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Doctoral Thesis

Electronic Properties of Organic Conductors

λ -(BEDT-STF)₂MCl₄ ($M = \text{Ga}, \text{Fe}$)

(有機伝導体 λ -(BEDT-STF)₂MCl₄

($M = \text{Ga}, \text{Fe}$) の電子物性)

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Chapter 1

Introduction

1.1 Two-dimensional organic conductors

Since the discovery of the first organic superconductor $(\text{TMTSF})_2\text{PF}_6$ (TMTSF = tetramethyltetraselenafulvalene) in 1980[1], many progress has been achieved in the physical and chemical fields of molecular superconductors[2]. The BEDT-TTF (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, hereafter “ET”) salt was synthesized in 1982[3] as rather two-dimensional material than TMTSF salts. The ET salts with polymeric anions such as $\kappa\text{-(ET)}_2X$ ($X = \text{Cu(NCS)}_2$ [4], $\text{Cu[N(CN)}_2\text{]Br}$ [5], etc.) show high superconducting transition temperature exceeding $T_c \approx 10$ K and many researches have been conducted to elucidate the mechanism of this superconducting phase. For another two-dimensional organic superconductors, $\lambda\text{-(BEDT-TSF)}_2M\text{Cl}_4$ and $\kappa\text{-(BEDT-TSF)}_2M\text{Cl}_4$ ($M = \text{Ga, Fe}$, BEDT-TSF = bis(ethylenedithio)tetraselenafulvalene, hereafter “BETS”)[6] show various interesting features. As mentioned later, $\lambda\text{-(BETS)}_2\text{GaCl}_4$ shows the SC phase below 5.5 K and λ - and $\kappa\text{-(BETS)}_2\text{FeCl}_4$, with the magnetic interaction between π and d electrons, shows the magnetic

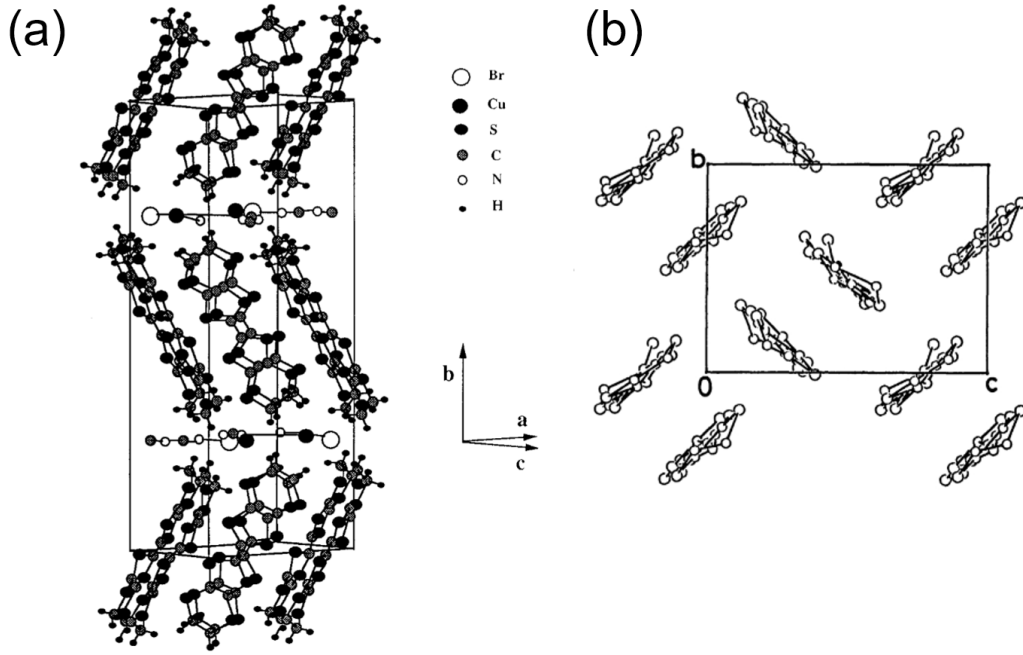


Figure 1.1: (a) Crystal structure of κ -(ET)₂Cu[N(CN)₂]Br. The ET molecules are shown as dimers. The anion molecule is in the plane perpendicular to the b -axis.[7] (b) Crystal structure viewed along the molecular long axis. Only ET molecules are depicted.[4]

field induced SC phase.

1.2 Organic superconductors with non-magnetic anion

1.2.1 κ -(ET)₂X

Quasi-two-dimensional organic superconductors κ -(ET)₂Cu(NCS)₂ and κ -(ET)₂Cu[N(CN)₂]Br are widely investigated because of its high temperature superconductivity exceeding 10 K. The typical crystal structure and band structure of κ -type salts are shown in Fig. 1.1[4, 7] and Fig. 1.2[7, 8], respectively. The highest occupied molecular orbital (HOMO) band in Fig. 1.2(a) is half-filled because of the dimerization of the ET molecules. The κ -type salt has a quasi-two dimensional Fermi surface as shown in Fig. 1.2(b). The phase diagram of

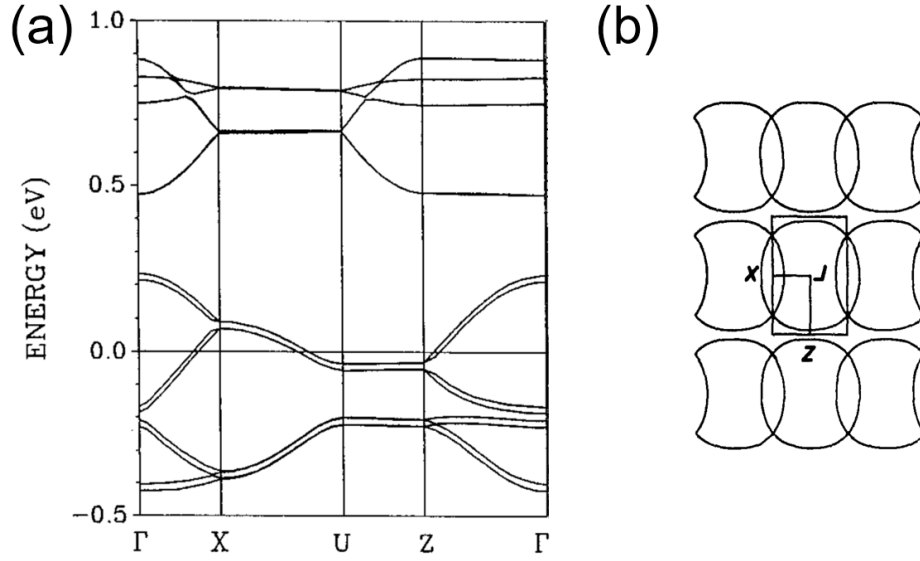


Figure 1.2: (a) Band structure of κ -(ET) $_2$ Cu[N(CN) $_2$]Br.[7] (b) Fermi surface.[8]

κ -type salts are summarized in Fig. 1.3[9].

Total behaviors of these salts are well explained in the phase diagram with U_{eff}/W , where U_{eff} is the effective on-site Coulomb repulsion energy on the ET dimers and W is the band width, which corresponds to the hydrostatic pressure. In this phase diagram, Cu(NCS) $_2$ and Cu[N(CN) $_2$]Br salts are located at the high pressure region and show the SC phase at 10.4 and 11.6 K, respectively[4, 5]. The SC transition temperature T_c increases gradually from the Cu(NCS) $_2$ salt to the Cu[N(CN) $_2$]Br salt, with increasing U_{eff}/W . On the other hand, the Cu[N(CN) $_2$]Cl salt located at low pressure region and it shows the antiferromagnetic (AF) transition at 30 K[8]. The Cu[N(CN) $_2$]Cl salt also shows the SC transition with $T_c \approx 13$ K at 30 MPa of hydrostatic pressure. From the various studies for these salts, it is known that the SC phase appears adjacently to the AF phase like a typical cuprates, which known as high T_c superconductors. From above relation between the SC and AF phases, it has

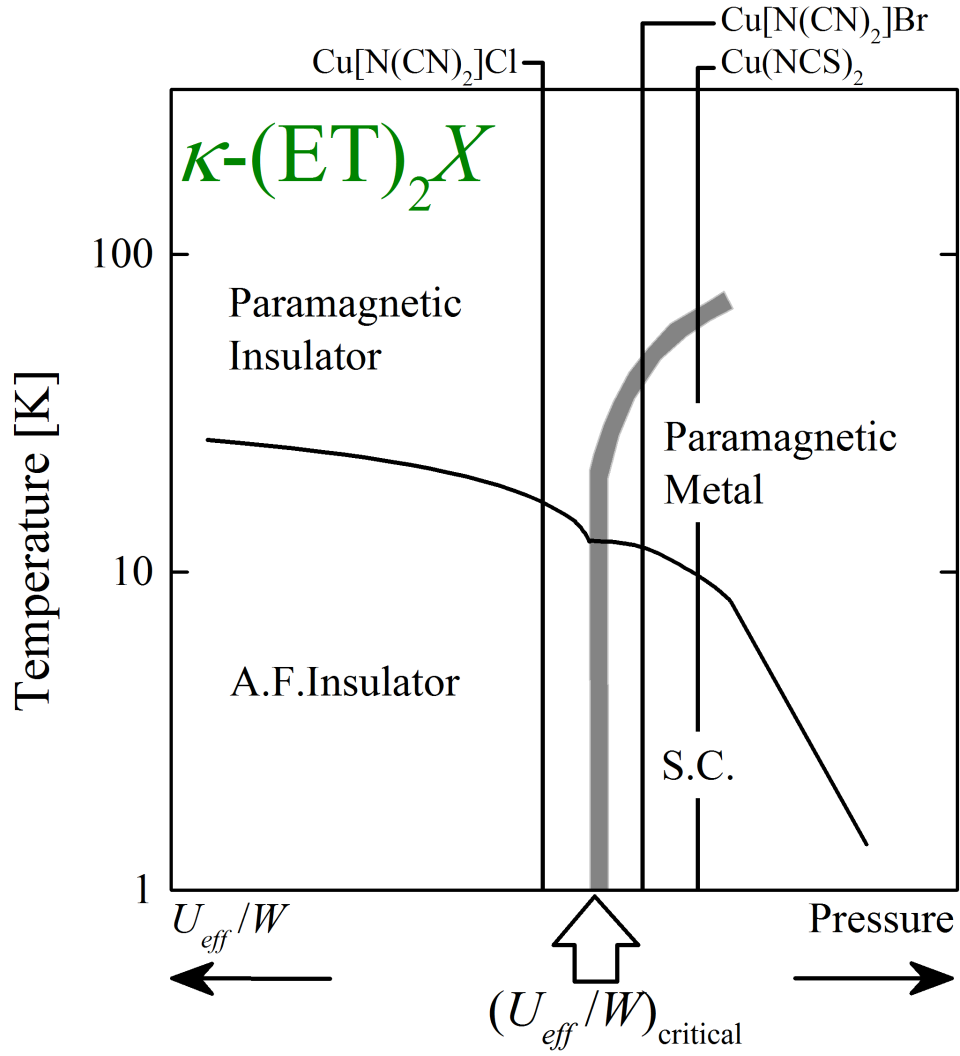


Figure 1.3: Phase diagram of $\kappa\text{-(ET)}_2X$. A.F. and S.C. denote antiferromagnetic and superconducting phases.[9]

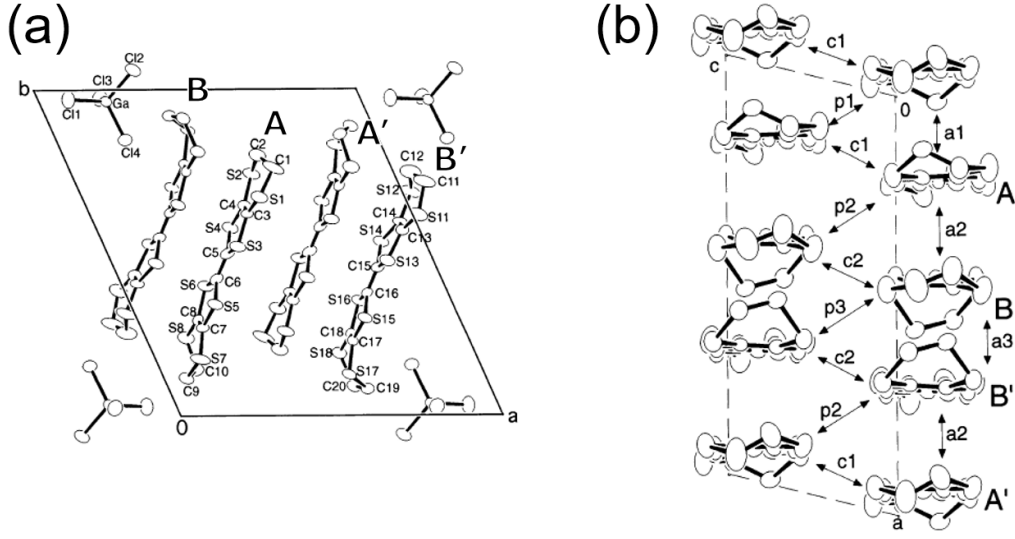


Figure 1.4: (a) Crystal structure of λ -(BETS) $_2$ GaCl $_4$. (b) Crystal structure viewed along the molecular long axis. Only ET molecules are depicted.[10]

been believed that the attractive interaction of the Cooper pair mediated by the AF spin fluctuation.

1.2.2 λ -(BETS) $_2$ GaCl $_4$

The λ -(BETS) $_2$ GaCl $_4$ is also known as a quasi-two-dimensional organic superconductor. The typical crystal structure of λ -(BETS) $_2$ GaCl $_4$ are shown in Fig. 1.4[10]. The overlap integrals between each molecule in Fig. 1.4(b) are estimated as $a1 = 9.3$, $a2 = -25.8$, $a3 = 8.1$, $c1 = -4.6$, $c2 = -2.8$, $p1 = 12.0$, $p2 = -6.1$, and $p3 = 1.8$ ($\times 10^{-3}$) and the band structure calculated from them is shown in Fig. 1.5[10]. According to the overlap integrals, there are dimers of (A-B) and (A'-B'). Because of this dimerization, the quarter-filled band structure is split into the half-filled upper bands and the full-filled lower bands. It has a cylindrical Fermi surface, which reflects the two-dimensionality, and its geometry is similar to that of κ -(ET) $_2$ X.

