

Selective observation of sublattice magnetization in the molecular π - d system λ -(BEDT-STF)₂FeCl₄ studied by ¹³C NMR

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We have performed ¹³C NMR measurements on λ -(BEDT-STF)₂FeCl₄ to reveal the mechanism of unconventional paramagneticlike behavior observed in λ -type molecular π - d systems. ¹³C NMR spectra and nuclear spin-lattice relaxation rate $1/T_1$ revealed that the π and $3d$ electron systems undergo an antiferromagnetic transition simultaneously at 16 K with the assistance of the π - d interaction. We found that the sublattice magnetizations of the π and $3d$ spins show different temperature dependence below T_N , which is derived from the magnetic coupling between the two sublattice systems with different magnetic natures. We discuss the relationship between the two different magnetization processes and the unconventional magnetic behavior in λ -type molecular π - d system.

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I. INTRODUCTION

Correlations between conducting electrons and localized spins cause various exotic physical properties. For example, large internal fields generated by localized spins lead to remarkable transport properties such as giant magnetoresistance and field-induced superconductivity (FISC) [1–3]. Magnetic interactions between localized spins mediated by conducting electrons stabilize novel spin structures, resulting in new functionalities. In organic compounds, molecular π - d systems have attracted considerable interest because the coexistence of itinerant π electrons with strong electron correlation and localized $3d$ electrons is realized in one material [4]. Due to the magnetic interaction between the π and $3d$ electrons, which is called π - d interaction, they exhibit unique conducting and magnetic properties, which are rarely observed in other systems. One of the most prominent phenomena is the FISC state, which is explained by the Jaccarino-Peter compensation mechanism [3,5,6]. Among the π - d systems, λ -type salts have been studied intensively due to the strong π - d interaction [7]. For example, λ -(BETS)₂FeCl₄ [BETS = bis(ethylenedithio)tetraselenafulvalene], which consists of organic donor molecules and magnetic anions with $S = \frac{5}{2}$ spins, shows a metal-insulator (MI) transition at 8.3 K, although λ -(BETS)₂GaCl₄, which is an isostructural compound with nonmagnetic anions, shows a superconducting transition at 5 K [8]. These facts indicate that the introduction of the localized $3d$ electrons changes the ground state of the π electron system drastically through the π - d interaction from the superconducting state to the insulating state. Even though many studies have been performed

for the insulating state, its mechanism is still under discussion [9–12]. This insulating state changes into the metallic state by applying magnetic fields of about 10 T and the FISC state is induced at around 30 T [3,13].

The magnetic nature in the insulating phase of λ -(BETS)₂FeCl₄ is also still under discussion. It has been believed that both the π and $3d$ electron systems undergo an antiferromagnetic transition simultaneously at 8.3 K, which triggers the MI transition [9,18,19]. However, heat-capacity measurements revealed a Schottky-type anomaly derived from the $3d$ spin degrees of freedom below T_{MI} [20]. From the result, the paramagnetic model, which suggests that the $3d$ electron system remains paramagnetic below T_{MI} and only the π electron system undergoes the antiferromagnetic transition accompanying a MI transition, was proposed [20,21]. The Schottky-type anomaly is inherent in the $3d$ spins passively polarized by the internal fields produced by the antiferromagnetically ordered π spins in the model. However, some contradictive results to the paramagnetic model have been reported and the necessity to modify the model is suggested [9,22]. Since the relationship between the origin of the unconventional magnetic state and that of the MI transition is expected, it is important to reveal the unconventional magnetic state realized in the insulating phase separately from the MI transition before studying the mechanism of the MI transition [23].

To study the unconventional magnetic state observed in λ -type salts, we focus on λ -(BEDT-STF)₂FeCl₄, where BEDT-STF is bis(ethylenedithio)diselenadithiafulvalene. From the previous works, it was confirmed that the substitution of S atoms for Se atoms corresponds to a negative chemical pressure effect, resulting in the increase of T_N from 8.3 K in λ -(BETS)₂FeCl₄ to 16 K in λ -(BEDT-STF)₂FeCl₄ [16,24]. In addition to the increase in the transition temperature, the negative chemical pressure changes the conducting properties of the π electron system. In contrast to λ -(BETS)₂FeCl₄, which

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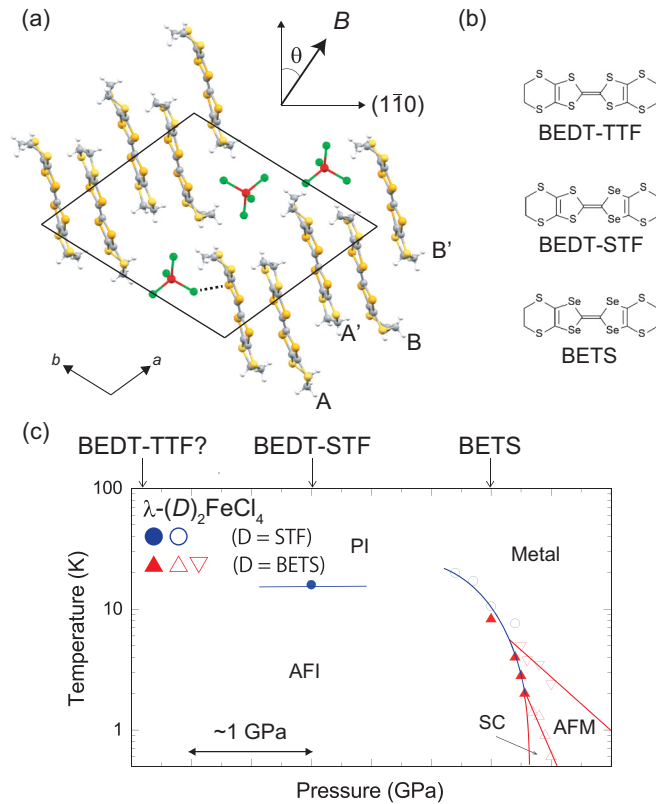


