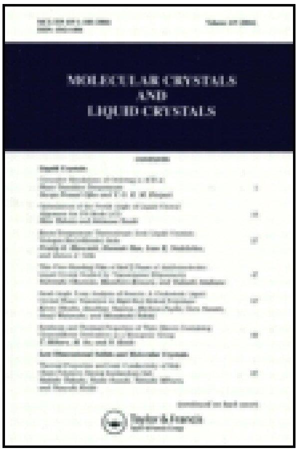

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Frequency Dependence Millimeter Wave ESR Measurements of Et 2 Me 2 P[Pd(dmit) 2] 2

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Frequency Dependence Millimeter Wave ESR Measurements of $Et_2Me_2P[Pd(dmit)_2]_2$

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We have performed the frequency dependence millimeter wave ESR measurements on $Et_2Me_2P[Pd(dmit)_2]_2$ single crystals at 4.2 K. Antiferromagnetic resonance (AFMR) was observed for $B // \boldsymbol{a}$ and $\boldsymbol{c}$. The hard axis is determined to be $\boldsymbol{a}$ axis by AFMR mode analyses. This result will be discussed in connection with the X- and Q-band ESR results at low temperature. We will also discuss about the magnetic anisotropy of the system and it turned out that this salt is the antiferromagnet with the easy axis type anisotropy.

Keywords millimeter wave ESR; dmit; AFMR; magnetic anisotropy

INTRODUCTION

A series of β'-(cation)$[Pd(dmit)_2]_2$ salts (cation = Me_4Z and Et_2Me_2Z; Z = P, As and Sb) has attracted much interest of many researchers due to its unique two-band electronic structure which is characterized by one-dimensional LUMO (lowest unoccupied molecular orbital) band and two-dimensional HOMO (highest occupied molecular orbital) band.[1] These salts exhibit insulating, metallic and superconducting phases depending on cation and pressure. For instance, the title compound Et_2Me_2P salt shows superconducting transition under pressure region from 6.9 to 10.4 kbar with $T_c = 4.0 - 1.8$ K[2], while the antiferromagnetic transition occurs under ambient pressure.[3] β'-Pd(dmit)$_2$ salts have almost the same crystal structure regardless of cations and the crystal structure is based on the stack of strongly dimerized Pd(dmit)$_2$ molecules. Under ambient pressure, these salts are all in the insulating phase which is considered to be Mott-Hubberd insulator.[1] The ground state of these salts under ambient pressure is suggested to be antiferromagnetic states except for Et_2Me_2Sb salts by the X-band ESR measurements.[3] The T_N of the title compound Et_2Me_2P salt is 18 K and that of Me_4P salt is 35 K, while an antiferromagnetic transition is not observed for Et_2Me_2Sb salt. This large cation dependence of T_N has been explained by the effect of the magnetic frustration in this system.[4] The main aim of this study is to gain information of the magnetic structure of these salts. We focus on the frequency dependence of ESR of Et_2Me_2P salt and the magnetic anisotropy of this salt in this paper.

EXPERIMENTAL

Millimeter wave ESR measurements using the pulsed magnetic field up to 15 T have been performed at 4.2 K in the frequency region from 80 to 315 GHz using Gunn oscillators.[5, 6, 7] X-band ESR measurements have been performed at around 3 K using a conventional X-band ESR spectrometer Bruker EMX 081 with the static magnetic field up to 0.86 T. Both measurements have been performed for all axes by preparing a large amount of $Et_2Me_2P[Pd(dmit)_2]_2$ single crystals aligned along each axis. Q-band ESR measurements have been also performed for ***a*** and ***c*** axes using a conventional Q-band ESR spectrometer Bruker ESP 300E with the static magnetic field up to 1.74 T. Several single crystals aligned along each axis were used and the observed temperature region was from 5 to 20 K.

