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Microscopic Observation of π Spin Polarization by *d* Localized Spin in λ Type BETS Based Organic Superconductors

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Abstract: In this study, ^{77}Se NMR measurements were carried out to detect the π spin polarization of the organic BETS (BETS = Bis(ethylenedithio)tetraselenafulvalene) molecule of the field induced superconductor, λ-(BETS)$_2$Fe$_{1-x}$Ga$_x$Cl$_4$, which shows a superconducting transition at relatively low magnetic field compared to the non-doped λ-(BETS)$_2$FeCl$_4$. From the analysis of the NMR spectrum at low temperature, it was clarified that the exchange interaction between π and 3*d* spins in the Ga doping system is smaller than that in the Fe salt. It is also clarified that the conduction π spins feel the "averaged" exchange field from the localized 3*d* spins at the dilute Fe sites.

Keywords: (BETS)$_2$Fe$_{1-x}$Ga$_x$Cl$_4$; π-*d* interaction; NMR

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1. Introduction

The organic charge transfer salt λ-(BETS)$_2$FeCl$_4$ has been attracting much physical interest due to the strong interaction between conducting π spins on the two-dimensional organic sheet and S = 5/2 3*d* localized spins at the Fe site [1]. The system shows a metal–insulator transition (MIT) with antiferromagnetic ordering at 8 K under zero magnetic field [1–4]. Application of a strong magnetic field decreases the MIT temperature. A magnetic field stronger than 11 T kills the MIT and the system remains metallic down to low temperatures. The MIT of the system has been considered as a cooperative transition between organic π and *d* spins [4]. However, another scenario was proposed as a result of the specific heat measurements presented by Akiba et al. [5]. The mechanism of the MIT and the details of the antiferromagnetic ordered state are still unclear [6]. The most drastic phenomenon of this material is magnetic field-induced superconductivity (FISC) [7,8]. The explanation of this unusual phenomenon is the compensation mechanism [9]: polarized 3*d* electrons produce a strong magnetic field through the exchange interaction with π conduction electrons, which cancels the applied field. The magnitude of the exchange field by localized *d* spin was evaluated experimentally and the compensation mechanism was evidenced by several studies [5,10,11] including our NMR studies [12,13]. The details of the FISC of the system were reviewed by Uji and Brooks [14].

On the other hand, an isostructural λ-(BETS)$_2$GaCl$_4$ (Ga salt, hereafter) is a pure π electronic system because there is no *d* spin on the anion site [15]. The Ga salt shows superconductivity around 5 K at zero magnetic field and the superconducting state is killed by a magnetic field (H_{C2} ~ 12 T) as in a conventional superconductor [16].

The π-*d* interaction of the system can be tuned by making alloy compounds λ-(BETS)$_2$Fe$_{1-x}$Ga$_x$Cl$_4$ [16,17]. The structural disorder effect is considered to be small because the size of the anions $FeCl_4$ and $GaCl_4$ is similar. In fact, in the Ga-doped system, the transition temperature, T_{MI}, decreases continuously with increasing x continuously [17] and the insulating phase disappears when x is larger than 0.25. The Ga doping also changes the field-induced phase. Uji et al. performed precise and systematic electrical resistivity measurements under various magnetic fields for different Ga contents and they proposed a global temperature-field phase diagram [17]. A schematic drawing of the temperature-field phase diagram is given in Figure 1. The dome-shaped FISC phase shifts towards the lower field side without broadening and the antiferromagnetic insulating (AFI) phase shrinks with Ga doping. Phenomenologically, the FISC phase of Ga-doped salt seems to be very similar to that of the Fe salt. The gravity center of the FISC dome, H_{max}, the magnetic field that gives the highest transition temperature, was observed at H_{max}~$32 \times (1 - x)$ in Tesla. The area of the FISC is not changed significantly by doping. The π-d exchange field seems to be homogeneous and reduced continuously by Ga doping. Several studies on the Ga-doped system have been carried out. Oshima et al. performed combined measurements of ESR and electrical resistance in the field-induced superconducting state of Ga 40% system [18]. They observed increases in the resistance in the superconducting state when the Fe spin polarization was disturbed by ESR [18]. This suggests that the π-d exchange field was modified by the ESR transition and, consequently, FISC was destroyed. Akiba et al. performed systematic heat capacity measurements on various samples with different Ga content x and evaluated the strength of the π-d interaction from the entropy analysis [19]. They reported that the π-d interaction decreased systematically with x as $J_{\pi d}$~J_0 $(1 - x)$, where $J_{\pi d}$ and J_0 are π-d interaction and that of the Fe salt, respectively. These reports suggest that the conduction π spins feel the "uniform" exchange field from the dilute Fe site. In the present study, we performed Se NMR measurements on a Ga-doped system, λ-$(BETS)_2(Fe_{1-x}Ga_x)Cl_4$, to investigate how the π-d interaction changes by the partial replacement of Fe with Ga, through detecting the π spin polarization quantitatively and microscopically.