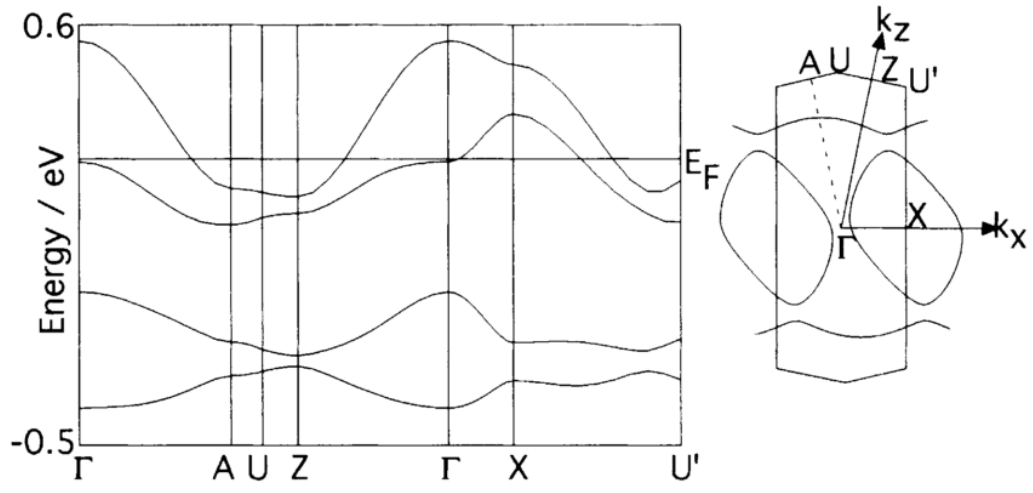


Figure 1.5: Band structure and Fermi surface of λ -(BETS) $_2$ GaCl $_4$. [10]

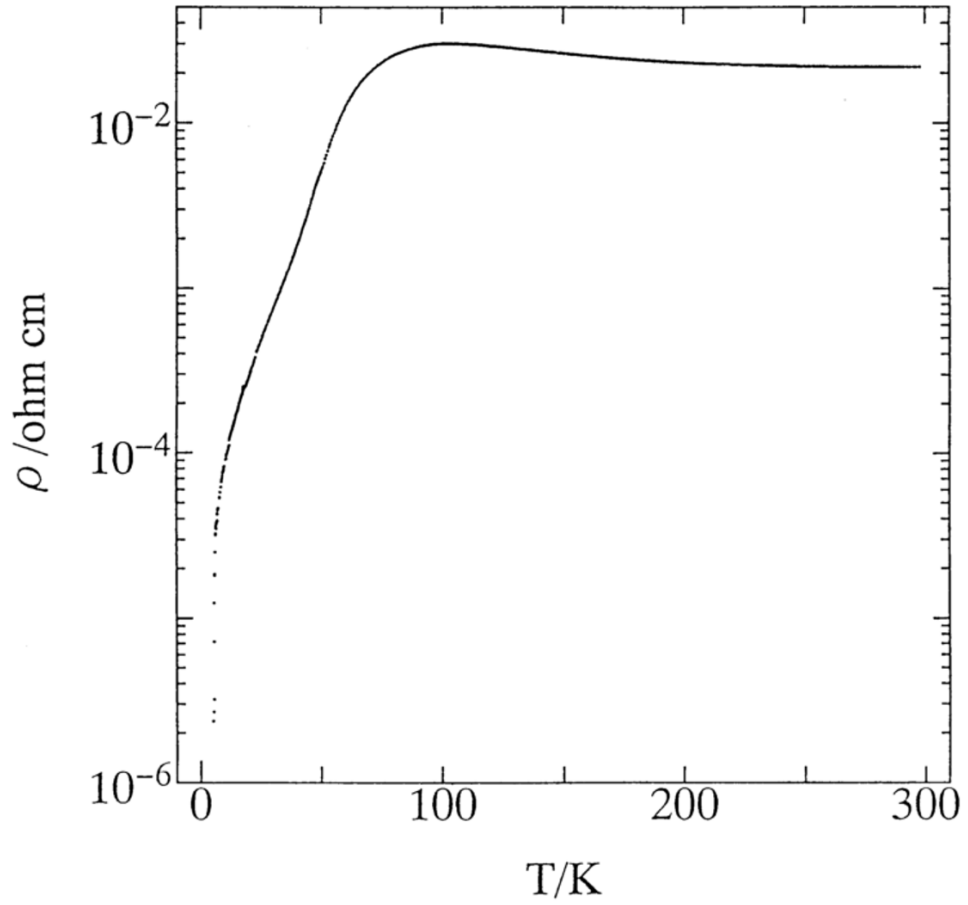


Figure 1.6: Temperature dependence of the resistivity of λ -(BETS) $_2$ GaCl $_4$. [11]

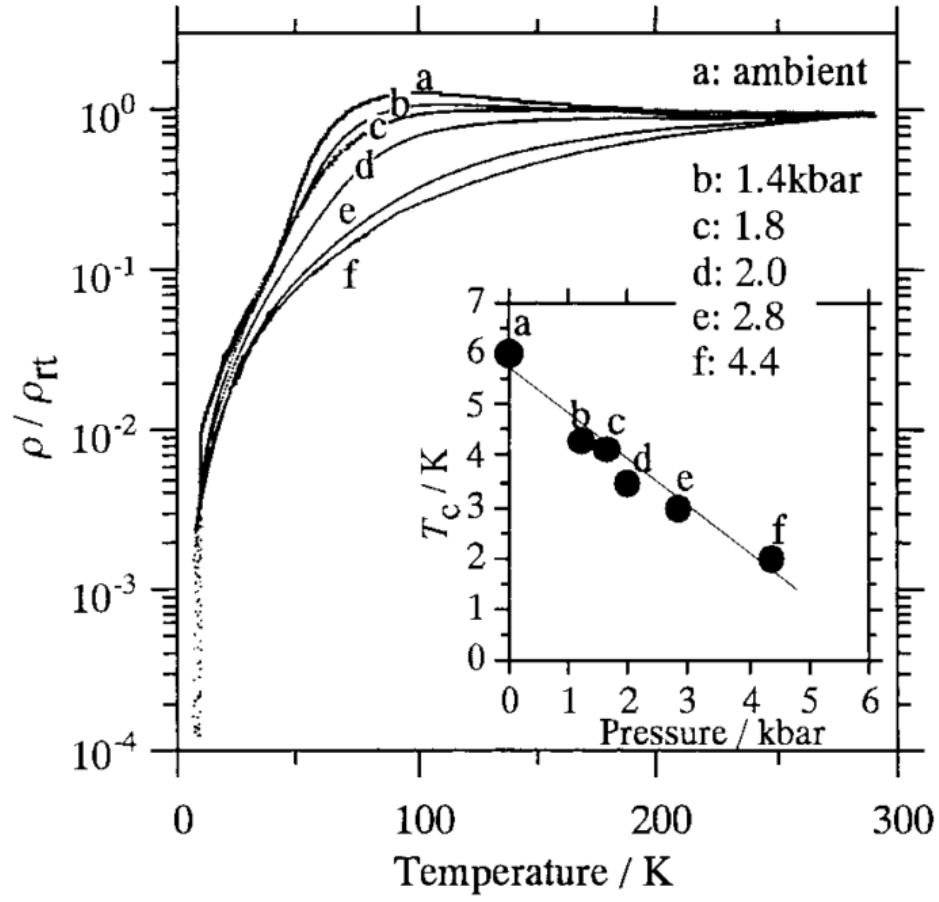


Figure 1.7: Pressure dependence of resistivity and T_c (midpoint) of λ -(BETS) $_2$ GaCl $_4$. [13]

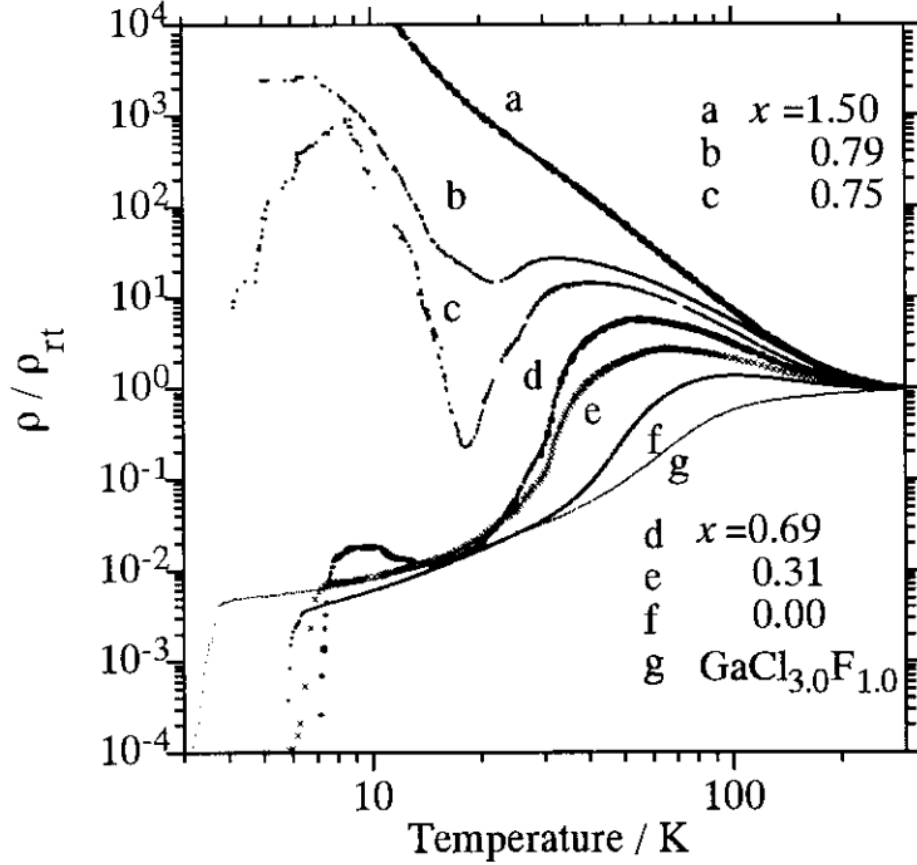


Figure 1.8: Temperature dependence of resistivity of λ -(BETS) $_2$ GaBr $_x$ Cl $_{4-x}$. Each resistivity is normalized by the respective room-temperature resistivity.[13]

Fig. 1.6 shows the resistivity with a broad hump structure at around 100 K and the SC phase with $T_c \approx 5.5$ K at ambient pressure[11]. The pressure dependence of resistivity is shown in Fig. 1.7[13]. With increasing pressure, the hump structure is suppressed and the broad metallic region appears above 0.20 GPa. The SC transition temperature decreases with increasing pressure and T_c is observed at 2 K under 0.44 GPa.

In the same analogy to κ -(ET) $_2$ X, the electronic correlation can be controlled by changing the anion as shown in Fig. 1.8[13]. The temperature dependence of resistivity for various Br contents is investigated by H. Tanaka *et*

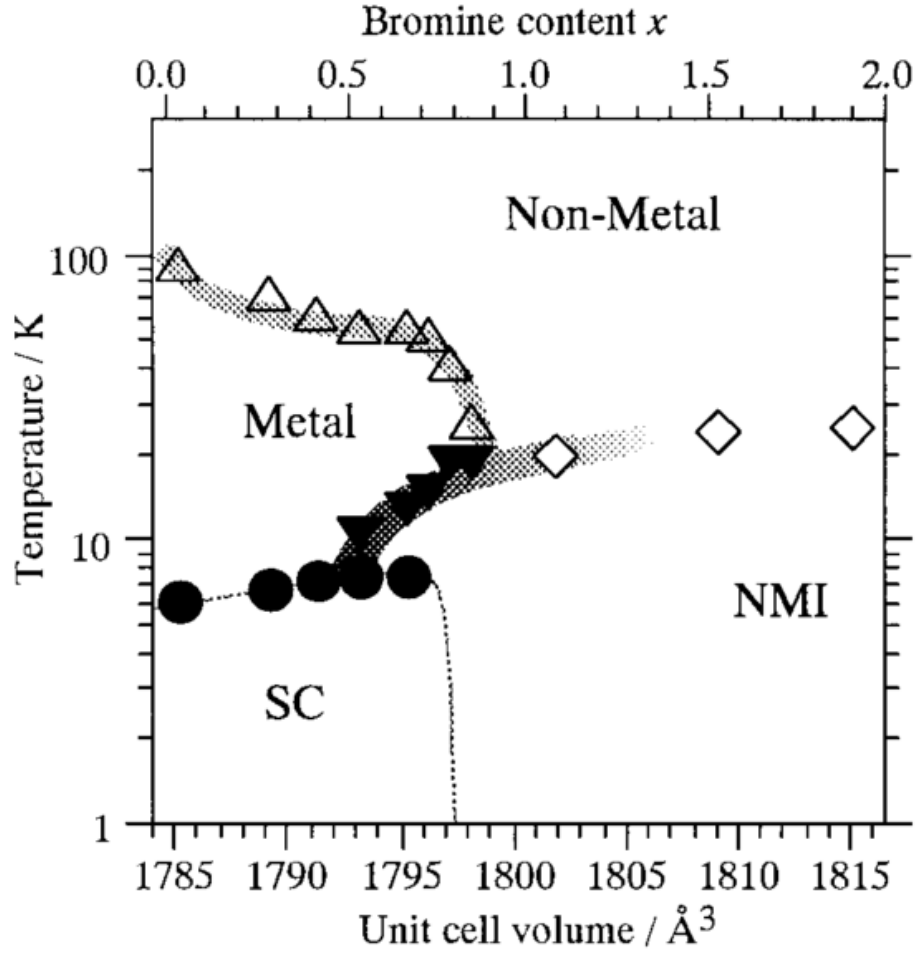


Figure 1.9: T - x phase diagram of λ -(BETS) $_2$ GaBr $_x$ Cl $_{4-x}$ proposed by the result of resistivity and susceptibility. The upper (lower) abscissa represents bromine content x (unit cell volume). [13]