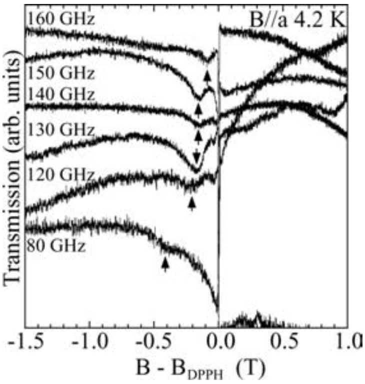

FIGURE 1 Frequency dependence ESR spectra at 4.2 K for *B*//***a***. AFMR is indicated by arrow. Horizontal axis is normalized by the resonance field of DPPH.

RESULTS AND DISCUSSION

Figure 1 shows the frequency dependence ESR spectra observed at 4.2 K for *B*//***a***. It is obvious that the resonance field of ESR indicated by arrow shifts to lower field side from the resonance field of DPPH as the frequency is decreased. The temperature dependence ESR measurements showed the increase of the linewidth around T_N, and the shift of the resonance field below T_N.[8] These results can be interpreted by the appearance of the internal magnetic field accompanied by the antiferromagnetic transition at T_N. Therefore, the observed resonance at 4.2 K is considered to be the antiferromagnetic resonance (AFMR). Figure 2 shows the frequency dependence of the *g*-value at 4.2 K. The *g*-value increases as the frequency is decreased for *B*//***a***, while the *g*-value seems to depend not much on the frequency for *B*//***c***. The frequency dependence of the *g*-value for *B*//***a*** can be explained well by the following AFMR mode for *B*//hard axis by the conventional two-sublattice AFMR theory.[9]

$$\left(\frac{\omega}{\gamma}\right) = \sqrt{B^2 + c_2} \tag{1}$$

where, ω, γ and c_2 are angular frequency, magnetogyric ratio and constant,

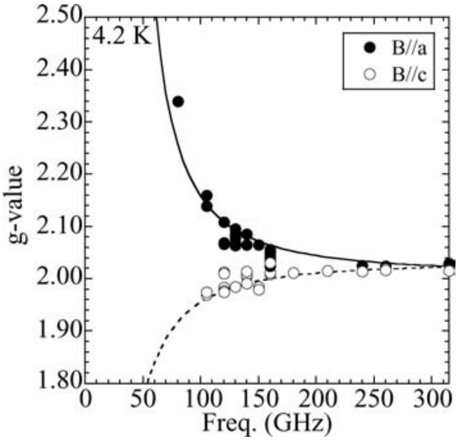

FIGURE 2 Frequency dependence of the g-values at 4.2 K. Solid and dotted lines are given by equations (1) and (2) in the text, respectively.

respectively. Solid line in Figure 2 indicates the frequency dependence of the g-value using equation (1) with $\sqrt{c_2} = 1.3$ T. According to the conventional two-sublattice antiferromagnetic theory[9], it is predicted that an antiferromagnet with the easy plane type anisotropy has the g-value which is independent of the frequency and its AFMR is observed at the same resonance field with its electron paramagnetic resonance (EPR) field when the external field is applied in the easy plane. The g-value does not depend much on the frequency for $B//\boldsymbol{c}$ as shown in Figure 2. However, it seems to be difficult to explain the AFMR of this salt by the easy plane type anisotropy. In the X-band ESR measurement, the integrated intensity decreased abruptly below T_N for all axes.[10] If ***bc*** plane is the easy plane, the integrated intensities at low temperature for $B//\boldsymbol{b}$ and $\boldsymbol{c}$ are expected to be comparable to those of EPR. On the other hand, the temperature dependence of the resonance field in the millimeter wave ESR measurement showed the shift to the higher field side for $B//\boldsymbol{c}$, the shift to the lower field side for $B//\boldsymbol{a}$ and the broadening out of the signal with the shift to the lower field side for $B//\boldsymbol{b}$ below T_N.[8] These results seem to suggest that the antiferromagnetic state of this salt has the easy axis type anisotropy and the easy axis is $\boldsymbol{c}$ axis. Taking these into account, the AFMR mode analysis for $B//\boldsymbol{c}$ has been made. The AFMR mode for $B//$easy axis ($B \geq$ spin flop field; B_{SF}) is given by the following equation according to the AFMR theory.[9]

