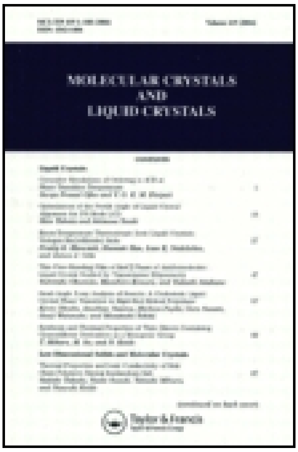

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Millimeter Wave ESR Measurements of $(DMET)_2FeBr_4$

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We have performed millimeter wave ESR measurements of $(DMET)_2FeBr_4$ single crystals, which consist of electric quasi 1D chain-based donor layers and magnetic Fe^{3+} square lattices, in the temperature region from 1.8 K to 70 K. We observed the splitting of absorption line at 130 GHz, and the estimate the exchange interaction between *d*-electrons and π-electrons. The temperature dependence of ESR at low temperature is discussed in connection with the conventional antiferromagnetic resonance (AFMR).

Keywords: DMET; π-*d* system; high field ESR

INTRODUCTION

TTF-based organic charge transfer complexes provides low dimensional electronic systems consisting of π-electrons. These compounds provide a large variety of features in their electronic systems, such as insulators, semiconductors, metals and superconductors, due to the Coulomb interaction and electron-phonon interaction. Moreover, as the insertion of localized magnetic moments of d-electrons into π-electron systems provides another aspect in the low dimensional conducting system[1-5], the π-d interaction systems have attracted much interest.

$(DMET)_2FeBr_4$ is an organic conductor which consists of quasi 1D chain-based donor and localized magnetic anion. The crystal structure is characterized by DMET donor conducting sheets and $FeBr_4$ magnetic sheets[5]. Due to the shortest inter-atomic distance between S and Br, which is comparable to the sum of corresponding van der Waals distances, the inter-layer interactions between donors and anions are expected[5]. Although the resistivity shows metallic behavior at high temperatures, a M-I transition at $T_{M\text{-}I}$ ~40 K occurs and the magnetic susceptibility shows a 3D antiferromagnetic transition at T_N=3.7 K[5]. The anisotropy of the magnetic susceptibility below T_N suggests that the easy axis is the a-axis. The magnetization curves show several anomalies and the magnetoresistance also shows anomalies which correspond to those in the magnetization curve. The conductivity is dominated by π-electrons and the magnetism is dominated by d-electrons. These results suggest the existence of interaction between π-electron and d-electron.

In this study, we will investigate the electronic state of the system by our high field ESR measurements.

EXPERIMENTAL

We performed the millimeter wave ESR measurements of $(DMET)_2FeBr_4$ single crystals in the temperature region from 1.8 K to

70K using the pulsed magnetic field up to 16 T. Gunn oscillators and backward wave oscillators were used as the light sources in the frequency region from 60 to 220 GHz. The details our experimental systems can be found elsewhere[6-8].

EXPERIMENTAL RESULTS & DISCUSSION

Figure 1 shows the temperature dependence of ESR spectra for *B//b* at 130 GHz in the temperature region from 8 K to 20 K. A broad resonance was observed at 20 K. As the line width of the observed resonance is comparable with that from the *d*-electron while the π–electron usually gives much sharper line width, it can be considered that the observed resonance mainly originated from *d*-electrons. Moreover, another sharp resonance started to appear in the higher field side in the temperature region below 15 K. As the broad resonance *d* in Figure 1 shifts to lower field side as the temperature is decreased, this seems to be the origin why we observed a new sharp resonance below 15 K. There is a possibility that this new sharp resonance is coming from the π–electron. Although the resonances from the *d*-electron and the π–electron are usually amalgamated to one resonance due to the exchange interaction between them, there is a possibility that we observe the split resonances in the high field ESR due the competition between the exchange interaction and the difference of Zeeman energy between two spins. In general, the amalgamation begins near the condition[9].

$$2J \approx \Delta g \mu_B H_0 \qquad (1)$$

where Δg is the difference of the *g*-values between the two spins, H_0 is the external magnetic field. The split of resonance occurs when the Zeeman energy exceeds the exchange interaction. The equation indicates that we can estimate the exchange interaction between two spins by investigating the EPR spectra. We can estimate the exchange

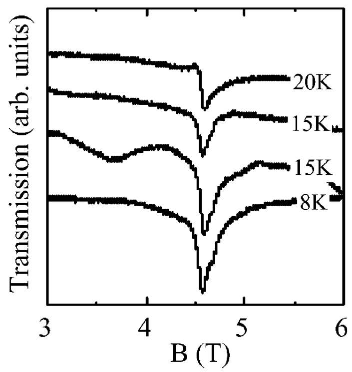

FIGURE 1 The Temperature dependence of ESR spectra for B//b of 130GHz.