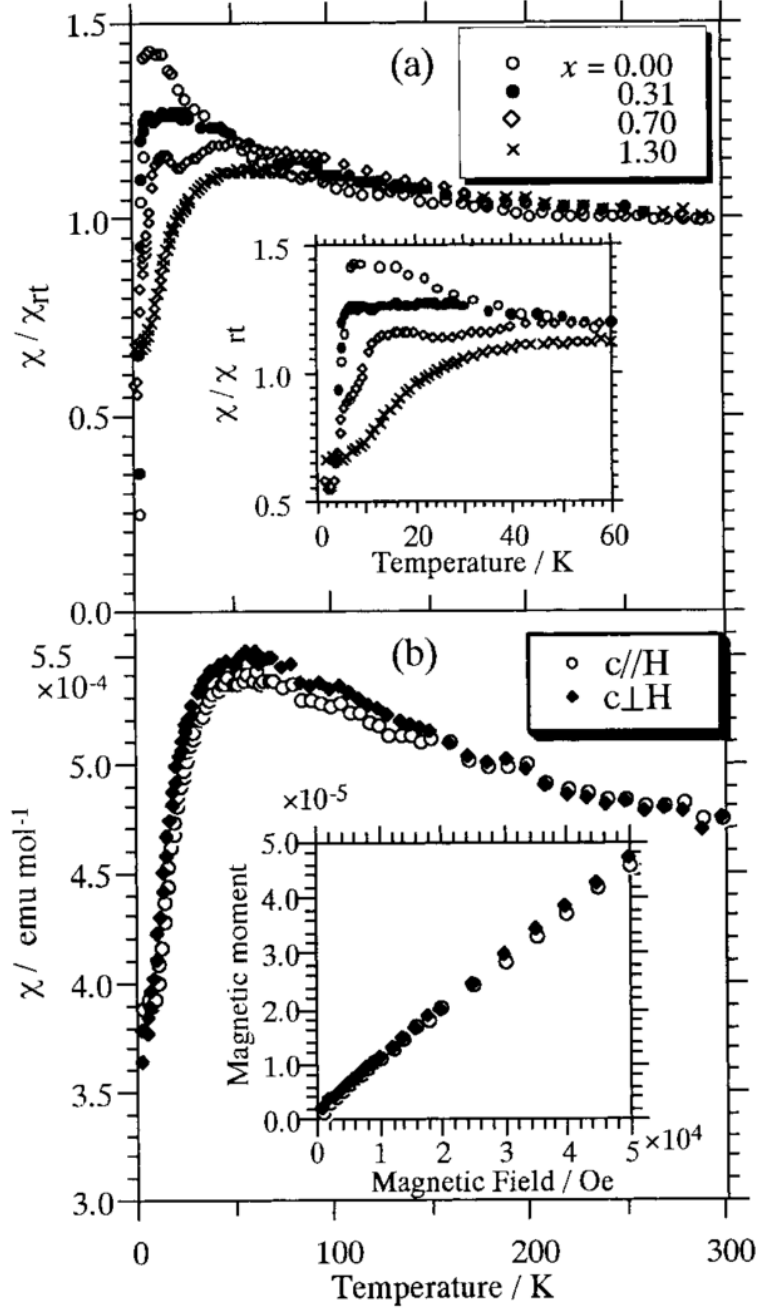


Figure 1.10: Magnetic susceptibilities of λ -(BETS) $_2$ GaBr $_x$ Cl $_{4-x}$. (a) Each susceptibility is normalized by the respective room-temperature susceptibility. (b) The magnetic susceptibility of λ -(BETS) $_2$ GaBr $_{1.3}$ Cl $_{2.7}$ perpendicular and parallel to the c -axis and inset shows field dependence of the magnetization measured at 5 K.[13]

	λ -(ET) ₂ GaCl ₄	λ -(STF) ₂ GaCl ₄	λ -(BETS) ₂ GaCl ₄
chemical formula	C ₂₀ S ₁₆ H ₁₆ GaCl ₄	C ₂₀ S ₁₂ Se ₄ H ₁₆ GaCl ₄	C ₂₀ S ₈ Se ₈ H ₁₆ GaCl ₄
a (Å)	16.246(5)	16.203(8)	16.172(3)
b (Å)	18.027(5)	18.316(9)	18.616(2)
c (Å)	6.533(7)	6.573(2)	6.607(2)
α (°)	98.20(5)	98.41(4)	98.38(2)
β (°)	97.48(6)	97.03(3)	96.75(3)
γ (°)	112.29(2)	112.42(4)	112.56(2)
V (Å ³)	1716(2)	1750(15)	1784.2(8)

Table 1.1: Lattice parameters of ET, us-BEDT-STF and BETS.[10]

al. In λ -(BETS)₂GaBr _{x} Cl_{4- x} , in which increasing x is regarded as decreasing the chemical pressure from the GaCl₄ salt, the SC phase appears for $x < 0.75$ and T_c increases with increasing x as shown in Fig. 1.9[13]. For $x > 0.75$, the SC phase is suppressed and the ground state is driven into the insulating phase. Since the magnetic susceptibility does not have an anisotropy (see Fig. 1.10) in the $x = 1.3$ salt, they mentioned about the magnetic state in the adjacent phase to the SC phase with the negative pressure region is, at least, not an AF ordered phase. Accordingly, H. Tanaka *et al.* pointed out that the adjacent phase of the SC phase is expected to be a non-magnetic insulating (NMI) phase. However, the detailed magnetic properties in these salts in NMI phase is not clear except for the static susceptibility. To clarify the mechanism of the SC phase in λ -type salts, more careful investigations are needed.

For another way to control the band width, the investigation for λ -GaCl₄ salts with various donor molecules were conducted by H. Mori *et al*[10]. They used as donor molecules ET, us-BEDT-STF, and BETS (see Fig. 1.11). us-BEDT-STF (STF) denotes unsymmetorical-bis(ethylenedithio)diselenadithiafulvalene, which is placed between the ET and BETS in their size of molecular orbital. The lattice parameters of these salts are listed in Table. 1.1. The tem-

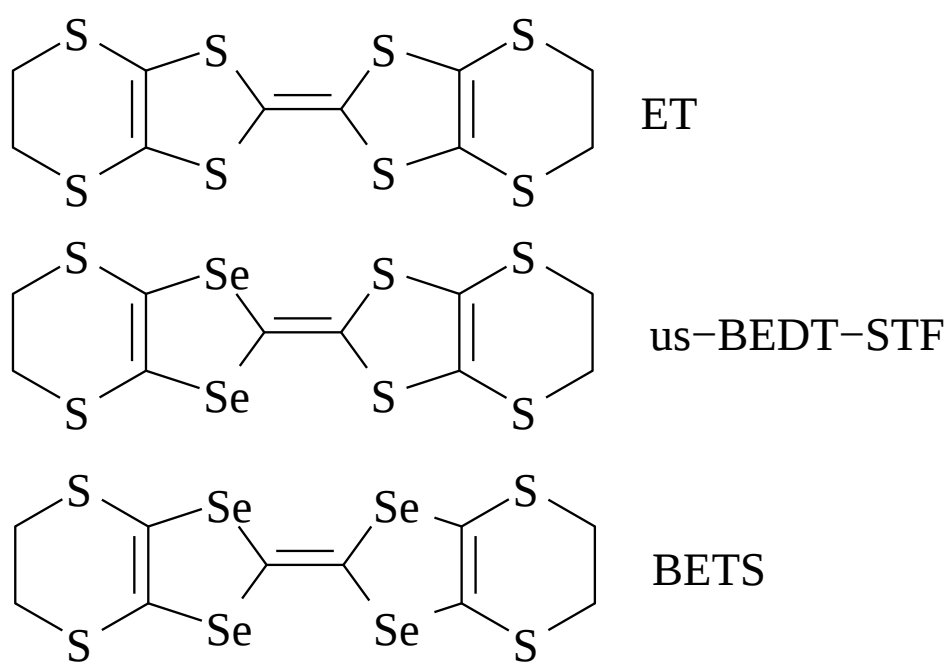


Figure 1.11: Molecular structures of ET, us-BEDT-STF and BETS.

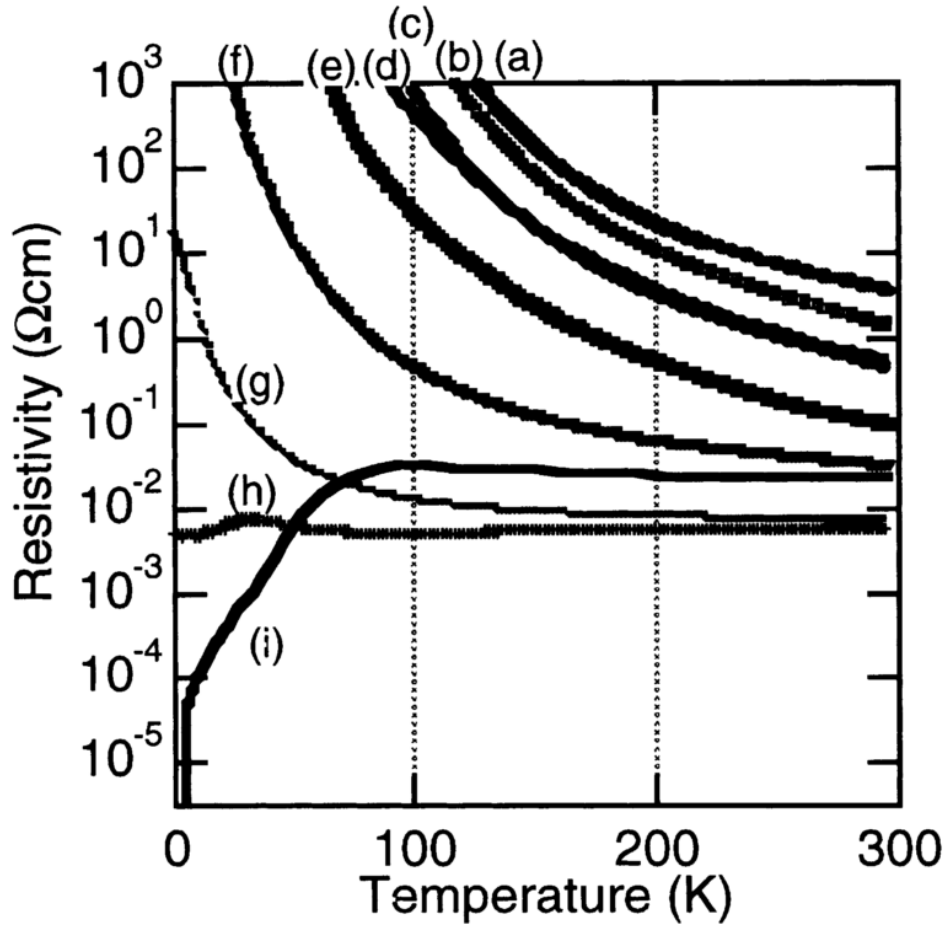


Figure 1.12: Pressure dependence of resistivity for λ -(ET) $_2$ GaCl $_4$ ((a) 1 bar, (b) 4.5 kbar, (c) 16.5 kbar), λ -(STF) $_2$ GaCl $_4$ ((d) 1 bar, (e) 4.5 kbar, (f) 13.5 kbar, (g) 17.3 kbar, (h) 18 kbar), and λ -(BETS) $_2$ GaCl $_4$ (i) 1 bar. [10]

perature dependence of the resistivity of λ - $D_2\text{GaCl}_4$ ($D = \text{ET}, \text{STF}, \text{BETS}$) at various pressure is shown in Fig. 1.12. The temperature dependence of resistivity change drastically from ET, STF, to BETS salts at ambient pressure; the semiconducting behavior is observed for the ET salt, the STF salt is a more conductive semiconductor, and the BETS salt shows a metallic behavior below 100 K and SC transition at 5.5 K. With increasing pressure, the resistivity of the ET salt decreases, and the temperature dependence of the resistivity in ET salt at 1.65 GPa is almost similar to that of the STF salt at ambient pressure. As increasing pressure on the STF salt, the resistivity decreases gradually similar to the pressure dependence of ET salt. However, up to 1.8 GPa, the SC transition does not appear in STF salt although the insulating behavior is completely suppressed at 1.8 GPa. According to these behavior of resistivity, we can speculate that the STF salt can be placed at the high pressure region of the ET salt in P - T phase diagram. However, it is not clear whether the STF salt can be placed at the negative pressure region of the BETS salt. Therefore, it is not clear whether the all of the λ - GaCl_4 salts can be placed in the universal phase diagram.

In the same report, it is pointed out that the ET salt shows the AF magnetic order below 13 K from the ESR measurement as shown in Fig. 1.13. The linewidth decreases gradually with lowering temperature, and increases rapidly below 13 K. The intensity is almost constant at high temperature region and decreases suddenly below 20 K. The g -values along the a , b , c -axes also start increasing below 20 K. These behaviors are the evidence for the occurrence of AF magnetic order below 13 K. According to these results of resistivity and

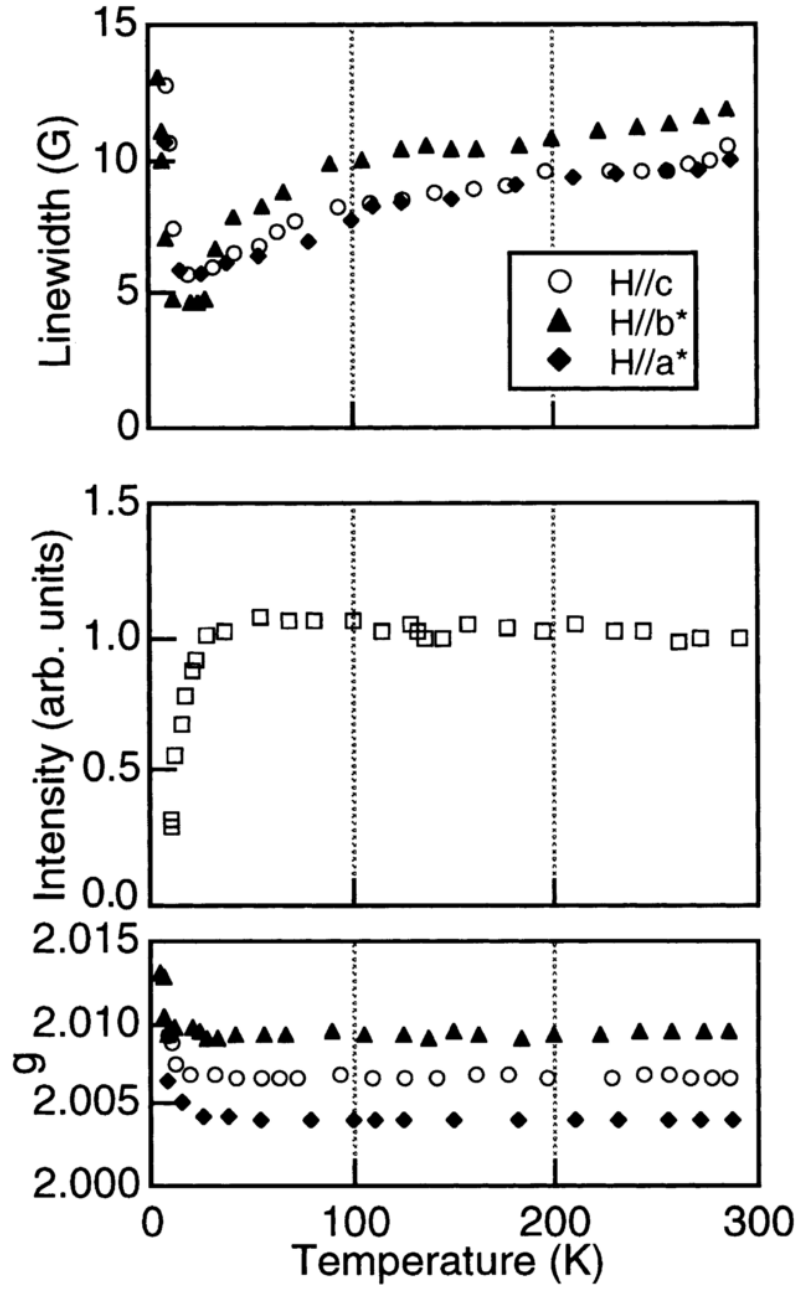


Figure 1.13: ESR measurement of λ -(ET) $_2$ GaCl $_4$. [10]