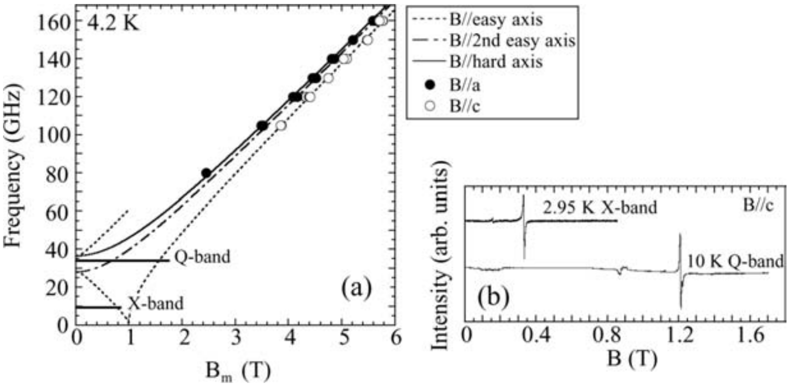

FIGURE 3 (a) Frequency - field diagram at 4.2 K. Bold solid lines indicate the observed magnetic field region in the X- and Q-band measurements. (b) ESR spectra for $B//\boldsymbol{c}$ obtained by X- and Q-band ESR measurements.

$$\left(\frac{\omega}{\gamma}\right) = \sqrt{B^2 - c_1} \qquad (2)$$

The dotted line in Figure 2 indicates the frequency dependence of the g-value using equation (2) with $\sqrt{c_1} = B_{SF} = 1.0$ T. Although the fitting parameter c_1 seems to have ambiguity as the observed AFMRs for $B//\boldsymbol{c}$ are limited above 105 GHz as shown in Figure 2, the obtained spin flop field has the similar value to that of Me$_4$P salt, which is 1.5 T and it is evaluated by the upturn of the magnetization curve at low temperature.[1] Figure 3(a) shows the frequency - field diagram at 4.2 K with the modified field $B_m = (g_{\mathrm{EPR}}/2)B$ using $g_{\mathrm{EPR}} = 2.01$ and $g_{\mathrm{EPR}} = 2.03$ for $B//\boldsymbol{a}$ and $\boldsymbol{c}$, respectively. This AFMR mode analysis suggests that AFMR can not be observed for $B//\boldsymbol{a}$ in X- (9.4 GHz) and Q-band (34 GHz) ESR while for $B//\boldsymbol{c}$ AFMRs can be observed at around 0.7 T and 1.5 T in X- and Q-band ESR, respectively. For $B//\boldsymbol{a}$, AFMR was not observed at low temperature in neither X- or Q-band ESR measurements and it is consistent with the AFMR mode for $B//$hard axis, while there seems to be no signal for $B//\boldsymbol{c}$ except for the signals around $g = 2$, which is mainly caused by impurity, as shown in Figure 3(b). It should be noted that β-Me$_4$N salt which undergoes the antiferromagnetic transition at 12

K has the small local magnetization of 0.22 μ_B[11] and Et_2Me_2P salt is considered to have similar small local magnetization.[4] This small local magnetization is considered to be related with the magnetic frustration.[4] Moreover, the intensity of AFMR gets weaker at lower frequency as shown in Figure 1 and it may be related with the fact that AFMR is not observed at X- and Q-band for $B//\boldsymbol{c}$. Further investigation is needed especially for the lower frequency region.

In summary, we performed millimeter wave, X- and Q-band ESR measurements on $Et_2Me_2P[Pd(dmit)_2]_2$ single crystals at low temperature. The AFMR is observed at 4.2 K for $B//\boldsymbol{a}$ and $\boldsymbol{c}$ by millimeter wave ESR measurements. The magnetic anisotropy of the system has been discussed and AFMR mode analysis suggest that $\boldsymbol{a}$ axis is the hard axis.

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