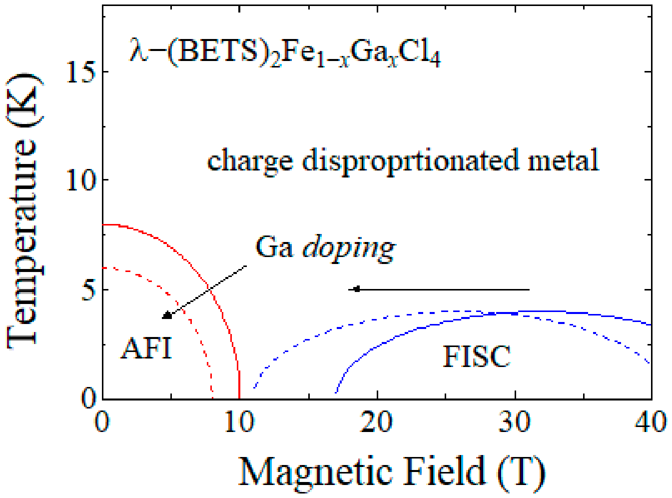

Figure 1. Schematic field-temperature phase diagram of λ-$(BETS)_2Fe_{1-x}Ga_xCl_4$, showing the effect of Ga doping.

2. Experimental Details

Single crystal samples were prepared by Zhou et al. at Nihon University by the electrochemical method using a mixture of Ga and Fe electrolytes. The Ga content is evaluated by the molar content of Ga and Fe electrolytes as $M_{Ga}/(M_{Ga} + M_{Fe})$, where M_{Ga} and M_{Fe} are molecular contents of Ga and Fe electrolytes, respectively. More precise estimations of the Ga content were obtained by the following two methods: (i) the electron probe microanalysis (EPMA) measurements and (ii) the heat capacity measurements. Akiba et al. reported that there is a clear relationship between Ga content and heat capacity [19]. The values of the Ga content thus agreed well with those in preparation.

A single crystal sample from the same batch which was characterized by the heat capacity measurements was used in the present study. The dimensions of the sample were ~0.1 × ~0.05 × ~3 mm^3. The natural abundance of NMR-active ^{77}Se isotopes contribute to the signal at a value of 7%.

The ^{77}Se NMR measurements were performed by a conventional pulsed NMR spectrometer with 9 T superconducting magnet. NMR spectrum was obtained by the fast Fourier transformation of the spin echo signal at a fixed magnetic field of 9 T. The typical pulse width was ~0.5 μs. In most of the present measurements, the *rf* pulse duration was short enough to cover the spectrum. The NMR frequency shift and the linewidth were defined as the first moment and the square root of the second moment of the spectrum, respectively. The sample and the NMR coil were mounted on a goniometer with the rotation axis along the needle axis (crystallographic *c*): the geometry of the experiments and analysis was almost the same as in our previous studies [13].