FIG. 1. (a) Crystal structure of λ -(D)₂FeCl₄ (D = donor molecules). A and B molecules are crystallographically equivalent with A' and B' molecules, respectively. The dashed line represents the Se/S-Cl contact, which contributes to the π - d interaction significantly. (b) Molecular structures of BEDT-TTF, BEDT-STF, and BETS. (c) p - T phase diagram of λ -(D)₂FeCl₄. PI = paramagnetic insulator phase, SC = superconducting phase, AFI = antiferromagnetic insulator phase, and AFM = antiferromagnetic metal phase. The data are cited from Refs. [14–17].

is metallic above T_N , λ -(BEDT-STF)₂FeCl₄ is insulating over the entire temperature range. Such a situation is desirable to study the unconventional magnetic state because the mechanism of the MI transition and that of the unconventional magnetic state can be discussed separately.

The crystal structure of λ -type salts and the molecular structures of BEDT-TTF, BEDT-STF, and BETS [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene] are shown in Fig. 1. In λ -type salts, organic donor molecules and inorganic anions form donor layers and anion layers, respectively, in the ac plane and these layers are stacked alternately. Since the transfer integral between A (A') and B (B') is much larger than others, the two donor molecules form a dimer in the donor layers. The pressure-temperature (p - T) phase diagram of λ -(D)₂FeCl₄ and the location of λ -(BEDT-STF)₂FeCl₄ and λ -(BETS)₂FeCl₄ are shown in Fig. 1(c) [14–17].

Previously, we performed ⁵⁷Fe Mössbauer measurements on λ -(BEDT-STF)₂FeCl₄ to investigate the magnetic properties of the $3d$ electron system and found that the temperature dependence of the magnetization of the $3d$ spins shows a unique multistep development below T_N [17]. At T_N of 16 K, one Mössbauer peak splits into sextet peaks due to the emergence of the hyperfine fields at the Fe sites. We found that

the increase in the hyperfine fields is small in the temperature range between 16 and 8 K. Below 8 K, the hyperfine fields show a steep increase. Since a Schottky-type anomaly is observed in the magnetic heat capacity of λ -(BEDT-STF)₂FeCl₄ below 8 K where the steep increase is observed, the multistep magnetization process is a key to reveal the mechanism of the paramagnetic-like behavior [25].

To reveal the unconventional magnetism induced by the π - d interaction, it is essential to investigate the magnetic properties of both the π and $3d$ electron systems separately. However, since the magnetic moment of π spins is small, the magnetic properties of the π spins are masked by those of the $3d$ spins with a large magnetic moment [9,16,18]. Such a situation makes it difficult to study the unconventional magnetic state from bulk magnetization measurements. Although ¹H NMR measurements have been performed on λ -(BEDT-STF)₂FeCl₄, the local fields at ¹H sites are predominantly determined by the dipole magnetic field arising from the $3d$ spins [16]. To observe the small π spin contribution selectively, we conducted ¹³C NMR measurements on λ -(BEDT-STF)₂FeCl₄. Since the enriched ¹³C sites located at the central C=C bond have strong coupling to the π spins of the highest occupied molecular orbital, we can investigate the magnetic properties of the π spins selectively. From the results of the selective investigation on the magnetic behavior of the π and $3d$ electron systems, we discuss the mechanism of unconventional magnetic behavior in λ -type salts and its relationship to the MI transition.

II. EXPERIMENT

Single crystals of λ -(BEDT-STF)₂FeCl₄ were prepared by the electrochemical oxidation of ¹³C-enriched BEDT-STF in the presence of TBAFeCl₄ (TBA = tetrabutylammonium) in chlorobenzene [26]. To eliminate the spectrum splitting derived from nuclear spin-spin coupling, namely, Pake doublet problem, the sulfur side of the carbon atom on the central C=C bond was enriched with the ¹³C isotope. We confirmed by x-ray diffraction measurements that the large surface of needlelike crystals of λ -(BEDT-STF)₂FeCl₄ corresponds to the (1 $\bar{1}$ 0) plane. In this study, $\theta = 0^\circ$ and the rotation direction are defined as shown in Fig. 1(a). The ¹³C NMR measurements were performed in the magnetic field of 6.1 T. The NMR spectra were obtained using a fast Fourier transformation of the echo signal with a $\pi/2$ - π pulse sequence, of which the first pulse length is 1.5 μ s. The NMR shifts were determined by fitting the spectra with a Lorentzian function. The nuclear spin-lattice relaxation rate $1/T_1$ measurements were performed using the conventional saturation-recovery method. The relaxation curves were fitted using a single exponential function expressed as $M(t) = M_0[1 - A \exp(-t/T_1)]$. In this study, we used two samples (samples No. 1 and No. 2). The experiments in Sec. III A were performed using sample No. 1 and those in Sec. III B were performed using samples No. 1 and No. 2.

III. RESULTS

A. Paramagnetic state

Figure 2(a) shows the angle dependence of the NMR spectra of λ -(BEDT-STF)₂FeCl₄ in the a^*b^* plane at 100 K.