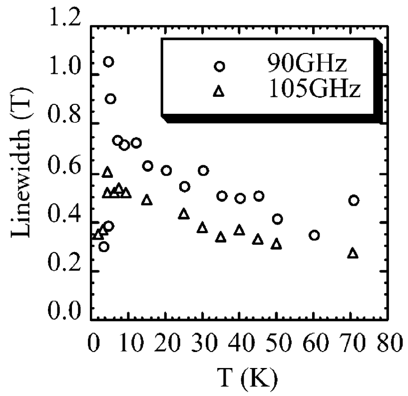

FIGURE 2 The temperature dependence of line width for B//a.

interaction between π-electrons and d-electrons by using the equation (1) and the exchange interaction $J_{\pi\text{-}d}$ is estimated as $J_{\pi\text{-}d}/k_B$=0.06 K by assuming g_{Fe}=2.04 at 35 K, g_{π}=2.00 and the frequency 130 GHz. We need detailed frequency dependence measurement for more detailed discussion.

Figure 2 shows the temperature dependence of line width for *B*//*a*–axis at 90 and 105 GHz. The line width increased below about 40 K as the temperature approached T_N. The behavior of line width indicates the antiferromagnetic ordering around T_N, which is consistent with the results of the magnetic susceptibility measurement[5].

Figure 3 shows the temperature dependence of *g*-values originated from *d*-electron for all principal axes at 150 GHz (*a*, *b*-axis) and 90 GHz (*c*-axis). The *g*-value for *B*//*a*, *b* increases as the temperature is decreased, but the g-value for *B*//*c* decreases as the temperature is decreased. There is a possibility that these shifts of *g*-values are due to the short range ordering above T_N. It is well known

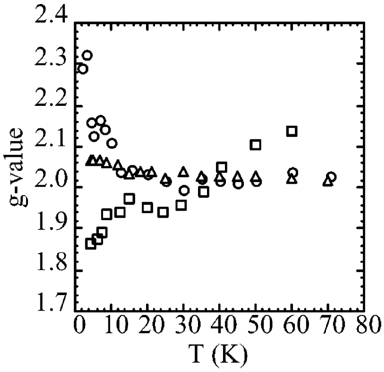

FIGURE 3 The temperature dependence of g-values a-axis (circles), b-axis (triangles), c-axis (squares).

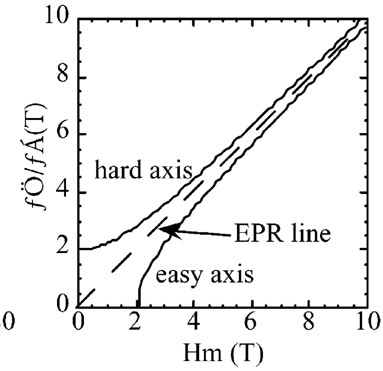

FIGURE 4 Frequency-field diagram of easy axis type atiferromagnet assuming two sub-lattice.

that the frequency-field diagram of a typical easy-axis type antife rromagnet assuming a two-sublattice takes the dependence shown in Figure 4. Figure 4 indicates that the resonance field for *B*//hard-axis decreases as the temperature is decreased, i.e. the *g*-value for *B*//hard-axis increase as the temperature is decreased. On the other hand, the g-value for *B*//easy-axis decreases as the temperature is decreased. However, the *g*-shifts for *B*//*a* (easy axis) and *c*(hard axis) do not coincide with the behavior of typical antiferromagnet shown in Figure 4. The results indicate that the magnetic structure of $(DMET)_2FeBr_4$ cannot be interpreted by a simple two sublattice antiferromagnet and suggest that further frequency dependence measurements are required below T_N.

SUMMARY

We performed the millimeter wave ESR measurements on $(DMET)_2FeBr_4$ single crystals in the temperature region from 1.8 K to 70K. We showed the rough estimate of the exchange interaction between π-electrons and d-electrons on $(DMET)_2FeBr_4$ from our high field ESR results. We also discussed about the temperature dependence of g-values of $(DMET)_2FeBr_4$ in connection with the typical antiferromagnetic resonance (AFMR).

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