The NMR shift of electronic origin, δf, should be expressed as

$$\delta f(\theta, T) = \gamma A(\theta)\chi^{\pi}(H_0 + JM(T)) \tag{1}$$

where γ, $A(\theta)$, χ^{π}, H_0, J and $M(T)$ are gyromagnetic ratio of ^{77}Se nucleus (8.127296 MHz/T) [13] hyperfine coupling constant, local susceptibility of the π spin system, external field, exchange interaction and Fe moment, respectively. The hyperfine coupling constant for ^{77}Se nuclei in the present system is known to be uniaxial, written as $A(\theta) = A^{\mathrm{iso}} + A^{\mathrm{ax}}(3\cos^2(\theta - \theta_0)\cos^2\phi_0 - 1)$, where $A^{\mathrm{iso}}/A^{\mathrm{ax}}$, θ, θ_0 and ϕ_0 are isotropic/axial components of the hyperfine coupling, the rotating angle in the *a***b**-plane and the orientation angles of the Se $4\mathrm{p}_z$ orbital with respect to the *a***b**-plane (θ_0 is 17.3°) and the angle between the π orbital of the Se and rotating plane (13.6°), respectively. The geometrical situation is shown in the inset of the Figure 2. In our previous reports on Fe and Ga salts, the values of hyperfine parameters were already obtained [13,20]. We used the Brillouin function of $S = 5/2$ for the temperature dependence of the Fe moment, $M(T)$, in Equation (1) as in the previous work [13].

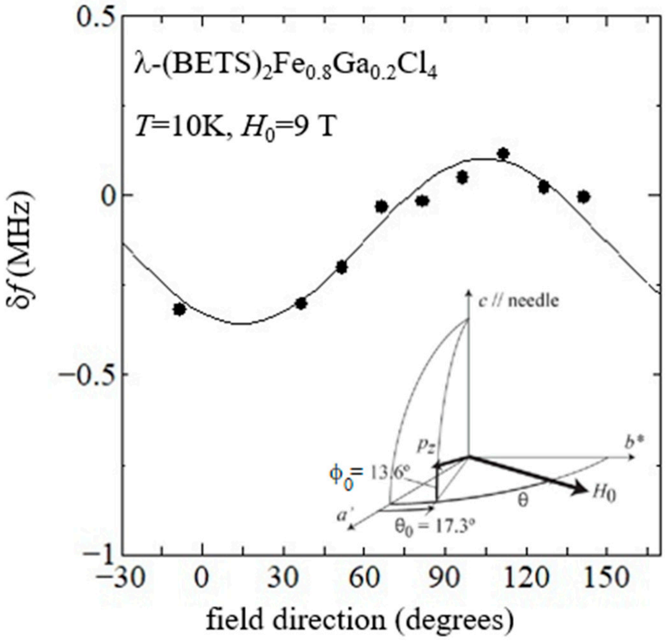

Figure 2. Angular dependence of the central shift, δf. The solid line is the calculated angular dependence assuming the exchange interaction JM(10K) = −20 T. The geometrical situation of the measurements is shown in the inset.

3. Results and Discussion

3.1. Evaluation of the Exchange Interaction

The NMR shift δf is a linear function of H_0 or M(T) under the fixed field or temperature, as shown in Equation (1), so that the temperature dependence of δf at a fixed magnetic field or the field dependence at a fixed temperature enables us to determine the exchange interaction J independently. The analysis of the temperature and field dependences of the NMR shift on the Fe salt gave the value of the low temperature (LT) exchange field JM(LT) as −32 T (J~5.4 T/μ_B) in our previous work [13]. We tried to perform similar measurements in the present study on the Ga-doped sample to evaluate the exchange interaction, J. However, the signal–noise ratio of the spectrum was poor due to the broadening, especially at low temperatures. Therefore, we decided to measure the angular dependence of the NMR spectrum at 10 K, where the linewidth was relatively narrow.

Figure 2 shows the angular dependence of δf for the Ga-doped sample, which exhibits a qualitatively similar sinusoidal angular dependence with opposite sign to the Ga salt and the same sign as the Fe salt [13,20]. The crystal structure and the hyperfine symmetry of the present Ga-doped sample are expected to be the same as the non-doped systems and we have chosen the same experimental geometry as those in our previous studies [13,20]. The observed NMR shift clearly indicates that the effective field at the Se nuclear site of the present system is opposite to the external field due to the negative exchange field produced by the localized d spin as observed in the pure Fe salt.