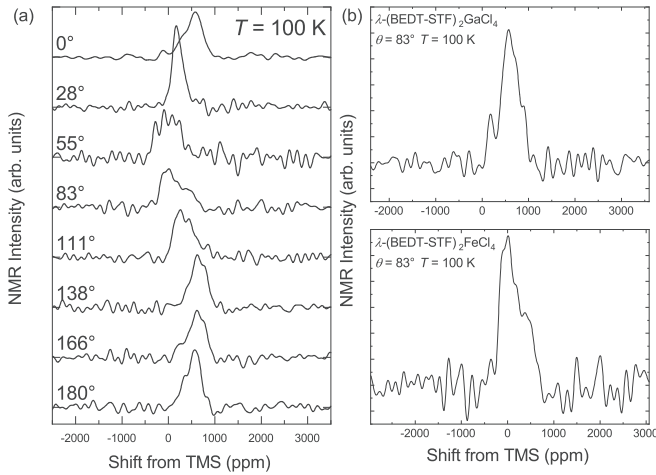


FIG. 2. (a) Angle dependence of the NMR spectra at 100 K in a^*b^* plane. A broad peak was observed in all directions because of the positional disorder effect. (b) NMR spectra of λ -(BEDT-STF) $_2$ GaCl $_4$ and λ -(BEDT-STF) $_2$ FeCl $_4$ at 100 K.

A broad peak was observed in all directions. We suggest that the broad peak is derived from a positional disorder of BEDT-STF molecules. In the case of λ -(BEDT-STF) $_2$ FeCl $_4$, there are two possible orientations of BEDT-STF molecule for each site, because BEDT-STF molecule is an unsymmetrical molecule due to the position of Se and S atoms. The x-ray diffraction measurements revealed that BEDT-STF molecules are randomly oriented in the crystal [26]. The NMR spectra of λ -(BEDT-STF) $_2$ FeCl $_4$ and λ -(BEDT-STF) $_2$ GaCl $_4$ measured at the same field direction of $\theta = 83^\circ$ are shown in Fig. 2(b). The linewidths of λ -(BEDT-STF) $_2$ FeCl $_4$ and λ -(BEDT-STF) $_2$ GaCl $_4$ are almost the same at $\theta = 83^\circ$ and are comparable with the splitting width of the two peaks in λ -(BETS) $_2$ GaCl $_4$ at $\theta = 83^\circ$ [27]. In λ -(BETS) $_2$ GaCl $_4$, which contains symmetrical BETS molecules, there are four donor molecules in a unit cell, and there are two crystallographically nonequivalent donor molecules which are indicated as A and B in Fig. 1(a). A' and B' are crystallographically equivalent with A and B , respectively, related by inversion symmetry. In addition, there are two crystallographically nonequivalent ^{13}C sites on the central C=C bond. Thus, there are four crystallographically nonequivalent ^{13}C sites in λ -(BETS) $_2$ GaCl $_4$. In the previous ^{13}C NMR study on λ -(BETS) $_2$ GaCl $_4$, two peaks of which the intensity ratio is 3:1 were observed when the magnetic field is applied in the a^*b^* plane, suggesting that three peaks are merged into one peak [27]. We can interpret that ^{13}C NMR spectra of λ -(BEDT-STF) $_2$ FeCl $_4$ have intensity distribution consisting of numerous ^{13}C sites with different surroundings, resulting in a unique broad peak.

Figure 3(a) shows the angle dependence of the NMR shift $[\delta(\theta)]$ of λ -(BEDT-STF) $_2$ FeCl $_4$ and λ -(BEDT-STF) $_2$ GaCl $_4$ at 100 K [28]. The phase of NMR shift of λ -(BEDT-STF) $_2$ FeCl $_4$ is shifted from that of λ -(BEDT-STF) $_2$ GaCl $_4$. The phase shift is caused by the $3d$ spin contribution to the Knight shift in λ -(BEDT-STF) $_2$ FeCl $_4$. Angle dependence of the NMR shift can be described as

$$\delta(\theta) = \sigma(\theta) + K(\theta) = \sigma(\theta) + \delta_\pi(\theta) + \delta_d(\theta), \quad (1)$$

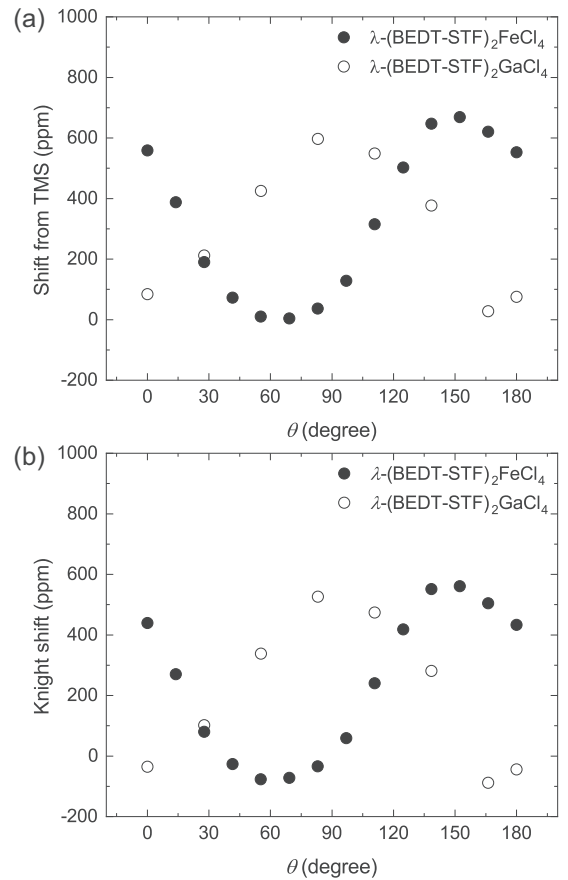


FIG. 3. Angle dependence of (a) the NMR shift and (b) the Knight shift at 100 K. The angle dependence of the Knight shift of λ -(BEDT-STF) $_2$ FeCl $_4$ is shifted from that of λ -(BEDT-STF) $_2$ GaCl $_4$ because of the contribution of $3d$ spins.

where σ and K are the chemical shift and the Knight shift, respectively. The Knight shift consists of δ_π and δ_d , where δ_π and δ_d are the Knight shift derived from the magnetization of the π spins and that of the $3d$ spins, respectively. The value of the chemical shift is inherent in the molecular structure and the valence of donor molecules. Thus, the chemical shift of λ -(BEDT-STF) $_2$ FeCl $_4$ and that of λ -(BEDT-STF) $_2$ GaCl $_4$ are the same. The angle dependence of the chemical shift is estimated assuming that the chemical shift tensor of BEDT-STF $^{0.5+}$ is the same as that of BEDT-TTF $^{0.5+}$ [29]. We assumed the four BEDT-STF molecules in a unit cell have the same angle dependence of the chemical shift in the a^*b^* plane because the four BEDT-STF molecules in a unit cell are almost parallel to each other. By subtracting the contribution of the chemical shift, the angle dependence of the Knight shift, which is shown in Fig. 3(b), was obtained.