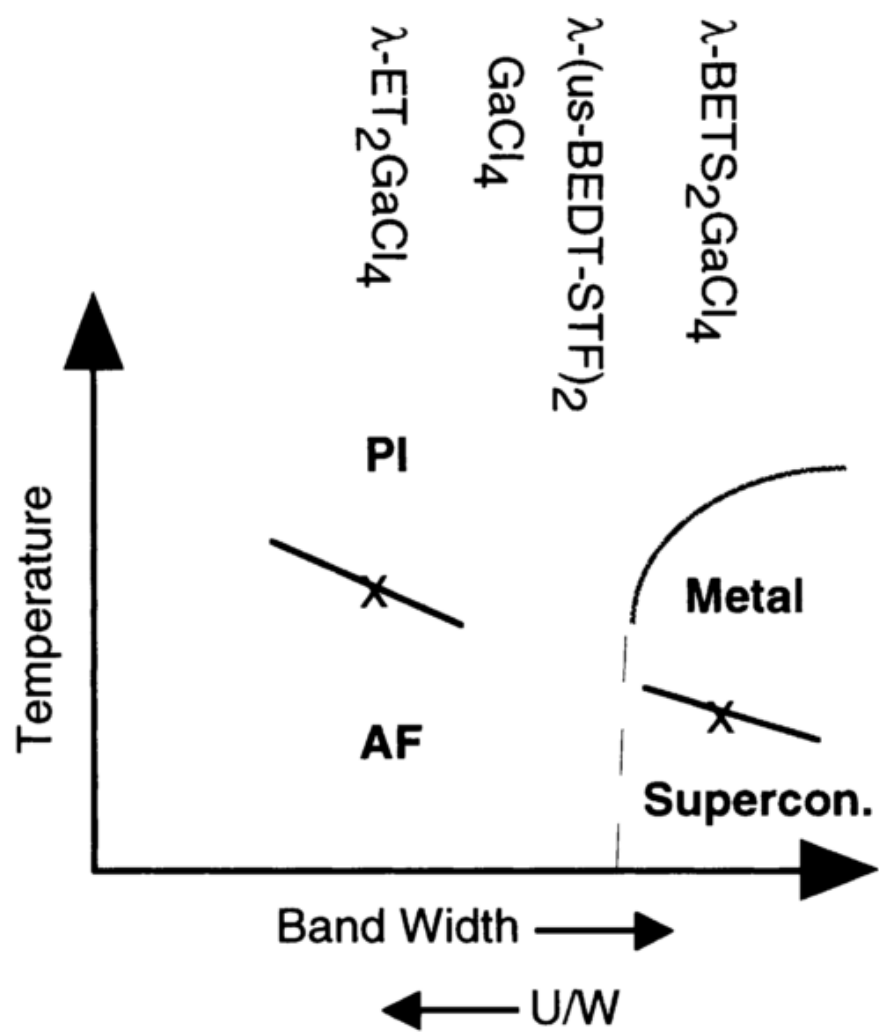


Figure 1.14: Electronic phase diagram of λ -type salts. [10]

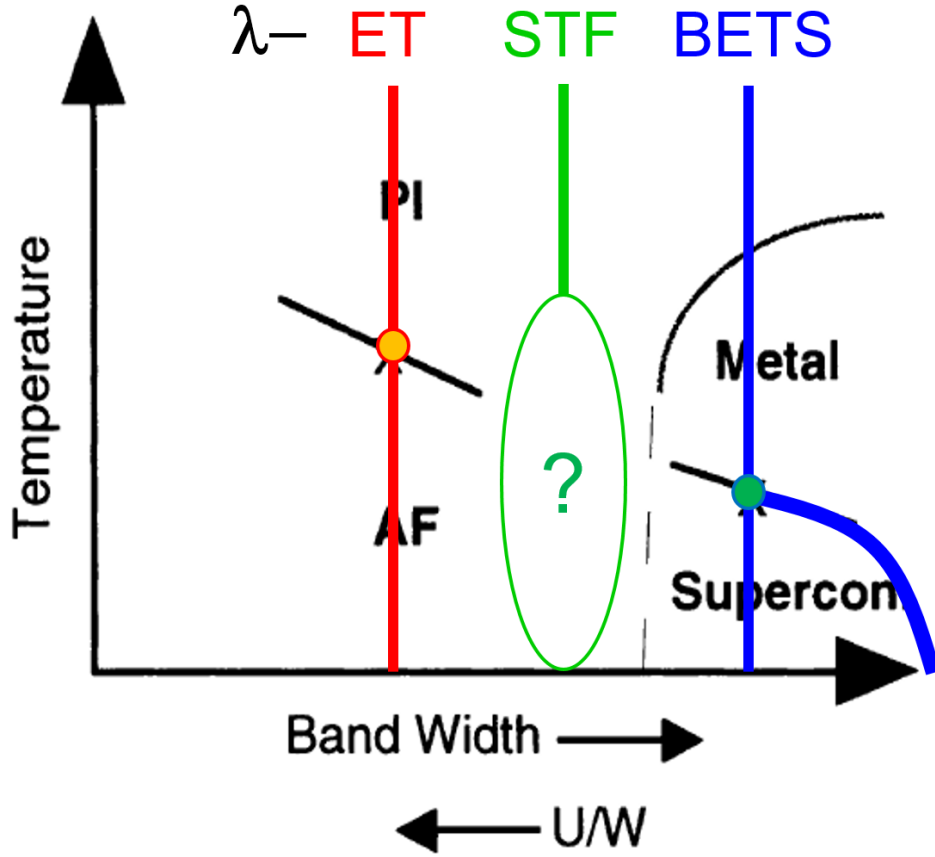


Figure 1.15: Electronic phase diagram of λ -type salts. We focused on the physical properties in the region marked as “?” in this study.

ESR measurements, as shown in Fig. 1.14, they proposed the phase diagram of λ -GaCl₄ salts.

1.2.3 Motivation

Since there is no investigation for magnetic properties of the STF salt, it is not clear the adjacent state of the SC phase in the BETS salt (see Fig. 1.15). However, it is expected that the AF magnetic state is close to the SC phase in the universal phase diagram in λ -GaCl₄ salts. This is similar to that in the family of κ -ET salts, where the AFI phase is observed as the ground state in

the low pressure region[9]. In κ -ET salts, a ^{13}C -NMR study in the normal phase above the SC and AFI phases[14] and an STM spectroscopy study in the SC phase[15] have been conducted. From these results, it is suggested that the SC state in the κ -ET salts has d -wave symmetry with line nodes and is driven by AF spin fluctuations. Accordingly, it is expected that in λ -type salts, the SC phase is stabilized at higher pressures and is enhanced by AF spin fluctuations. However, it is not clear whether the AFI phase in λ -ET salts is adjacent or not to the SC phase in λ -BETS salts. Although many investigations have been done, the origin of the SC phase in λ -type salts is not yet clear and remains an open question. Therefore, the understanding of the electronic properties of λ -(STF) $_2$ GaCl $_4$ becomes very important for clarifying the mechanisms of the SC state in the λ type salts. In this study, we have measured the electrical resistivity under pressure and the magnetic properties at ambient pressure in λ -(STF) $_2$ GaCl $_4$.

1.3 Organic $\pi - d$ interacting system

Study of the $\pi - d$ interacting system has been one of the most intensely investigated-topics in the field of strongly correlated electron systems. Low-dimensional organic conductors are important examples of the $\pi - d$ system and in particular, the quasi-two-dimensional organic conductor λ -(BETS) $_2$ FeCl $_4$ is well-known as the first organic material to show a magnetic-field induced superconductivity[16]. The magnetic field dependence of resistivity in λ -(BETS) $_2$ FeCl $_4$ is shown in Fig. 1.16.

The occurrence of the field-induced SC phase is well explained by the

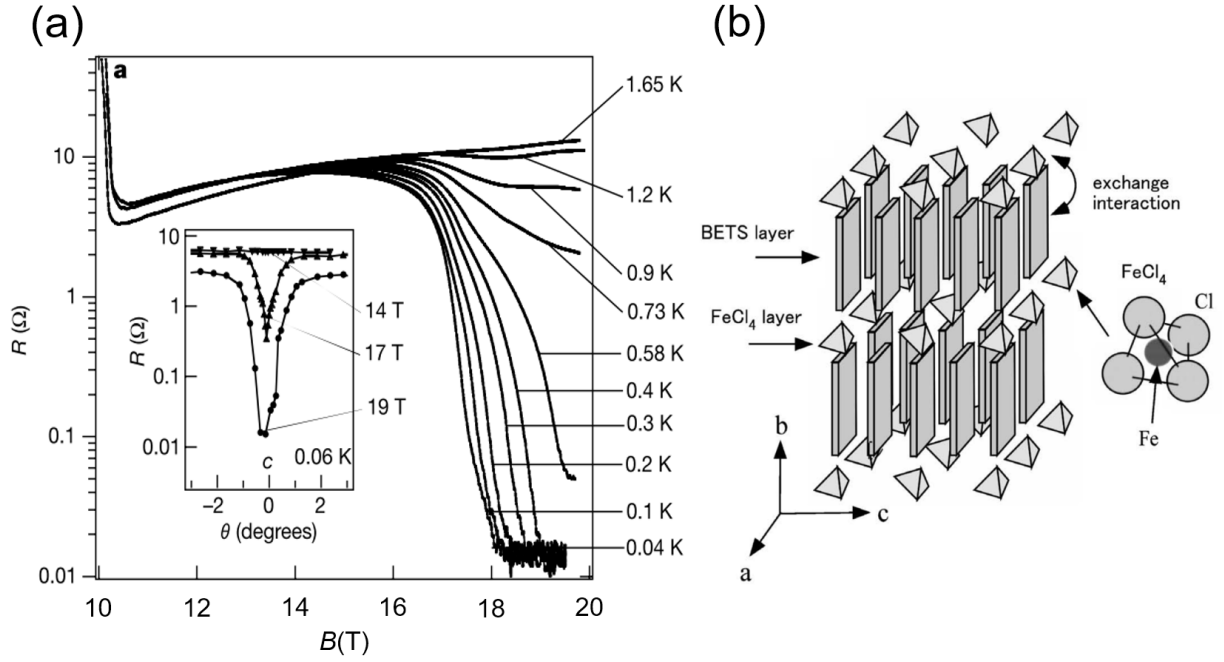


Figure 1.16: (a) Interlayer resistance of λ -(BETS) $_2$ FeCl $_4$ when the magnetic field is applied parallel to the c -axis, which is in the conduction layer. The inset shows the field-direction dependence of the resistance under the field in the b^* - c plane. (b) Schematic drawing of the structure of λ -(BETS) $_2$ FeCl $_4$. [16]

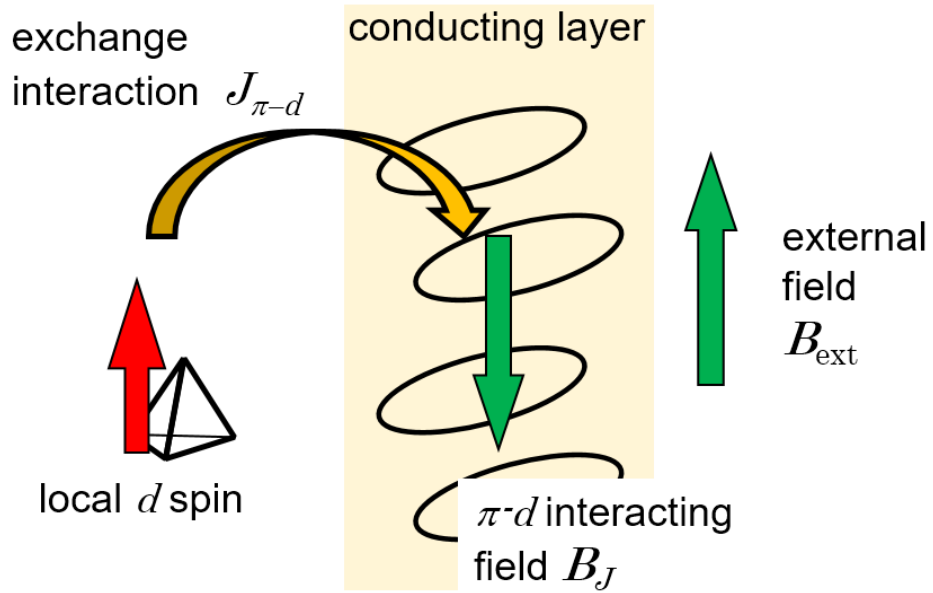


Figure 1.17: Schematic drawing of the Jaccarino-Peter compensation mechanism.