The solid line in Figure 2 is the calculated frequency shift assuming that the exchange interaction, J, is isotropic because we did not observe the angular dependence of the exchange interaction in the Fe salt. We also assumed that the hyperfine parameter, $A(\theta)\chi^{\pi}$, for the Ga-doped system should be given by a molar average of those for the pure salts as $A(\theta)\chi^{\pi}(\mathrm{G20}) = 0.8\,A(\theta)\chi^{\pi}(\mathrm{Fe}) + 0.2\,A(\theta)\chi^{\pi}(\mathrm{Ga})$, where χ^{π}(G20), χ^{π}(Fe) and χ^{π}(Ga) are the π spin susceptibility of the Ga 20%, Fe and Ga salts, respectively. The hyperfine parameters of Fe and Ga salts obtained from Refs [13] and [20] are listed in Table 1. The best fit was obtained by $H^{\mathrm{eff}} = H_0 + JM(10\mathrm{K}) \sim -11$ T. The strength of the applied field in the present study was $H_0 = 9$ T. Therefore, the exchange interaction at 10 K was obtained as $JM(10\mathrm{K}) = -20$ T. Considering the temperature dependence of the Fe moment given by the Brillouin function, the exchange field at low temperatures was estimated as $JM(0\mathrm{K}) = -25$ T (J~5 T/μ_B), which is 20% smaller than that of Fe salt, as expected.

Table 1. NMR parameters of the Ga and the Fe salts obtained by Refs [13,20].

Material	$A^{\mathrm{iso}}\chi^{\pi}$ (%)	$A^{\mathrm{ax}}\chi^{\pi}$ (%)	$\Delta\chi^{\pi}/\chi^{\pi}$	Reference
Ga salt	0.1	0.28	0.3	[20]
Fe salt	0.08	0.19	0.7	[13]

We also measured the temperature dependence of the NMR shift, δf, in the temperature range between 10 and 100 K at a fixed field orientation (θ~30 deg) as in the earlier report (Figure 10 of [13]). The results are plotted as a function of Fe moment in Figure 3. In this geometry, the $A(\theta)\chi^{\pi}$(G20) was estimated to be $0.8A(\theta)\chi^{\pi}(\mathrm{Fe}) + 0.2\,A(\theta)\chi^{\pi}(\mathrm{Ga}) = 0.29\%$. The solid line indicates the calculated values using the Equation (1) with $J = -5$ T/μ_B, mentioned above. The experimental data agree well with the calculation.

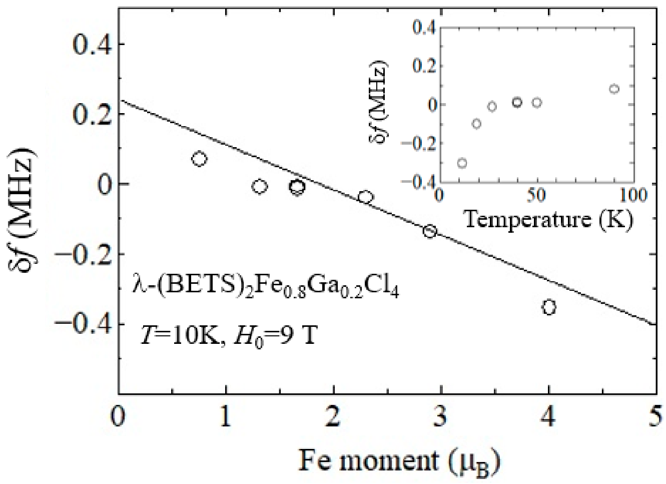

Figure 3. Temperature dependence of the NMR shift, δf obtained at the field orientation of 30 degrees; the horizontal axis is taken as the magnitude of the Fe moment at each temperature. The solid line indicates the calculated values taking J~5 T/μ_B. The inset shows the NMR shift as a function of temperature.

From the angular and temperature dependences of the NMR shift, it was clarified that the exchange interaction between π conduction spin and Fe moment in the Ga-doped salt is homogeneously reduced as Ga doping. The amount of the reduction of the J value of 20% is consistent with the Ga content $x = 0.2$. Although there is a broadening of the spectrum at low temperatures below ~5 K, no appreciable change in the spectrum such as a peak split due to the local inhomogeneity was observed. This indicates that the conduction π spins are polarized uniformly by the "averaged" exchange field from the localized 3*d* spins at the dilute Fe sites.

3.2. Linewidth Analysis: Charge Disproportionation

We reported an unexpected broadening of the ^{77}Se-NMR spectrum at low temperatures in the pure Fe and Ga salts [20]. From the analysis of the angular dependence of the linewidth, we concluded that the broadening is due to charge disproportionation (CD) in the BETS layer. Since the donor arrangement of the conducting layers is quite similar to the non-doped systems, the CD is also expected in the present system. In fact, we observed that the linewidth of the present salt shows a similar angular dependence. Results at 10 K are shown in Figure 4.