In the case of λ -(BEDT-STF) $_2$ GaCl $_4$, only the π spins contribute to the Knight shift, which is described as

$$K = \delta_\pi(\theta) = A_\pi(\theta)\chi_\pi(T), \quad (2)$$

where $A_\pi(\theta)$ is the hyperfine coupling constant for the π electron. $\chi_\pi(T)$ is the magnetic susceptibility of λ -(BEDT-STF) $_2$ GaCl $_4$, which was estimated as $\chi_\pi = 5.32 \times 10^{-4}$ emu/mol at 100 K [24].

In the case of λ -(BEDT-STF)₂FeCl₄, the 3*d* spins of Fe ions generate the dipolar field at the ¹³C sites. The contribution of the dipolar field for the Knight shift is described as

$$\delta_d(\theta) = A_{\text{dip}}(\theta)\chi_d(T), \quad (3)$$

where $A_{\text{dip}}(\theta)$ and $\chi_d(T)$ are a dipolar coupling constant including the demagnetization effect and the magnetic susceptibility of the 3*d* spins, respectively. χ_d was estimated as 3.8×10^{-2} emu/mol at 100 K [16]. The angle dependence of the dipolar field for λ -(BETS)₂FeCl₄ is given in Ref. [30]. According to the previous work, the amplitude of $\delta_d(\theta)$ is approximately two times larger than that of $\delta_\pi(\theta)$ in λ -(BEDT-STF)₂GaCl₄ at 100 K and the phase of the angle dependence of $\delta_d(\theta)$ is shifted from that of $\delta_\pi(\theta)$. Thus, the dipolar field makes a significant contribution for the Knight shift in λ -(BEDT-STF)₂FeCl₄.

In addition, the 3*d* spins generate the exchange field for the π spins, which modulates $\delta_\pi(\theta)$ as

$$\delta_\pi(\theta) = A_\pi(\theta)\chi_\pi(T)[1 + J_{\pi d}\chi_d(T)]. \quad (4)$$

However, the modulation of the $\delta_\pi(\theta)$ is expected to be small. From the observation of the maximum T_c in FISC phase at 33 T, $J_{\pi d}$ of λ -(BETS)₂FeCl₄ is estimated as $J_{\pi d} \simeq -6.6$ T/ μ_B . If the $J_{\pi d}$ of λ -(BEDT-STF)₂FeCl₄ is as large as that of λ -(BETS)₂FeCl₄, $J_{\pi d}\chi_d$ is estimated as $J_{\pi d}\chi_d \simeq -0.45$. Note that $J_{\pi d}$ of λ -(BEDT-STF)₂FeCl₄ is expected to be smaller than that of λ -(BETS)₂FeCl₄ because of the substitution effect of S atom for Se atom. We will discuss the details in the discussion part. These results suggest that the different angle dependence of the Knight shift between λ -(BEDT-STF)₂FeCl₄ and λ -(BEDT-STF)₂GaCl₄ is mainly attributable to the dipolar field.

Figure 4(a) shows the temperature dependence of the NMR spectra at $\theta = 83^\circ$. The temperature dependence of the NMR shift and the linewidth are summarized in Figs. 4(b) and 4(c). The magnetic susceptibility of λ -(BEDT-STF)₂FeCl₄ (χ) is expressed as $\chi = \chi_\pi + \chi_d$. Thus, the Knight shift is described as

$$K = A_\pi\chi_\pi(1 - J_{\pi d}\chi_\pi) - A_{\text{dip}}\chi_\pi + (A_\pi\chi_\pi J_{\pi d} + A_{\text{dip}})\chi. \quad (5)$$

The K - χ plot between 100 and 200 K is shown in Fig. 4(d). The temperature dependence of the magnetic susceptibility of λ -(BEDT-STF)₂FeCl₄ is cited from Ref. [16]. Since the temperature dependence of χ_π above 100 K is small, the first and second terms of Eq. (5) are regarded as constant [24]. Therefore, the inclination of the K - χ plot is mainly determined by the third term, namely, $A_\pi\chi_\pi J_{\pi d} + A_{\text{dip}}$. The large negative inclination of the K - χ plot also supports the dominant contribution of $A_{\text{dip}}(\theta)$ for the Knight shift.