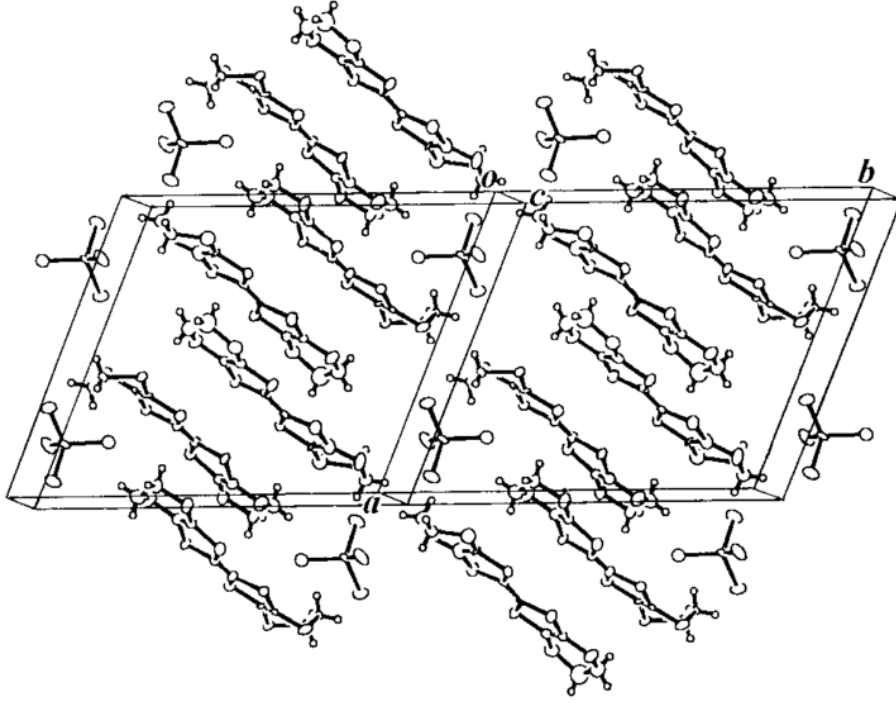


Figure 1.18: Crystal structure of λ -(BETS) $_2$ FeCl $_4$. [19]

Jaccarino-Peter compensation mechanism[17]. The schematic image of the Jaccarino-Peter mechanism is shown in Fig. 1.17. In the case of present π - d system, an external magnetic field $\mathbf{B}_{\text{ext}}$ arrange the local d spins $\mathbf{s}_d$ is compensated by the π - d interacted field $\mathbf{B}_J = (J_{\pi d}/g\mu_B)\mathbf{s}_d$, which is antiparallel to external field, where $J_{\pi d}$ is exchange coupling constant between π - and d -spins ($J_{\pi d} < 0$).

1.3.1 Physical properties in λ -(BETS) $_2$ FeCl $_4$

The crystal structure and energy band of λ -(BETS) $_2$ FeCl $_4$ is shown in Fig. 1.18[19] and Fig. 1.19[12], which is isostructural to λ -(BETS) $_2$ GaCl $_4$. It has a quasi-two-dimensional conduction in the BETS layer of the a - c plane and the anion layer, which does not contribute to the band structure.

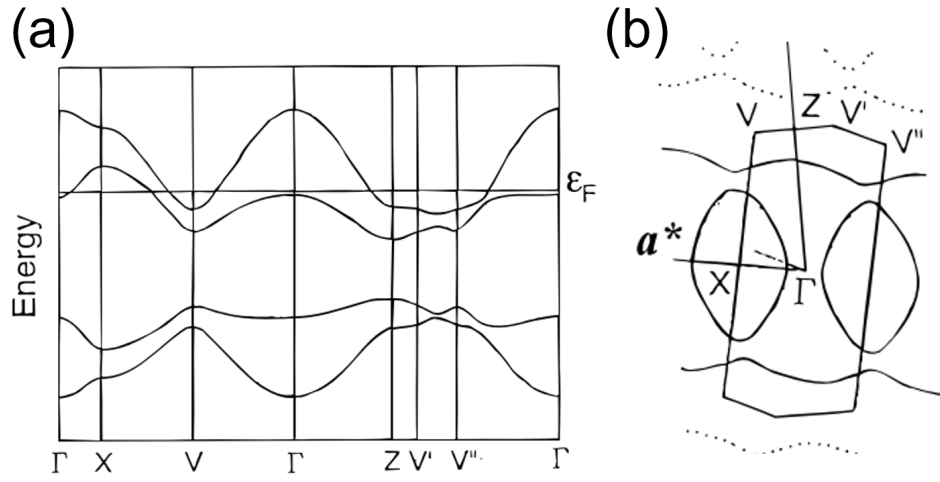


Figure 1.19: (a) Band structure and (b) Fermi surface of λ -(BETS) $_2$ FeCl $_4$ [12].

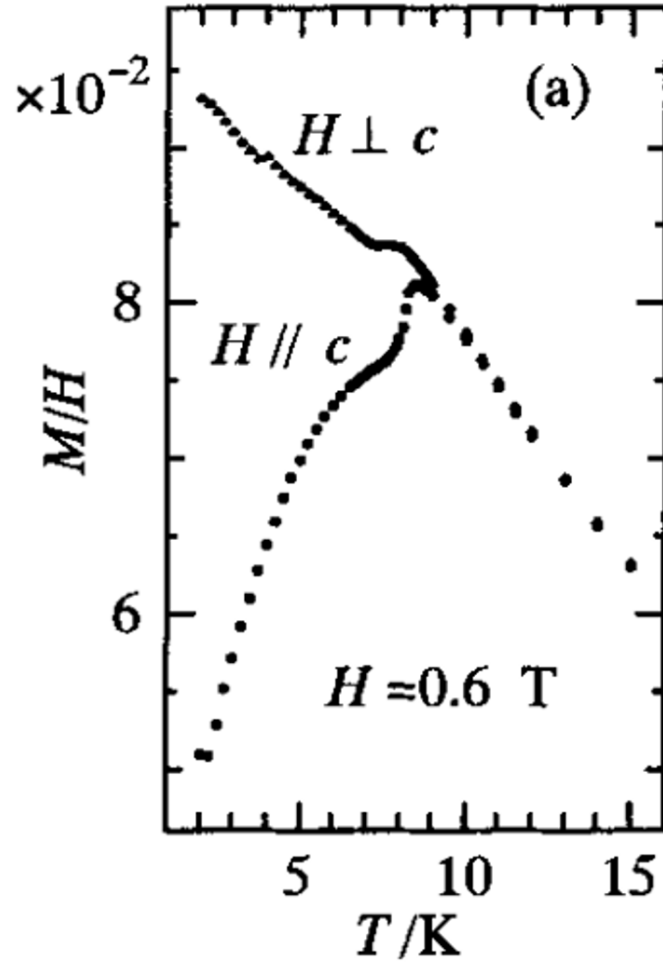


Figure 1.20: Temperature dependence of the static susceptibility of λ -(BETS) $_2$ FeCl $_4$. [18]

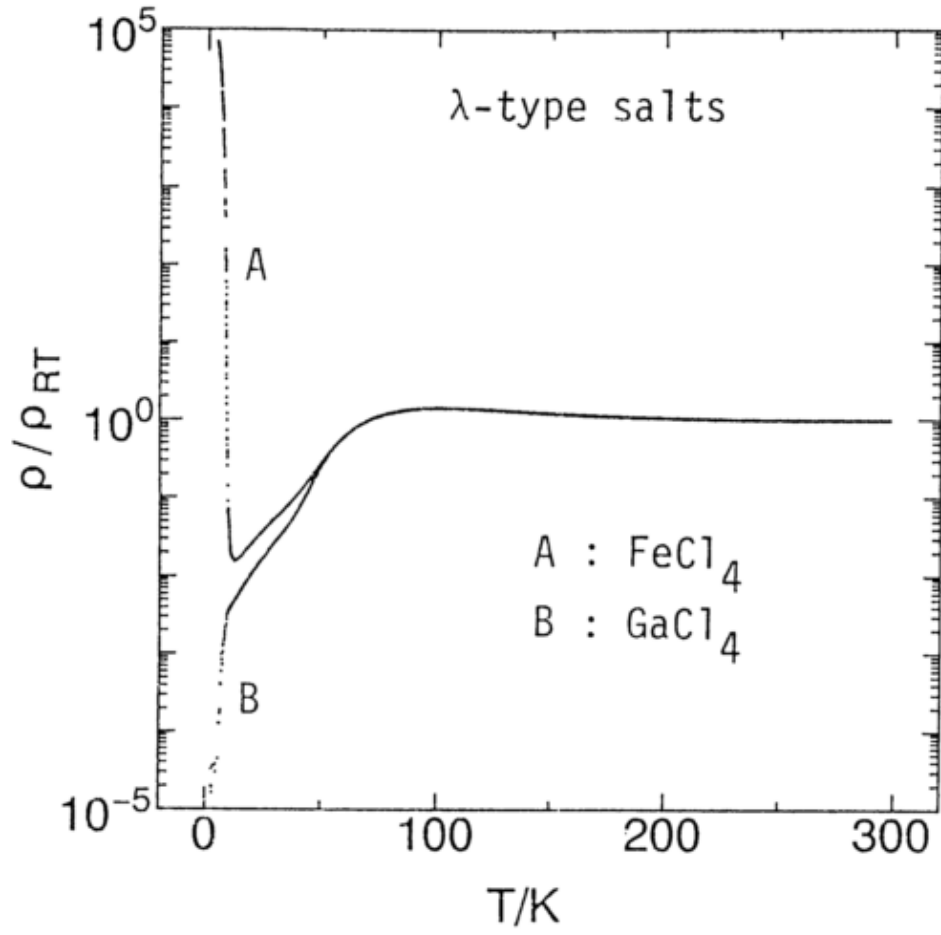


Figure 1.21: Temperature dependence of the resistivity normalized by the value at room temperature of λ -(BETS) $_2$ GaCl $_4$ and λ -(BETS) $_2$ FeCl $_4$. [11]

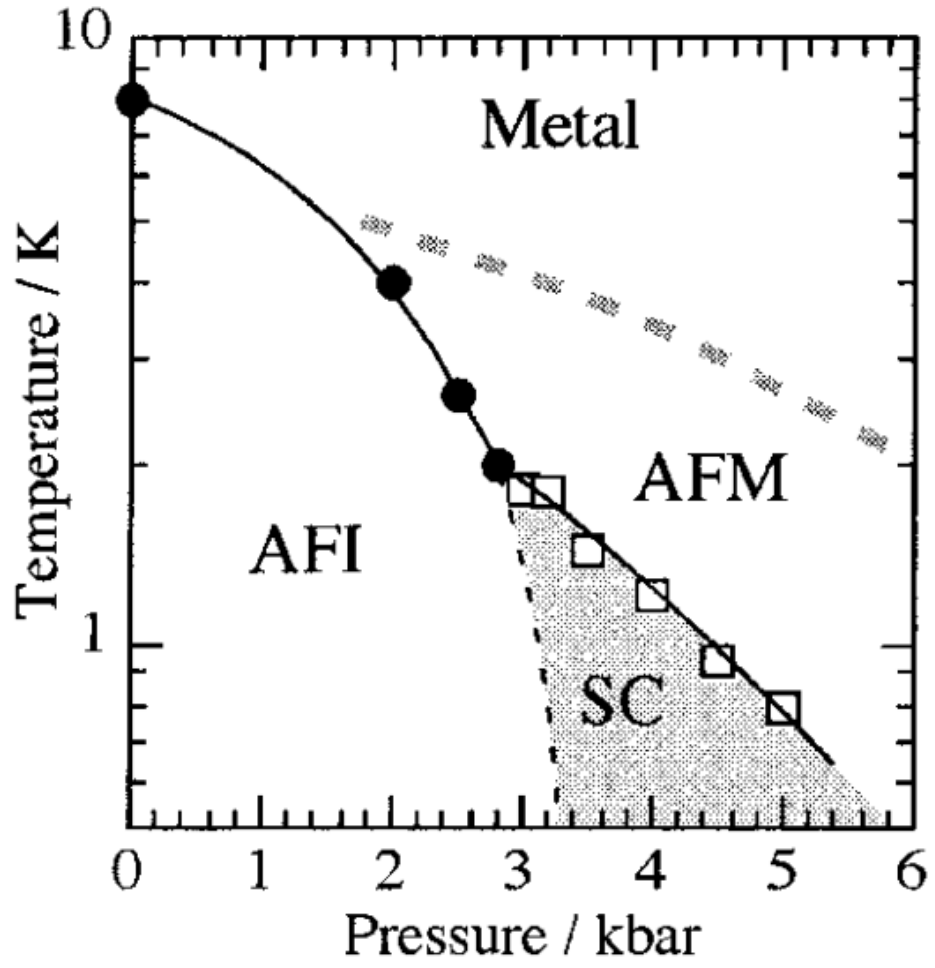


Figure 1.22: P - T phase diagram of λ -(BETS)₂FeCl₄ obtained from the resistivity measurements. AFI: antiferromagnetic insulator, AFM: antiferromagnetic metal.[13]

The temperature dependence of the static susceptibility is shown in Fig. 1.20. At high temperature region, the susceptibility shows a Curie-Weiss-type temperature dependence with $S = 5/2$ and the Weiss temperature $T_W = -15$ K. With magnetic field applied parallel to the c -axis, the susceptibility shows a sharp drop and anisotropy below 8.3 K, which reflect the AF magnetic transition. As shown in Fig. 3.32, the resistivity in λ -(BETS) $_2$ FeCl $_4$ shows a metal-insulator (MI) transition at 8.3 K, which is the same temperature to the AF magnetic transition. The P - T phase diagram of λ -(BETS) $_2$ FeCl $_4$ is shown in Fig. 1.22. Closed circles and open squares in the phase diagram are obtained by the resistivity measurements.

Since the susceptibility of the $3d$ -spin moments shows the Curie-Weiss type behavior above T_{AF} and an anisotropy below T_{AF} , for a long time, it has been believed that the AF magnetic order in the λ -(BETS) $_2$ FeCl $_4$ is caused by the ordering of $3d$ spin system in anion layer.[18, 19, 20].

