in the 1/3 magnetization plateau region, the temperature dependence of \( \Delta B_{\text{res}} \) shows a broad maximum at about 4 K. The behaviour for \( B//c \) is somewhat different from other two axes. The temperature dependence of \( \Delta B_{\text{res}} \) at 135 GHz shows a maximum at about 3 K, whereas monotonous shift of \( \Delta B_{\text{res}} \) was observed at 190 GHz. Peculiar feature is the moderate shift at 190 GHz. The shift at 190 GHz was smaller than that at 135 GHz (gapless region) and at 357 GHz (1/3 magnetization plateau region). Along the \( c \)-axis, considerably small intermolecular magnetic exchange coupling is expected as compared with that for other two axes. Therefore, the behaviour for \( B//c \) is possibly related to the spin-spin correlation within a molecule.

4.2.3. Field dependence of the resonant field
We also examined the field dependence of the resonant field (\( B_{\text{res}} \)) at 1.6 K for \( B//a, b, c \). Tiny deviations from the paramagnetic line was observed. The resonant field of paramagnetic state (\( B_{\text{para}} \)) was calculated by \( B_{\text{para}} = \frac{h \nu}{g_i \mu_B} \), where \( g_i (i = a, b, c) \) is the principal value estimated by X-band ESR at room temperature. The observed shift of the resonant field was calculated by

\[
\delta B_{\text{res}} = B_{\text{res}} - B_{\text{para}} - N_i M, \quad (I = a, b, c)
\]

where \( N_i \) is the demagnetizing factor by using the approximation of ellipsoid[15] and \( M \) is the observed magnetization value. Figure 5 (a) shows the field dependence of \( \delta B_{\text{res}} \). The anisotropic behaviour was observed. Above 10 T, positive and negative slope was observed for \( B//b, c \) and for

\[ B//a, \text{ respectively.} \]

\[ \text{The largest demagnetizing factor is expected for} \ B//a, \text{ and the contribution is less than} 20\%. \]

\[ \text{The correction of demagnetizing field does not change the sign of the slope of} \ \delta B_{\text{res}} \text{ against} \ B. \]

\[ \text{The homogeneity of the pulsed field is about 0.01\% of the applied field for} 1\text{mm discrepancy.} \]

\[ \text{At} 25 \text{T, the inhomogeneity is} 2.5 \text{mT, which corresponds to about} 4\% \text{ of} \ \Delta B_{1/2} \text{ and a quarter of the observed shift of} \ \delta B_{\text{res}}. \]

\[ \text{The field dependence at any field direction involves the contribution showing} \]

\[ \text{Figure 5. (a) Field dependence of resonant fields in BIPNNBNO crystals. The deviation from the paramagnetic line is plotted. Black, green, and red circles represent the observed data for} B//a, b, \text{ and} c, \text{ respectively. Solid curves are guide for eyes.} \ (b) \text{ Schematic illustration of the magnetic model of BIPNNBNO.} \]
positive field dependence, which is considered as the effect of the thermal excitations. The anisotropic change of the slope above 10 T should be related to the anisotropic magnetic exchange coupling. Then we can conclude that the \( a \)-axis is the direction along which dominant magnetic exchange couplings work between spins.

5. Conclusion

We have performed high-frequency ESR measurements of single crystals of BIPNNBNO. The temperature dependence of \( \Delta B_{1/2} \) and \( \Delta B_{\text{res}} \) differs between the gapped, gapless, and plateau region. In the field dependence of \( B_{\text{res}} \), small deviation from \( B_{\text{para}} \) was observed. Because of the very small anisotropy of organic radical, the efficiency of analysing \( \delta B_{\text{res}} \) has been demonstrated. From the results of the temperature and field dependences of \( B_{\text{res}} \), the different behaviour was observed for \( B // a \) from that for \( B // b, c \). It can be related to the magnetic exchange coupling. Although two-dimensional network is spread within the \( ab \) plane, the larger molecular overlap is expected along the \( a \)-axis, which means that the dominant magnetic exchange couplings work along the \( a \)-axis. The schematic magnetic model of BIPNNBNO is shown in figure 5 (b). We can see two kinds of intermolecular antiferromagnetic exchange couplings, which will yield frustrated spin structure. Recent study of the specific heat in magnetic field also suggests that the antiferromagnetic coupling along the \( a \)-axis is crucial, especially the coupling between \( S = 1 \) units [17].

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