B. Antiferromagnetic state

The temperature dependence of the NMR spectra and $1/T_1$ below 100 K were measured under the magnetic field applied at $\theta = 38^\circ$, where the NMR spectrum is the sharpest in order to obtain the highest intensity and to trace clearly the peak or spectrum splitting. Figure 5(a) shows the temperature dependence of the NMR spectra below 100 K. The NMR spectra below 20 K were obtained by the recombination of

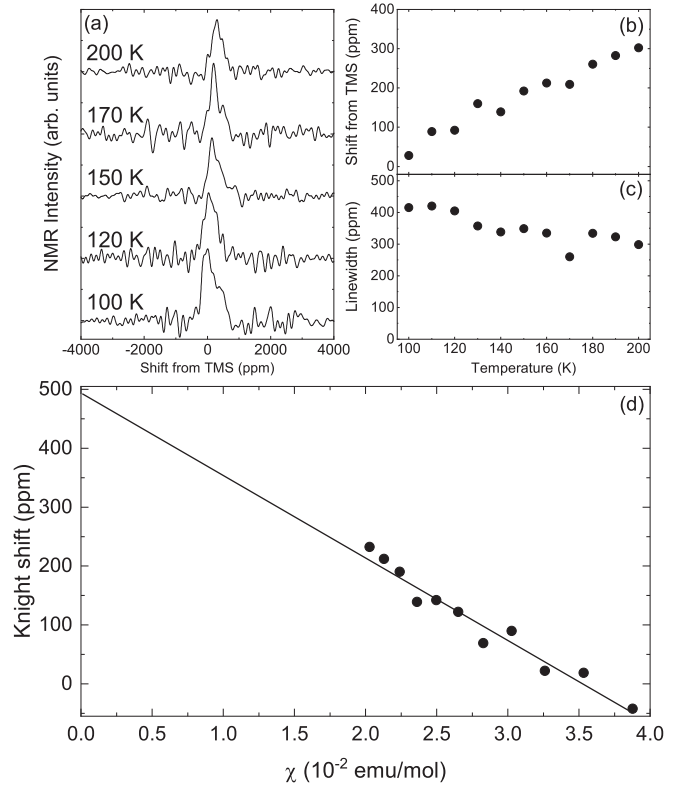


FIG. 4. (a) Temperature dependence of the NMR spectra of λ -(BEDT-STF)₂FeCl₄ at $\theta = 83^\circ$. Temperature dependence of (b) the NMR shift and (c) the linewidth. (d) K - χ plot between 100 and 200 K. The negative inclination originates from the contribution of the 3*d* spins. The magnetic susceptibility data are cited from Ref. [16].

several FT spectra. Figures 5(b) and 5(c) show the temperature dependence of the NMR shift and the linewidth above T_N , respectively. With decreasing temperatures, the NMR peak becomes broad and shifts to the lower frequency. Such relatively large temperature dependence of the NMR shift and the line broadening are ascribed to the development of the magnetization of the 3*d* spins. Below 16 K, the one peak splits into two peaks, indicating the development of the internal fields at the ¹³C sites due to an antiferromagnetic ordering. We emphasize that our results prove the development of the local fields inherent in the π spins since ¹³C NMR detects the magnetic properties of the π electrons sensitively. The two discrete NMR peaks below 16 K suggest that the spin structure of the π electron system is a commensurate antiferromagnetic structure. The splitting width of the NMR spectrum saturates at $\Delta F \simeq 0.3$ MHz below 12 K. The splitting width of 0.3 MHz corresponds to approximately 30 mT of the hyperfine field (B_{hf}) at the ¹³C sites. Here, B_{hf} is defined using the spectrum splitting width $\Delta F(T)$ as $\Delta F(T) = \gamma_N B_{\text{hf}}(T)$, where $\gamma_N = 10.705$ MHz/T is a gyromagnetic ratio of ¹³C. A commensurate antiferromagnetic state of the π electron system has been reported in λ -(BEDT-TTF)₂GaCl₄, which is located on the most negative pressure side in the p - T phase diagram of λ -(D)₂GaCl₄ salts [31]. The splitting width of λ -(BEDT-STF)₂FeCl₄ is in good agreement with that of λ -(BEDT-TTF)₂GaCl₄, of which the splitting width is estimated

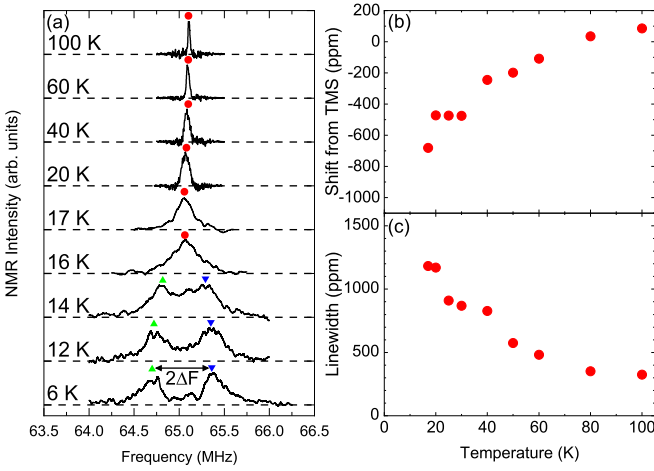


FIG. 5. (a) Temperature dependence of the NMR spectra of sample No. 1 at $\theta = 38^\circ$. A broad peak splits into two discrete peaks at 16 K, indicating that the development of the local fields at ^{13}C sites due to an antiferromagnetic ordering. Temperature dependence of (b) the NMR shift and (c) the linewidth.

as about 0.3 MHz. These results suggest that the ground state of the π electron system is likely to be a Mott insulating state as with λ -(BEDT-TTF) $_2$ GaCl $_4$, and there is also a commensurate antiferromagnetic phase in the negative pressure side in the p - T phase diagram of λ -(D) $_2$ FeCl $_4$ salts [31]. Although the molecular structures of BEDT-STF, BEDT-TTF, and BETS are different, the molecular packing of donor layers is common to the all λ -type salts. Thus, it is plausible that once the π electron system undergoes a magnetic transition, the magnetic ground states of the π electron system are the same. We suppose that the introduction of the π - d interaction works to stabilize the antiferromagnetic ordering of the π electron system for λ -(BEDT-STF) $_2$ FeCl $_4$ and that the magnetic ground states of the π electron system stabilized by the π - d interaction in magnetic anion salts are intrinsically the same with those of nonmagnetic anion salts. Therefore, the results of the ^{13}C NMR measurements on the λ -type salts with magnetic and nonmagnetic anions are similar to each other because ^{13}C NMR measurements detect the magnetic properties of the π electron system selectively. However, unlike the two discrete peaks in λ -(BEDT-STF) $_2$ FeCl $_4$, four discrete NMR peaks were observed in λ -(BEDT-TTF) $_2$ GaCl $_4$. This discrepancy suggests that although the introduction of the π - d interaction stabilizes the commensurate antiferromagnetic ordered state, the magnetic ordered structure of the π electron system is modified from the intrinsic magnetic structure observed in λ -(D) $_2$ GaCl $_4$ salts.