1.3.2 π -ordering model

In a recent study based on thermodynamic properties, H. Akiba *et al.* proposed that the π spin state is AF ordered and the $3d$ spin state is in the internal magnetic field arising from the π spin sites [21]. The open circles in Fig. 1.23 show the temperature dependence of the spin specific heat ΔC . A sharp peak structure was observed at 8.3 K, which cooperative with MI transition and a broad hump structure that appears to be a Schottky-type anomaly was found on a lower temperature. This hump anomaly suggests that the existence of the discrete energy levels due to the Zeeman effect, i.e. the existence of the

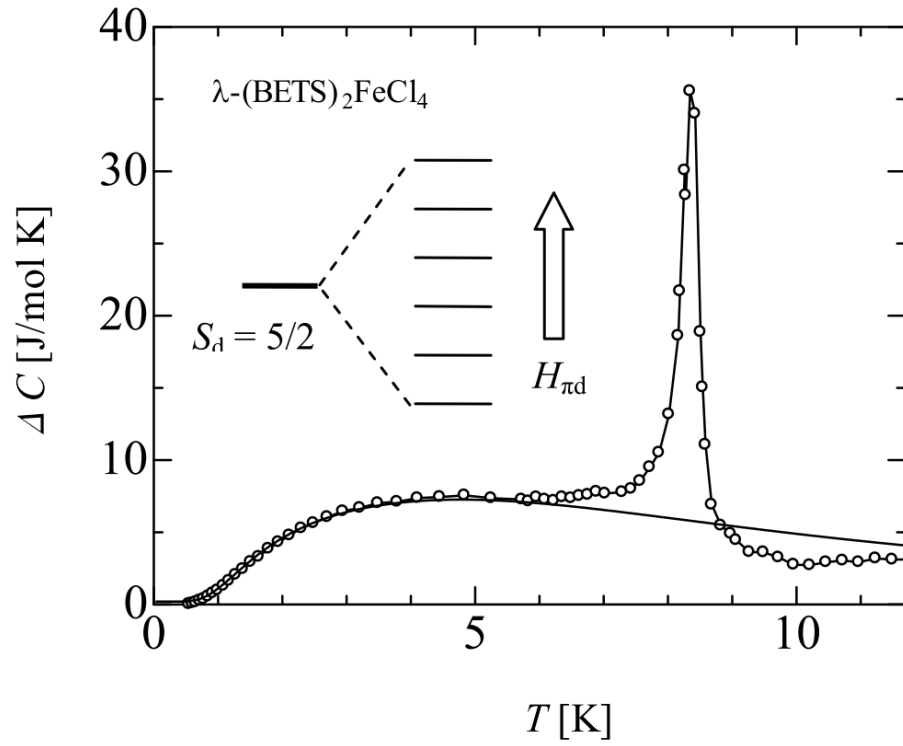


Figure 1.23: Temperature dependence of the excess specific heat ΔC of λ -(BETS)₂FeCl₄ obtained by subtracting the lattice and electric specific heats estimated for λ -(BETS)₂GaCl₄. [21]

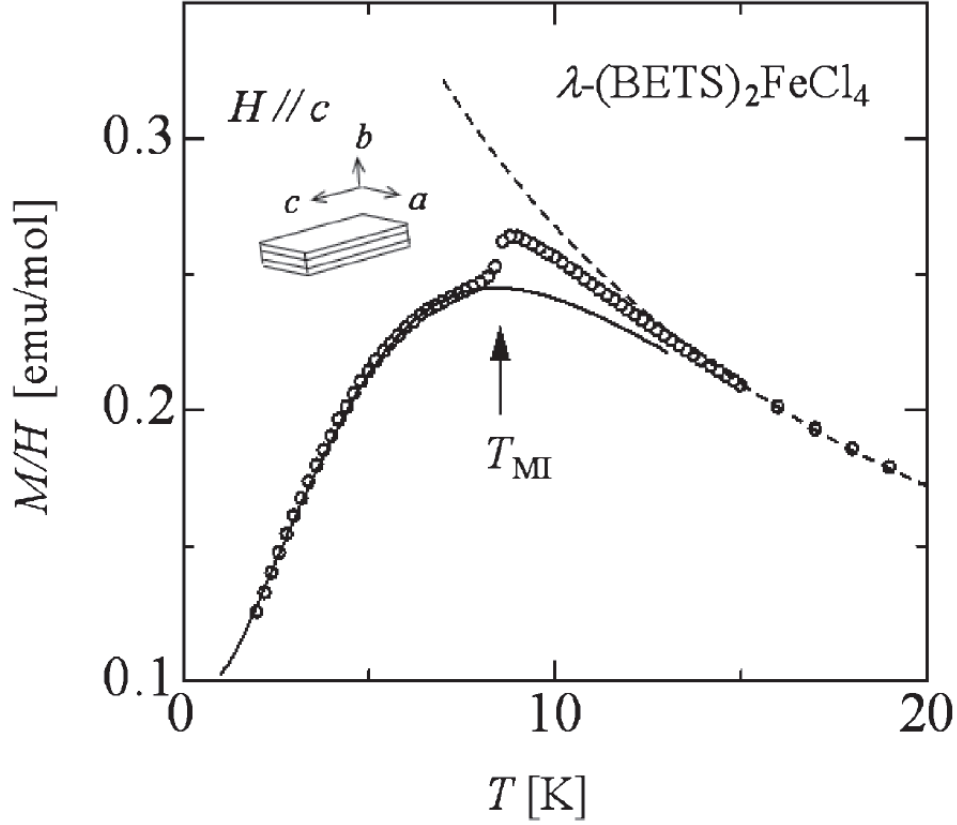


Figure 1.24: Temperature dependence of the magnetic susceptibility M/H of λ -(BETS) $_2$ FeCl $_4$ under external magnetic field parallel to the c -axis.[22]

free spin system in the internal field given by the AF ordered spin system.

The solid curve in Fig. 1.23 is the temperature dependence of the spin specific heat for the paramagnetic spin system with $S = 5/2$ split into six levels under an effective magnetic field $\mu_0 H_{\pi-d} \approx 4$ T. This description supposes that the $3d$ spin system behaves paramagnetically and AF ordered π spin system gives the internal field $H_{\pi-d}$ to the d -spin system.

This model also describes the temperature dependence of the magnetic susceptibility[22]. Figure 1.24 shows the magnetic susceptibility of the FeCl $_4$ salt observed under the application of an external field $\mu_0 H_{\text{ext}} = 0.1$ T parallel to the c -axis. Above $T_{\text{AF}} = 8.3$ K, the magnetic susceptibility shows the Curie-

Weiss-type behavior for the $3d$ spin ($S = 5/2$). It shows the characteristic shoulder type anomaly, which corresponds to the region where the Schottky-type specific heat is observed. As mentioned above, the Schottky-type specific heat can be explained by the Zeeman splitting of the paramagnetic $3d$ -spin system under the internal field $H_{\pi-d}$, which is given by the exchange interaction $J_{\pi-d}$ with AF-ordered π -spin system. Since the alternating internal field, which is given by the sublattices of the AF ordered π -spin system, arrange the $3d$ spins, the magnetization of the $3d$ -spin system would be canceled out and gradually decrease with decreasing temperature in the AF phase.

According to these studies for specific heat and magnetic susceptibility of λ -(BETS) $_2$ FeCl $_4$, they proposed that the AF phase of this salt below 8.3 K occurs by the ordering of π -spin system and the degree of freedom in d -spin system is remained. Here after, this model is called “ π -ordering model” in this paper.

1.3.3 Motivation

The AF phase in λ -(BETS) $_2$ FeCl $_4$ had been believed to be caused by the ordering of the d -spin system. However, it was reported that the specific heat and magnetic susceptibility of λ -(BETS) $_2$ FeCl $_4$ at ambient pressure can be explained by the “ π -ordering model”. In the π - d system, there are three magnetic interaction, π - π , π - d , and d - d interaction. However, the “ π -ordering model” ignores the interaction between d -spins (d - d interaction). To determine the effect of the d - d interaction is one of the main topics in π - d interacting system. In λ -(BETS) $_2$ FeCl $_4$, since the MI transition, AF transition, and

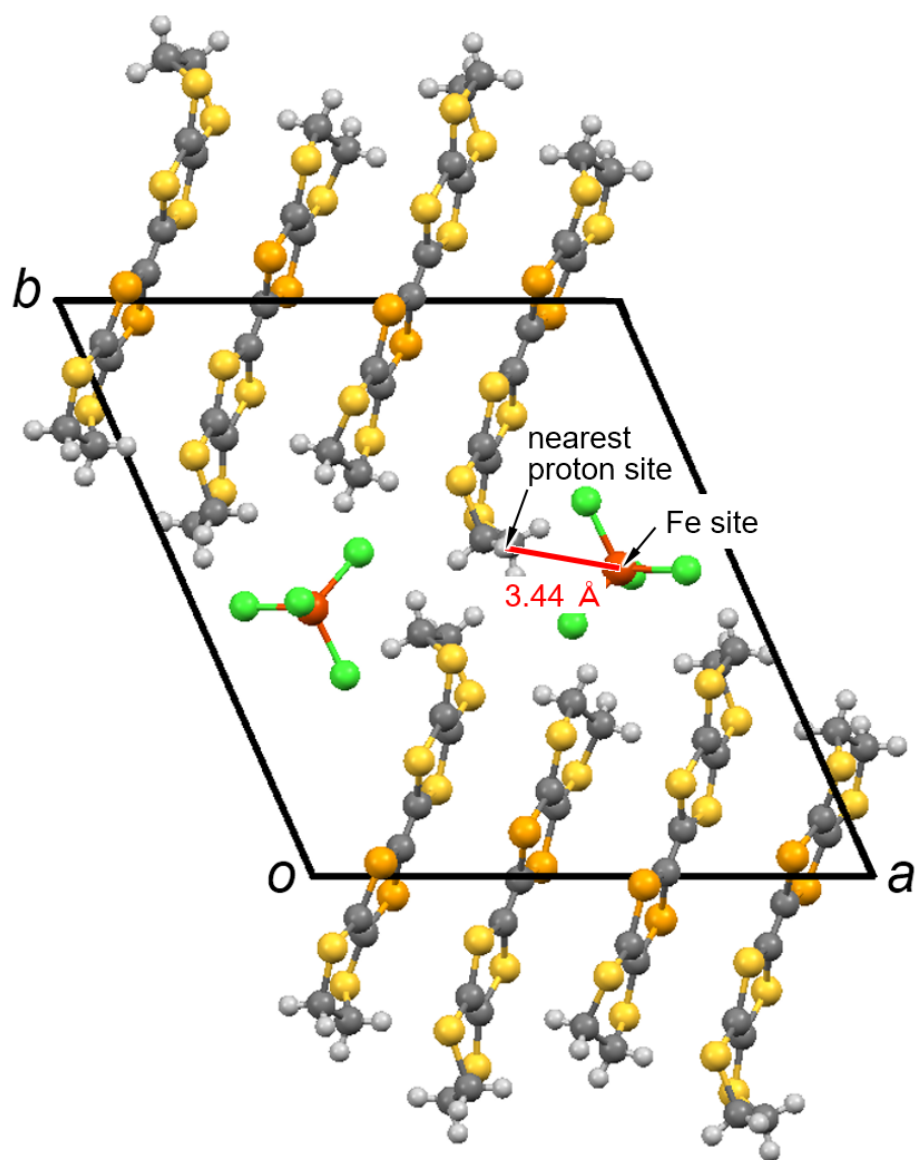


Figure 1.25: Crystal structure of λ -(STF) $_2$ FeCl $_4$

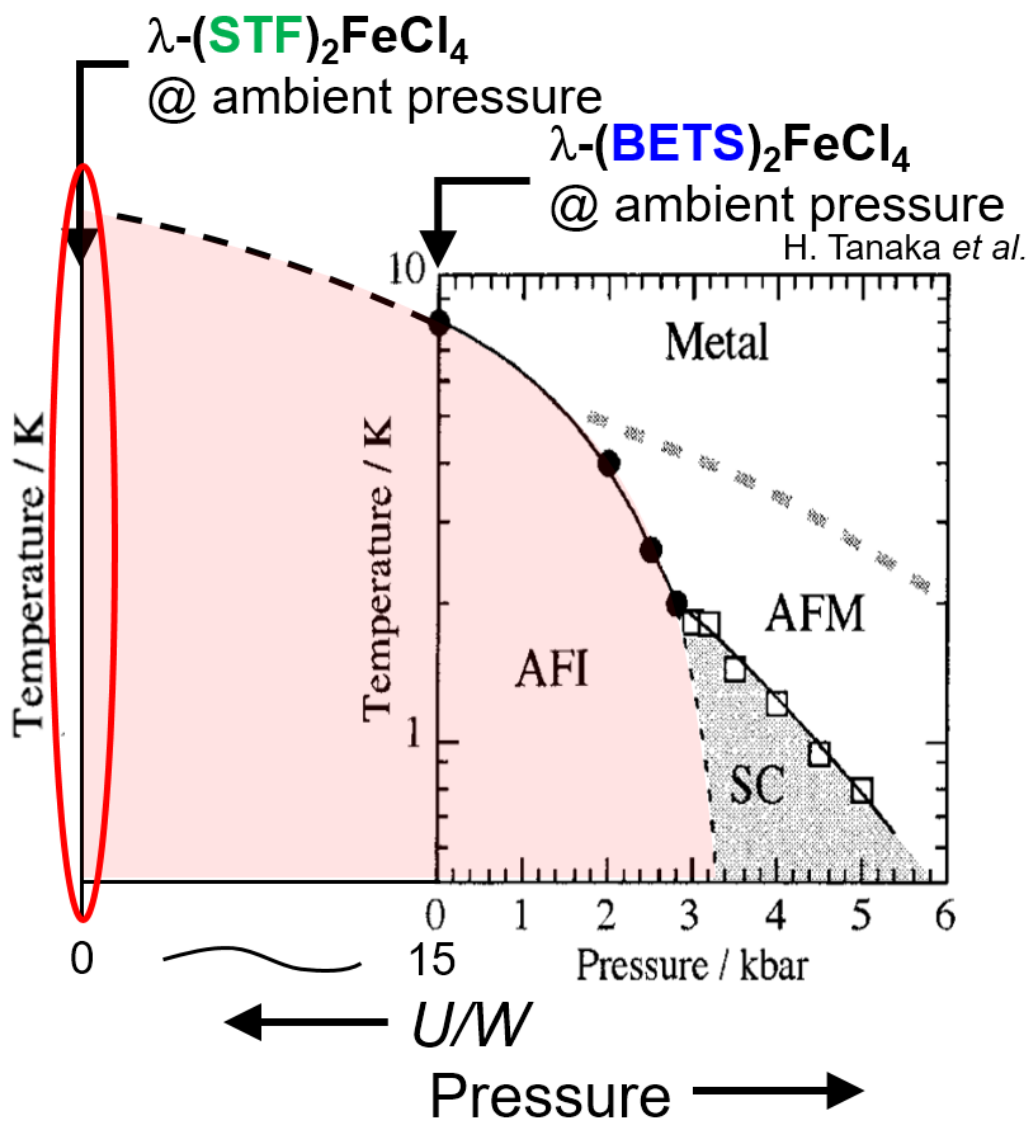


Figure 1.26: Schematic drawing of the expansion of the P - T phase diagram of the λ -FeCl₄ salts given in Fig. 1.22.

anisotropy of the susceptibility appears at the same moment, the situation is more complicated.

To solve these problems in the AF transition of λ -(BETS)₂FeCl₄ salts, we focused on λ -(STF)₂FeCl₄, which is isostructural to λ -(BETS)₂FeCl₄[23] (Fig. 1.25). In the same analogy to the λ -GaCl₄ salts, λ -(STF)₂FeCl₄ is expected to be located at the negative pressure region to λ -(BETS)₂FeCl₄. As shown in Fig. 1.26, the AF transition temperature in the BETS salt decreases with increasing pressure, i.e. with decreasing the electronic interaction U_{eff}/W . Therefore, λ -(STF)₂FeCl₄ is expected to have the AF phase with higher T_{AF} than that of λ -(BETS)₂FeCl₄. Moreover, λ -(STF)₂FeCl₄ is expected to have a wide insulating phase in the whole temperature range similar to the GaCl₄ salt. We can investigate the pure effect of the AF transition without MI transition. To elucidate the mechanism of the AF transition in the λ -FeCl₄ salts, we carried out the resistivity under high pressure and magnetic properties measurements at ambient pressure for λ -(STF)₂FeCl₄.