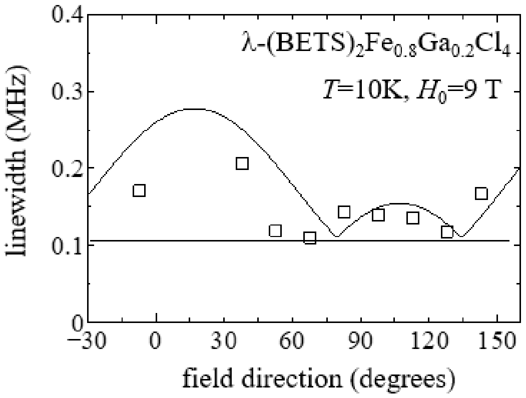

Figure 4. Angular dependence of the line width. The horizontal dashed line corresponds to the width of non-electronic origin. The solid line is the calculated value assuming charge disproportionation in the two-dimensional BETS conducting sheet. Details are given in the text.

To examine the angular dependence of the linewidth, we calculated the line width with the following assumptions. (i) We considered two independent contributions of angular dependent hyperfine component of the electronic origin, Δf_{el}, and of angular independent non-electronic component, Δf_{ne}, as was the case in the pure salts. (ii) The former is expressed as $\Delta f_{\mathrm{el}} = \gamma A(\theta)\Delta\chi^{\pi}$. Here, $\Delta\chi^{\pi}$ is the degree of the spatial inhomogeneity of the spin susceptibility and it should be proportional to the degree of CD. The ratios, $\Delta\chi^{\pi}/\chi^{\pi}$, for the Fe and Ga salts were obtained as 0.7 and 0.3, respectively, at low temperatures. For the present alloy system, we simply took this value as an adjusting parameter. (iii) We took the minimal value of the linewidth observed at 80 and 130 degrees as the latter contribution, Δf_{ne}. (iv) We calculated the linewidth as

$$\Delta f_{\mathrm{obs}} = \sqrt{\Delta f_{\mathrm{el}}^2 + \Delta f_{\mathrm{ne}}^2} \tag{2}$$

The solid curve in Figure 4 indicates the calculated angular dependence with $\Delta\chi^{\pi}/\chi^{\pi} = 0.4$. The basic features were well reproduced while the experimental data were rather scattered.

There are some remarks on the value of $\Delta\chi^{\pi}/\chi^{\pi}$. (i) As mentioned above, the ratio $\Delta\chi^{\pi}/\chi^{\pi}$ should be proportional to the degree of CD on the BETS layer. The CD in the Fe salt was much more enhanced compared with that in the Ga salt, the mechanism of which was not clarified. We do not have any reasonable estimate of the degree of CD in the alloy system. (ii) The degree of CD in the pure salts was temperature-dependent; the large broadening was observed at low temperatures. (iii) The expected total line width at around θ~30 degrees is comparable to (or larger than) the *rf* excitation pulse width. In such a case, the *rf* pulse might not cover the whole spectrum and it was difficult to detect the linewidth with high accuracy. From the present measurements, we only claim that the existence of CD was confirmed in the alloy system as in the pure Fe and Ga salts. The temperature dependence of the CD and the quantitative comparison with the pure salts will be addressed in a future investigation.

4. Conclusions

In this study, ^{77}Se NMR measurements of λ-(BETS)$_2$Fe$_{1-x}$Ga$_x$Cl$_4$ with 20% Ga doping (x = 0.2) were performed. From the analysis of the angular dependence of Se NMR spectra, relatively small π-d exchange interaction was obtained as −25 T, which is 20% smaller than that of Fe salt. The amount of reduction of J is consistent with the Ga content. It was confirmed microscopically that the itinerant conduction spins feel the effectively uniform exchange field from the dilute Fe sites. We also observed charge disproportionation in the two-dimensional BETS conducting sheet in the Ga-doped system.

Author Contributions: K.-i.H. and T.T. designed this study. The single crystal samples were prepared by B.Z.; H.A. and Y.N. evaluated the Ga content, x, by the heat capacity analysis. K.-i.H. performed NMR experiments and analyzed the data. K.-i.H. and T.T. wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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