Figure 6 shows the temperature dependence of $1/T_1$ below 150 K. These measurements were performed for two different single crystals, which are indicated as sample No. 1 (closed symbol) and sample No. 2 (open symbol), respectively. The symbols in Fig. 6 correspond to those indicated at the top of peaks in Fig. 5(a). With decreasing temperatures, $1/T_1$ increases gradually. Below 30 K, $1/T_1$ shows a sudden increase, which is ascribed to the critical slowing down, and a sharp peak was observed at 16 K, where the finite hyperfine fields at Fe sites were detected by ^{57}Fe Mössbauer

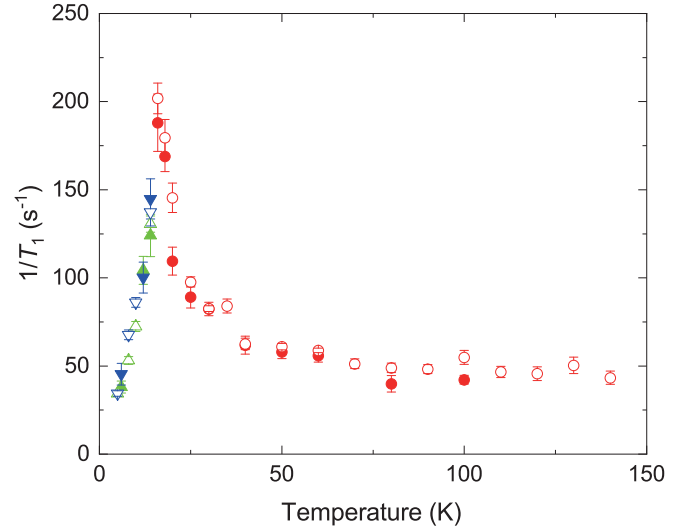


FIG. 6. (a) Temperature dependence of $1/T_1$. Closed symbols and open symbols represent the results of samples No. 1 and No. 2, respectively. Two triangle symbols correspond to the peaks at the low-frequency site and the high-frequency site below T_N as indicated in Fig. 5. A sharp peak observed at 16 K is ascribed to the antiferromagnetic transition.

measurements. These results demonstrate that the π electron system undergoes an antiferromagnetic transition at 16 K simultaneously with the $3d$ electron system. Note that the ^{13}C NMR and ^{57}Fe Mössbauer measurements were performed under magnetic fields of 6.1 and 0 T, respectively, but both measurements detected the magnetic transition temperature at 16 K. In addition, the ^1H NMR measurements performed around 3 T also revealed that the antiferromagnetic transition occurs at 16 K [17]. Thus, the magnetic field effect on the T_N is negligibly small in the low magnetic field region. Such weak field dependence of the T_N in low magnetic field was also confirmed in λ -(BETS) $_2$ FeCl $_4$ [9].

IV. DISCUSSION

In λ -(BEDT-STF) $_2$ FeCl $_4$, there are three types of magnetic interactions, namely, the magnetic interactions between π electrons ($J_{\pi\pi}$), $3d$ electrons (J_{dd}), and π and $3d$ electrons ($J_{\pi d}$). $J_{\pi d}$ connects the two different magnetic systems, namely, the π electron system and the $3d$ electron system. If we assume that $|J_{\pi\pi}/k_B|$ in λ -(BEDT-STF) $_2$ FeCl $_4$ is almost the same as that in λ -(BEDT-STF) $_2$ GaCl $_4$, $|J_{\pi\pi}/k_B|$ is estimated to be the order of 10^2 K [24]. However, the π electron system of λ -(BEDT-STF) $_2$ GaCl $_4$ shows no magnetic phase transition down to 2 K confirmed by ^{13}C NMR and magnetic susceptibility measurements [24,28]. As a possible origin of the suppression of a long-range magnetic ordering, the randomness due to the positional disorder of unsymmetrical BEDT-STF molecules and the frustration effect coupled with the low dimensionality were suggested [24]. J_{dd} should be almost the same between λ -(BEDT-STF) $_2$ FeCl $_4$ and λ -(BETS) $_2$ FeCl $_4$ because the nearest Fe-Fe distance of λ -(BEDT-STF) $_2$ FeCl $_4$ is comparable with that of λ -(BETS) $_2$ FeCl $_4$. Referring the theoretical calculation for λ -(BETS) $_2$ FeCl $_4$ by Mori *et al.*, $|J_{dd}/k_B|$ is

estimated to be 0.64 K, which is weak to form an antiferromagnetic order of the $3d$ electron system at 16 K [32]. These facts suggest that the antiferromagnetic ordering in λ -(BEDT-STF) $_2$ FeCl $_4$ at 16 K is realized due to the cooperation between the π and $3d$ electron systems. Both the π and $3d$ electron systems cannot show any long-range magnetic orderings individually at 16 K, but the π - d interaction affords a three-dimensional interaction network by coupling the π and $3d$ electron systems and stabilizes the antiferromagnetically ordered state of both the π and $3d$ spins. Actually, the stabilization of the antiferromagnetic order by the π - d interaction has been theoretically suggested [33,34].