Chapter 2

Experimental

2.1 Sample synthesis

Single crystals of λ -(us-STF)₂GaCl₄ and λ -(us-STF)₂FeCl₄ were synthesized by the standard electrochemical oxidation of us-STF (40 mg) with the tetrabutylammonium salt of GaCl₄⁻¹ (300 mg) and FeCl₄⁻¹ (300 mg) in the solvent of chlorobenzene (100 ml).

The typical size of the sample crystals are $3 \times 0.5 \times 0.1 \text{ mm}^3$. We determined their crystal structures by X-ray diffraction using XtaLAB P200 (RIGAKU). For GaCl₄ salt, $a = 16.207 \text{ \AA}$, $b = 18.293 \text{ \AA}$, $c = 6.579 \text{ \AA}$, $\alpha = 98.488^\circ$, $\beta = 97.040^\circ$ and $\gamma = 112.330^\circ$, and for FeCl₄ salt, $a = 16.202(3) \text{ \AA}$, $b = 18.286(4) \text{ \AA}$, $c = 6.5645(16) \text{ \AA}$, $\alpha = 98.443(6)^\circ$, $\beta = 96.799(7)^\circ$ and $\gamma = 112.347(3)^\circ$. They are consistent with a previous report[10, 23].

2.2 Electric resistivity

We measured the electrical resistivity for three samples of λ -(STF)₂GaCl₄ (Ga-#0, Ga-#1, Ga-#2) and four samples of λ -(STF)₂FeCl₄ (Fe-#0, Fe-#1,

Sample	size (mm ³)	cryostat	magnet	cell diameter & pressure medium
Ga-#0	$0.10 \times 0.28 \times 1.17$	⁴ He	-	-
Ga-#1	$0.07 \times 0.48 \times 2.57$	⁴ He	-	6mm, Daphne7373
Ga-#2	$0.06 \times 0.37 \times 1.78$	⁴ He	PPMS	4mm, Daphne7474
Fe-#0	$0.25 \times 0.05 \times 1.37$	⁴ He	-	-
Fe-#1	$0.12 \times 0.13 \times 2.50$	⁴ He	-	5mm, Daphne7373
Fe-#2	$0.01 \times 0.08 \times 1.08$	³ He	-	4mm, Daphne7474
Fe-#3	$0.12 \times 0.32 \times 1.50$	³ He	17T SC magnet	5mm, Daphne7474

Table 2.1: List of the resistivity measurements setups for each samples of λ -(STF)₂GaCl₄ (Ga-#1, Ga-#2) and λ -(STF)₂FeCl₄ (Fe-#1, Fe-#2, Fe-#3).

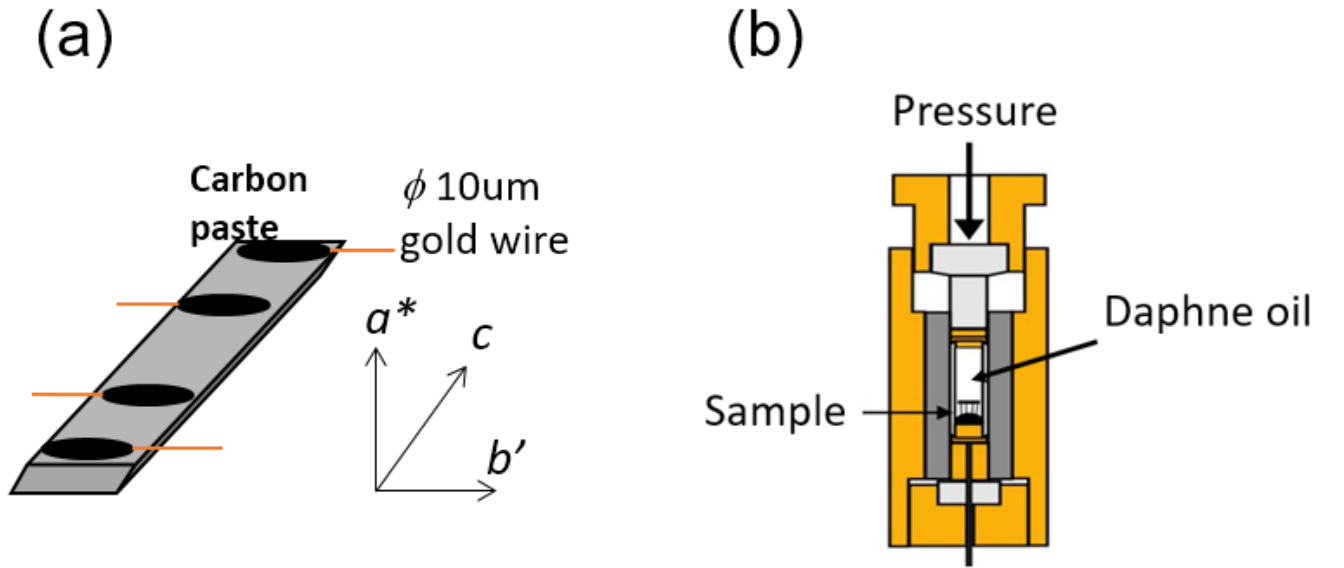


Figure 2.1: (a) Setup for resistivity measurements for λ -(STF)₂GaCl₄ and λ -(STF)₂FeCl₄. (b) Structure of the hybrid high pressure cell.

Fe-#2, Fe-#3). The experimental method for each samples are shown in Table. 2.1. Electrical leads of 10 μm gold wire were attached to the samples with carbon paste. The samples Ga-#0 and Fe-#0 were measured at ambient pressure. The samples Ga-#1, Ga-#2, Fe-#1, Fe-#2, and Fe-#3 were mounted inside a beryllium-copper and NiCrAl hybrid clamp cell, whose inner diameters are 6, 5, and 4 mm. As a pressure medium, Daphne 7373 or Daphne 7474 oil were used. At low temperatures, the pressure efficiency of the high pressure cells were calibrated by measuring the SC transition temperature of Pb below 7 K.

The electronic resistivity measurements were conducted by the DC four-probe method in the temperature range of 2-300 K. The current flow was parallel to the c -axis, which is the long axis of the crystals, in the conducting a - c plane. To avoid self heating and non-linear effects, the current was limited to 100 μA or less. The lowest current was 1 nA for a maximum resistance of 10 M Ω .

The magnetoresistivity measurements were performed in the PPMS (Quantum Design) for the sample Ga-#2, and the 17/19T SC magnet up to 17 T for the sample Fe-#3. For sample Ga-#2, the magnetic field was applied along the a^* -axis up to 9 T, and for sample Fe-#3, the magnetic field was applied parallel to the c -axis up to 17 T.

2.3 Magnetic susceptibility

The susceptibility measurements were performed using an MPMS SQUID magnetometer (Quantum Design).

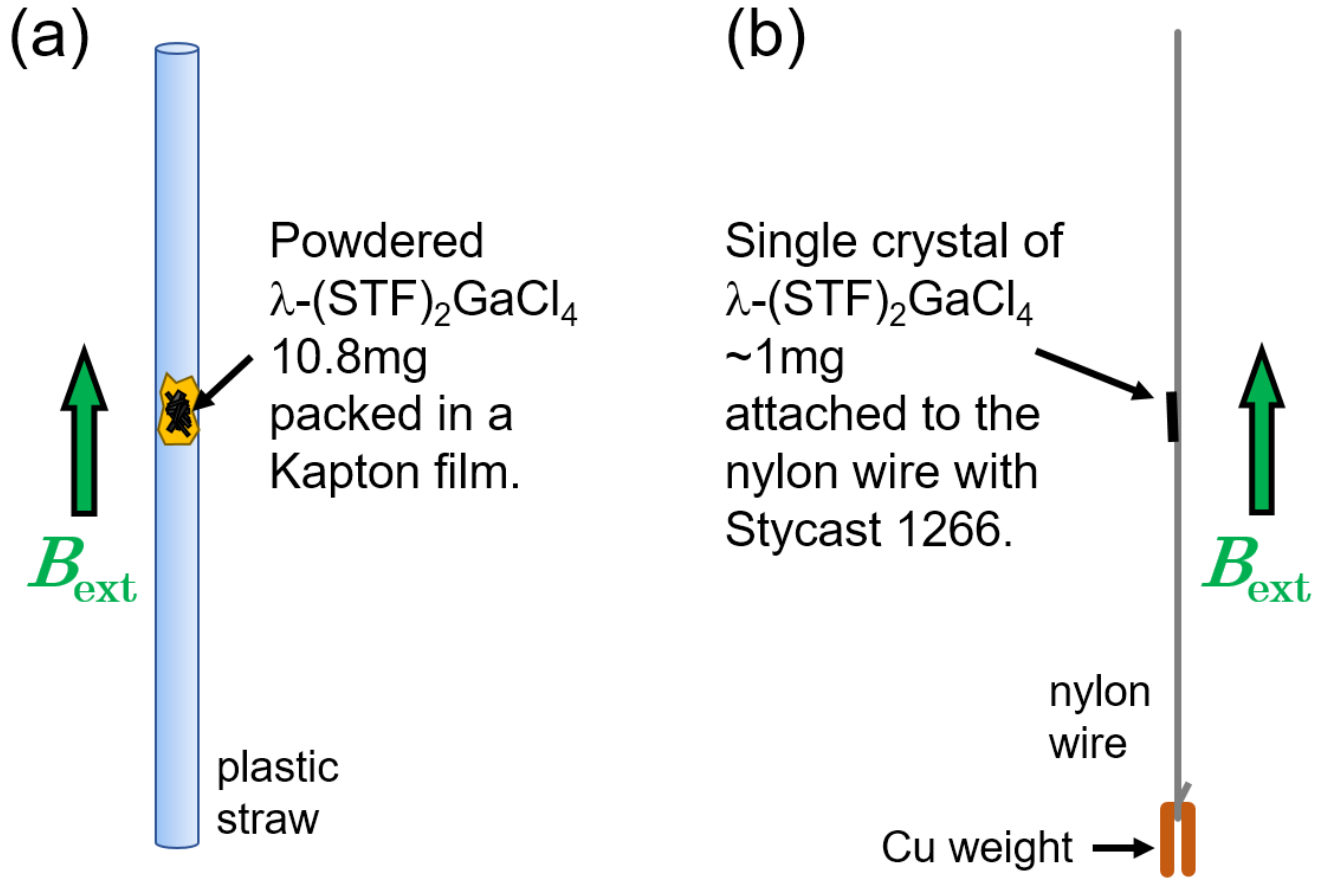


Figure 2.2: Setup for susceptibility measurements for λ -(STF) $_2$ GaCl $_4$ of (a) powdered sample, and (b) single crystal.

λ -(STF) $_2$ GaCl $_4$

A static susceptibility measurements for λ -(STF) $_2$ GaCl $_4$ were performed on a powdered sample of 10.8 mg and a single crystal of $\sim$ 1 mg. under an external magnetic field B of 1.0 T. As shown in Fig. 2.2(a) and (b), the powdered sample packed in a Kapton sheet was placed inside a plastic straw, and the single crystal sample was attached to the nylon line with a small amount of the Stycast 1266.

The background signal of the sample holder was separately measured and

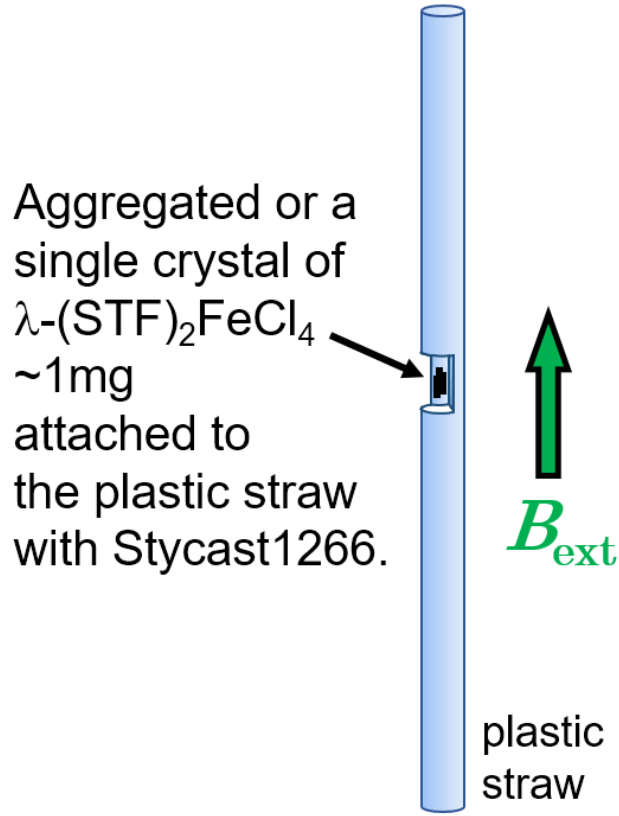


Figure 2.3: Setup for susceptibility measurements for $\lambda\text{-(STF)}_2\text{GaCl}_4$ of an aggregated sample.

subtracted from the result of the sample measurements. We measured the susceptibility for the powdered STF monocrystals and the GaCl_4 anion to estimate core diamagnetism and obtained -3.80×10^{-4} emu/mole.

$\lambda\text{-(STF)}_2\text{FeCl}_4$

A static susceptibility measurements for $\lambda\text{-(STF)}_2\text{FeCl}_4$ were performed on an aggregate of crystals of ~ 1.2 mg aligned along the c -axis, and a single crystal of ~ 0.1 mg under the external magnetic field up to 5 T. A external magnetic field is applied parallel and perpendicular to the c -axis and measurements

with $B_{\text{ext}} \perp c$ and $B_{\text{ext}} // c$ were conducted for the same sample. As shown in Fig. 2.3, the aggregated sample or a single crystal are attached to the plastic straw with the Stycast 1266. As the sample spaces, a part around the sample of plastic straw was cut and folded on the inside.

The signals of the core diamagnetism, the sample holder, and the Curie-tail contribution from the magnetic impurities were ignored since the spin contribution of the sample is a thousand times larger than such signals.