From the previous works on λ -(BETS) $_2$ FeCl $_4$, it is suggested that the atomic contact between Se and Cl indicated in Fig. 1(a) by a dashed line makes a significant contribution to the π - d interaction [22,32]. Because the two Se atoms are replaced with S atoms, of which the atomic radius is smaller than Se atom, the π - d interaction is expected to become smaller in λ -(BEDT-STF) $_2$ FeCl $_4$. However, T_N of λ -(BEDT-STF) $_2$ FeCl $_4$ is larger than that of λ -(BETS) $_2$ FeCl $_4$. We consider that such discrepancy is derived from the itineracy of the π electron system. In λ -(BEDT-STF) $_2$ FeCl $_4$, the π electron system is insulating over the entire temperature range. On the other hand, the π electron system in λ -(BETS) $_2$ FeCl $_4$ is metallic above T_{MI} of 8.3 K. At high-temperature region, such itinerant character prevents the development of the magnetization of the π electron system, resulting in the drastic suppression of T_N .

Next, we would like to focus on the temperature dependence of the sublattice magnetization for the π and $3d$ electron systems. Because the hyperfine fields estimated by ^{13}C NMR measurements are proportional to the magnetic moment localized at the ^{13}C sites, the temperature dependence of the hyperfine fields corresponds to that of the magnetization of the π electron system. Similarly, the temperature dependence of the hyperfine fields at ^{57}Fe sites estimated by ^{57}Fe Mössbauer measurements corresponds to that of the magnetization of the $3d$ electron system [17]. Figure 7 shows the temperature dependence of the hyperfine fields at the ^{13}C and ^{57}Fe sites. As discussed in Ref. [17], the hyperfine fields at the ^{57}Fe sites show a steplike development below T_N . On the other hand, the hyperfine fields at the ^{13}C sites show a sudden increase at 16 K, and saturate below 12 K. Since there is no significant anomaly in the temperature dependence of the hyperfine fields at ^{13}C sites, the steplike increase of the magnetization of the $3d$ electrons is independent of the magnetization process of the π electron system, and the origin of the steplike increase is ascribed to the $3d$ electron system.

Now, we discuss a possible interpretation of the peculiar two different magnetization processes and the relationship between the magnetization process and the paramagneticlike behavior. We consider the two different sublattice magnetizations are caused by the coupling between the two different magnetic systems, namely, the π electron system with large $J_{\pi\pi}$ and the $3d$ electron system with small J_{dd} . At T_N of 16 K, both the π and $3d$ electron systems undergo an antiferromagnetic transition cooperatively with the assistance of $J_{\pi d}$. In the case of the π electron system, $|J_{\pi\pi}/k_B|$ is large compared with T_N . Therefore, the magnetic fluctuation is suddenly suppressed below T_N , resulting in the sudden sat-

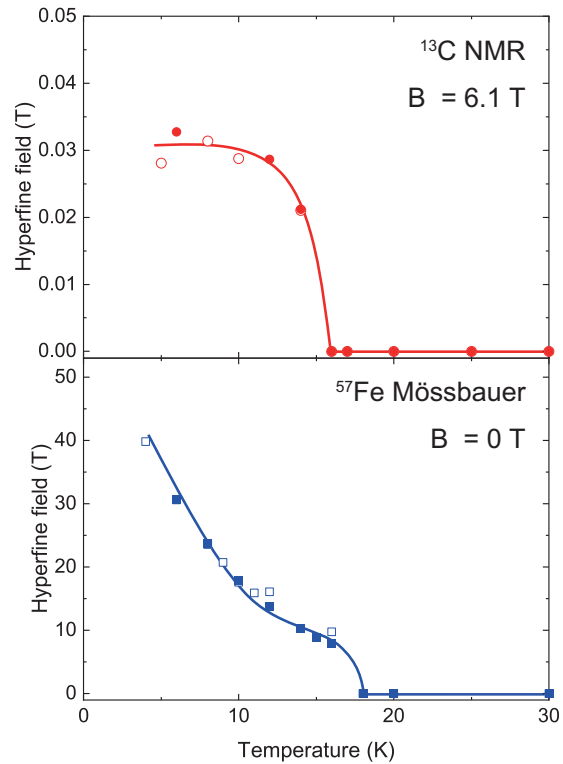


FIG. 7. Temperature dependence of the hyperfine fields at ^{13}C sites and ^{57}Fe sites estimated by ^{13}C NMR and ^{57}Fe Mössbauer measurements. The results of closed and open symbols in ^{13}C NMR are obtained using samples No. 1 and No. 2, respectively. The results of ^{57}Fe Mössbauer measurements are cited from Ref. [17]. Although the hyperfine fields at the ^{57}Fe sites show a steplike development below T_N , those at the ^{13}C sites suddenly saturate just below T_N . These results suggest that the π and $3d$ electron systems show different sublattice magnetizations as a function of temperature.

uration of the magnetization. On the other hand, the magnetic fluctuation of the $3d$ spins remains because of the small J_{dd} and the magnetization of the $3d$ electron system increases gradually below T_N . As a result, the π and $3d$ electron systems show the different magnetization process below T_N . This gradually increasing process of the magnetization of the $3d$ electron system was observed as if paramagnetic $3d$ spins are passively polarized under an internal magnetic field in the heat capacity and magnetic susceptibility [34]. Such magnetic coupling between the two sublattice systems with different magnetic natures through the π - d interaction causes the unique magnetic behaviors in molecular π - d systems. Our experimental results are consistent with the theoretical study using the simplest effective models constructed to explain the stabilization mechanism of the antiferromagnetic ordered state in λ -(BETS) $_2$ FeCl $_4$ [33]. The theoretical study suggests that the magnetization of the $3d$ electron system shows a small increase at high temperatures near T_N , but when the temperature approaches to the mean-field transition temperature of the $3d$ electron system, the magnetization of the $3d$ electron system shows a steep increase and saturates. Although the $3d$ electron system shows such an unusual steplike development of the magnetization below T_N , the magnetization of the π electron system shows a simple magnetization process

like usual Heisenberg antiferromagnets. As confirmed from Fig. 7, the hyperfine fields of the $3d$ electron system show the steplike development below T_N , and those of the π electron system show the conventional magnetization process as the model predicted. If we adopt $|J_{dd}/k_B|$ of 0.64 K, the mean-field transition temperature of the $3d$ electron system is estimated to be 3.7 K, which roughly corresponds to the temperature where the hyperfine fields of the $3d$ electron system show a steep increase and saturate [32]. We emphasize that the different sublattice magnetization process and the steplike development in λ -(BEDT-STF) $_2$ FeCl $_4$ were observed due to the fully insulating nature of the π electron system. Since the π electron system is insulating over the entire temperature range, the antiferromagnetic ordered state can survive at higher temperatures, and the weakly polarized magnetization of the $3d$ spins was clearly observed. On the other hand, the magnetic order is suppressed in λ -(BETS) $_2$ FeCl $_4$ due to the itinerant nature of the π electrons. Thus, the weakly polarized region of the $3d$ electron system was not observed.

In addition to the ^{57}Fe Mössbauer measurements, an anomalous behavior around 8 K was reported in some experiments, and the possible contribution of J_{dd} has been discussed. For example, the anisotropy of magnetic susceptibility and the enhancement of the ^1H NMR shift were observed below 8 K [16]. In the previous study by ^{57}Fe Mössbauer measurements, we also discussed the contribution of J_{dd} to the steep increase of the magnetization of the $3d$ electron system below 8 K [17]. From the present ^{13}C NMR study, we revealed that the magnetization of the π electron system is almost saturated at 12 K as confirmed in Fig. 7. This fact supports that J_{dd} can be responsible for the steep increase in the $3d$ electron system. Since $|J_{dd}/k_B|$ is relatively small compared with T_N , the magnetization of the $3d$ spins is thermally fluctuated just below T_N . However, at low temperatures comparable with the energy scale of J_{dd} , the J_{dd} can contribute to the enhancement of the magnetization of the $3d$ spins, which can be observed as the emergence of the anisotropy in the magnetic susceptibility below 8 K. This scenario is consistent with the experimental facts that λ -(BEDT-STF) $_2$ FeCl $_4$ and λ -(BETS) $_2$ FeCl $_4$ show a steep increase of the hyperfine fields at the Fe sites in the same temperature range even though T_N is different [17,35]. The substitution of Se atoms for S atoms modulates the itinerancy and magnetic coupling of the π electron system, leading to the decrease in T_N . However, J_{dd} remains almost the same in both salts and contributes to the magnetization process in the same manner. For further discussion on the relationship between the steplike magnetization process and J_{dd} in more detail, the study on the magnetic nature of the mixed anion systems of λ -(BEDT-STF) $_2$ Fe $_x$ Ga $_{1-x}$ Cl $_4$ is now in progress.

Finally, we would like to mention the relationship between the magnetic ordering and the insulating mechanism in λ -(BETS) $_2$ FeCl $_4$. Because the steep increase in the magnetization of the $3d$ electron system and a broad Schottky-type anomaly were observed in both salts, it is plausible to consider that the magnetic nature of both salts in the insulating state is essentially the same [17,25]. As confirmed in this study,

the π - d interaction works to stabilize the antiferromagnetic ordering for both the π and $3d$ electron systems. The same mechanism should work for λ -(BETS) $_2$ FeCl $_4$. We speculate that the stabilization of the long-range magnetic ordering by the π - d interaction can contribute to the MI transition. In the case of λ -(BETS) $_2$ FeCl $_4$, the metallic state is expected to be intrinsically stable because the metallic state is stable in λ -(BETS) $_2$ GaCl $_4$ down to $T_c = 5$ K. On the other hand, the introduction of the $3d$ spins and the strong π - d interaction works to stabilize the antiferromagnetic order. Actually, the insulating state is changed into the metallic state by suppressing the antiferromagnetic order in λ -(BETS) $_2$ FeCl $_4$ by magnetic fields, indicating that the stability of the insulating state is linked to that of the antiferromagnetic ordering. Thus, the π - d interaction causes a competition between a metallic and an antiferromagnetic insulating states in λ -(BETS) $_2$ FeCl $_4$. With decreasing temperatures, the stability of the antiferromagnetic insulating state overcomes that of the metallic state, resulting in the MI transition. Note that in the case of κ -(BETS) $_2$ FeX $_4$ ($X = \text{Cl}, \text{Br}$), which are other π - d interacting systems with smaller π - d interaction, only the $3d$ electron system undergoes an antiferromagnetic transition whereas the π electron system remains metallic below T_N and undergoes a superconducting transition [7]. We suppose that the emergence of the MI transition may depend on the delicate balance among the itinerancy and the magnetic coupling.

V. SUMMARY

In summary, we have performed ^{13}C NMR measurements on λ -(BEDT-STF) $_2$ FeCl $_4$. From the NMR spectrum splitting and the peak in $1/T_1$, we confirmed that the π and $3d$ electron systems undergo an antiferromagnetic transition simultaneously at 16 K. We found that the π and $3d$ electron systems show different sublattice magnetization process below T_N as a function of temperature. The magnetization of the π electron system saturates just below T_N , although that of the $3d$ electron system shows a steplike development. We interpret that the different sublattice magnetization is inherent in the coupling effect of the π electron system with large $J_{\pi\pi}$ and the $3d$ electron system with small J_{dd} , which is the unique situation in the molecular π - d system. We suppose that the gradually increasing process of the magnetization of the $3d$ electron system is related to the paramagneticlike behavior and that the stabilization of the long-range magnetic ordering by the π - d interaction is related to the insulating mechanism.

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