2.4 Proton nuclear magnetic resonance

λ -(STF)₂GaCl₄

We conducted the proton nuclear magnetic resonance (¹H-NMR) measurements for λ -(STF)₂GaCl₄. The ¹H-NMR spectrum measurements were conducted for the single crystal, whose long axis corresponds to the c -axis under the static magnetic field of 2.37 T, which applied perpendicular to the c -axis, in the SC magnet. The reference frequency corresponds to the ¹H nuclei is 100.73 MHz. The ¹H-NMR spectra were obtained as the fast Fourier transformation (FFT) processed spin-echo signal. All spectra were obtained applying the individual frequency 100.73 MHz and the spectrum in the range of 100.73 ± 0.1 MHz is responsible, for the performance of the LC-circuit and receiver in the measurement setup equipments. The spectrum measurements were performed in the temperature range of 200-2 K. The temperature below 4.2 K is achieved by the pumping of ⁴He.

Spin-lattice relaxation time T_1 measurements were conducted for the powdered sample of λ -(STF)₂GaCl₄ below 4.2 K down to 1.3 K. T_1 is estimated

from the intensity of the free induction decay (FID) obtained by the spin-echo method. The static magnetic field of 0.93 T is applied by the electromagnet. The FID intensity at the time t is proportional to the magnetization $M(t)$ and the measurements for various t gives the relaxation curve. The relaxation process is given as

$$M(t) = M_0 \left(1 - A_0 e^{-t/T_1}\right), \quad (2.1)$$

where M_0 is the magnetization at the thermal balanced limit and A_0 is the parameter to correct the division at $t = 0$. Therefore, we estimated T_1 by the linear fitting of the semilogarithmic plot of $M_0 - M(t)/A_0 M_0$.

λ -(STF)₂FeCl₄

The ¹H-NMR measurements for the needle-like single crystal were conducted for λ -(STF)₂FeCl₄ in the temperature range of 70 - 4.2 K. As shown in Fig. 2.4, the sample are attached to the glass stage, which can be rotated in the polarizing coil, by a small amount of silicon vacuum grease. The polarizing coil (number of turns is 10) is made by the ϕ 0.3 mm Cu line, whose coating were completely removed. The external magnetic fields of 3.117 ± 0.15 T, corresponding to the reference frequency of 132.5 MHz, were applied perpendicular to the c -axis in the SC magnet.

Field-swept spectra were obtained by the FFT of the spin-echo signal with a $\pi/2$ - π pulse sequence with static frequency 132.5 MHz. T_1 is estimated from the intensity of the FID curve obtained by the spin-echo method. We estimated T_1 using the same analysis to that in λ -(STF)₂GaCl₄.

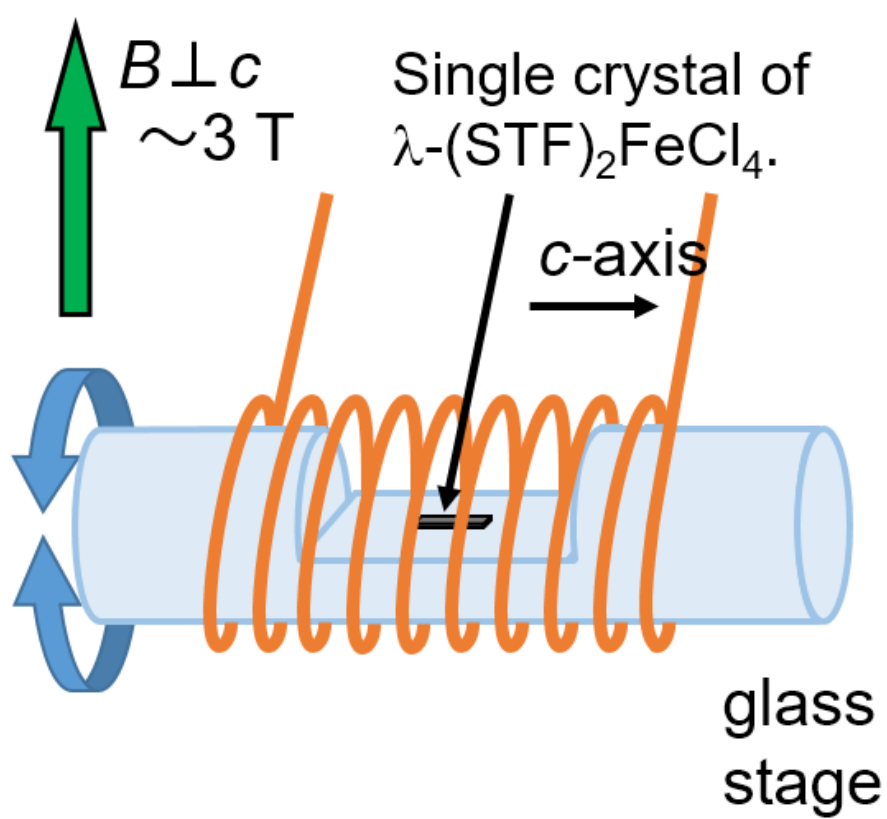


Figure 2.4: Sample mount for ^1H -NMR measurements for the single crystal of $\lambda\text{-(STF)}_2\text{FeCl}_4$.

Chapter 3

Results and discussion

3.1 λ -(STF)₂GaCl₄

3.1.1 Electrical resistivity

Figure 3.1 shows the temperature dependence of the electrical resistivity in λ -(STF)₂GaCl₄ at various pressures above 1.10 GPa for sample #0 and #1. Below 1.10 GPa, the resistivity monotonically increased with decreasing temperature. At 1.22 GPa, the divergence of resistivity below 50 K is suppressed and it shows a sudden drop below 5.1 K. In the range from 1.27 GPa to 1.35 GPa, the insulating behavior at high temperature region is suppressed gradually and it shows a local maximum structure, which was due to the mild insulator-metal (IM) transition around 25-50 K. The IM transition temperature T_{IM} shifts higher and the peak is broadened with increasing pressure. Above 1.60 GPa, this peak disappeared and a very wide metallic phase appeared.

The extended figure for the low temperature region is shown in Fig. 3.3. The resistivity shows sharp drop at 5.90, 5.90, 5.95 and 5.20K for 1.27, 1.31,

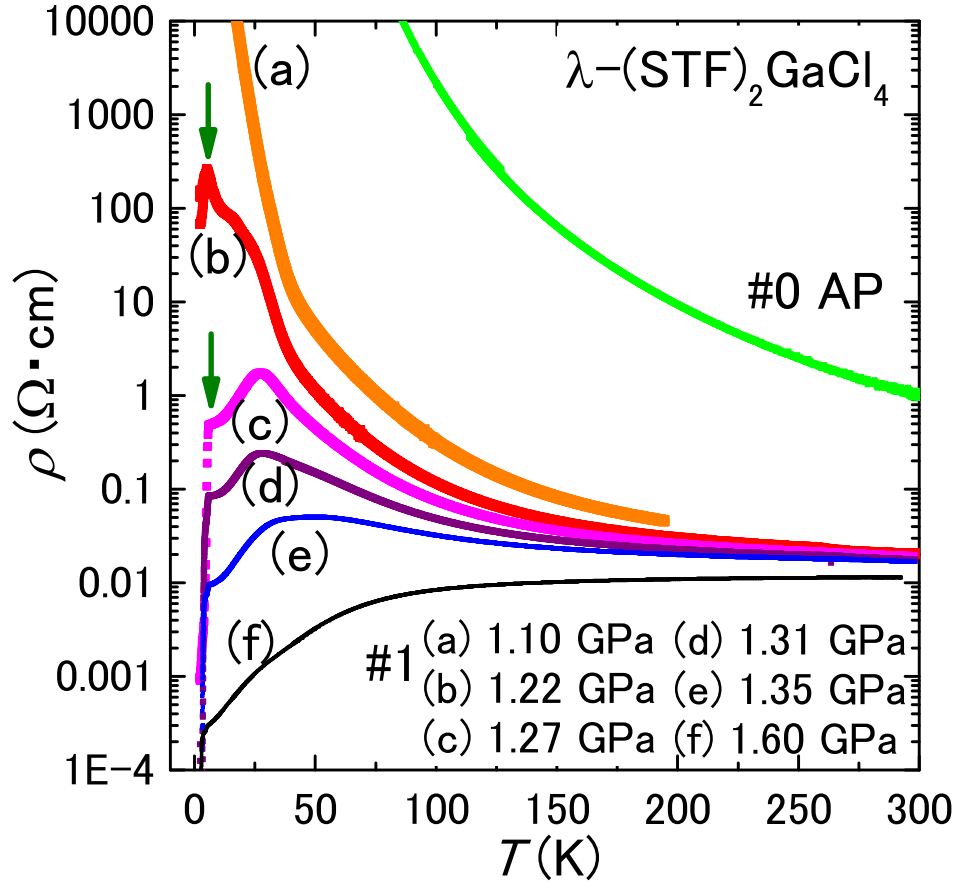


Figure 3.1: Temperature dependence of the electrical resistivity of $\lambda-(\text{BEDT-STF})_2\text{GaCl}_4$ at various pressures: ambient pressure for sample $\#0$, (a) 1.10, (b) 1.22, (c) 1.27, (d) 1.31, (e) 1.35, (f) 1.60 GPa for sample $\#1$.

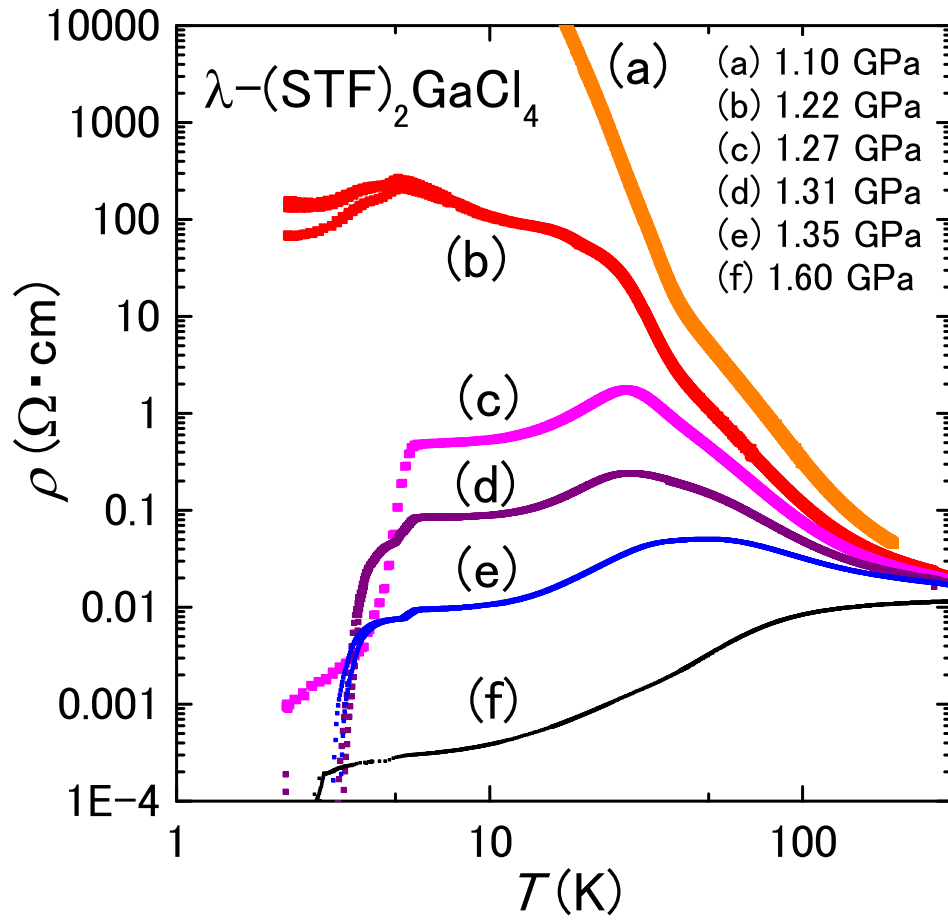


Figure 3.2: Logarithmic plot for horizontal axis of Fig. 3.1.

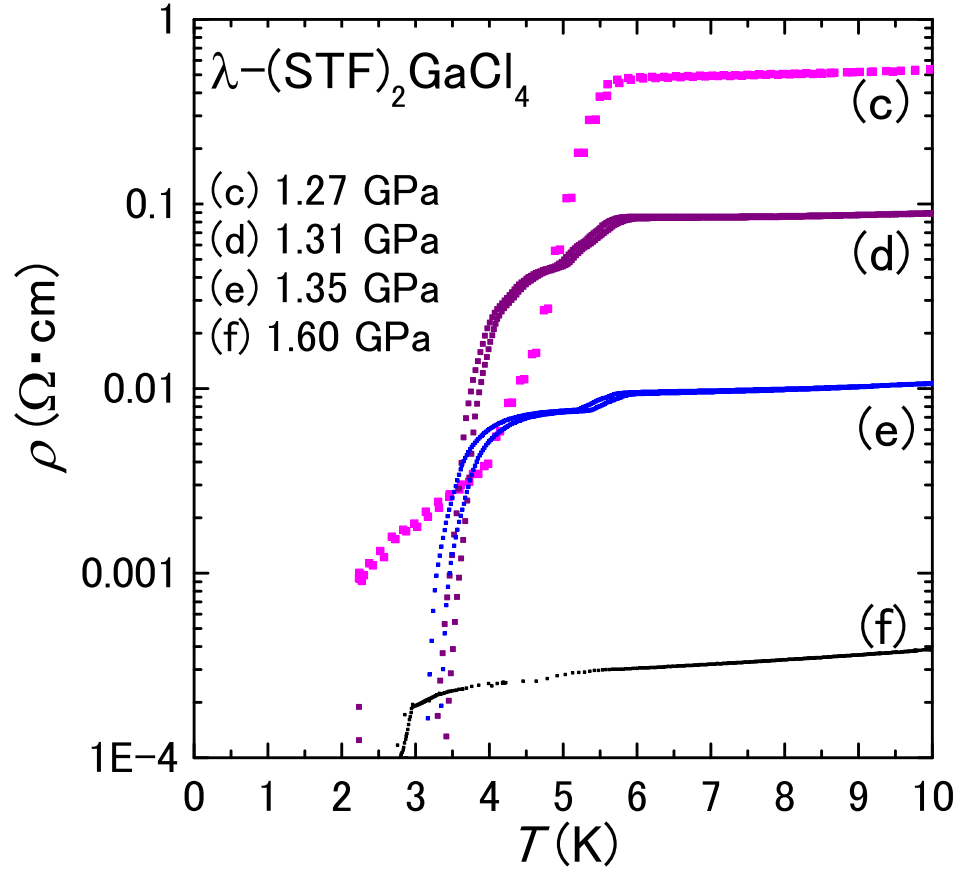


Figure 3.3: Enlarged view of the Fig. 3.1 for the low temperature region.

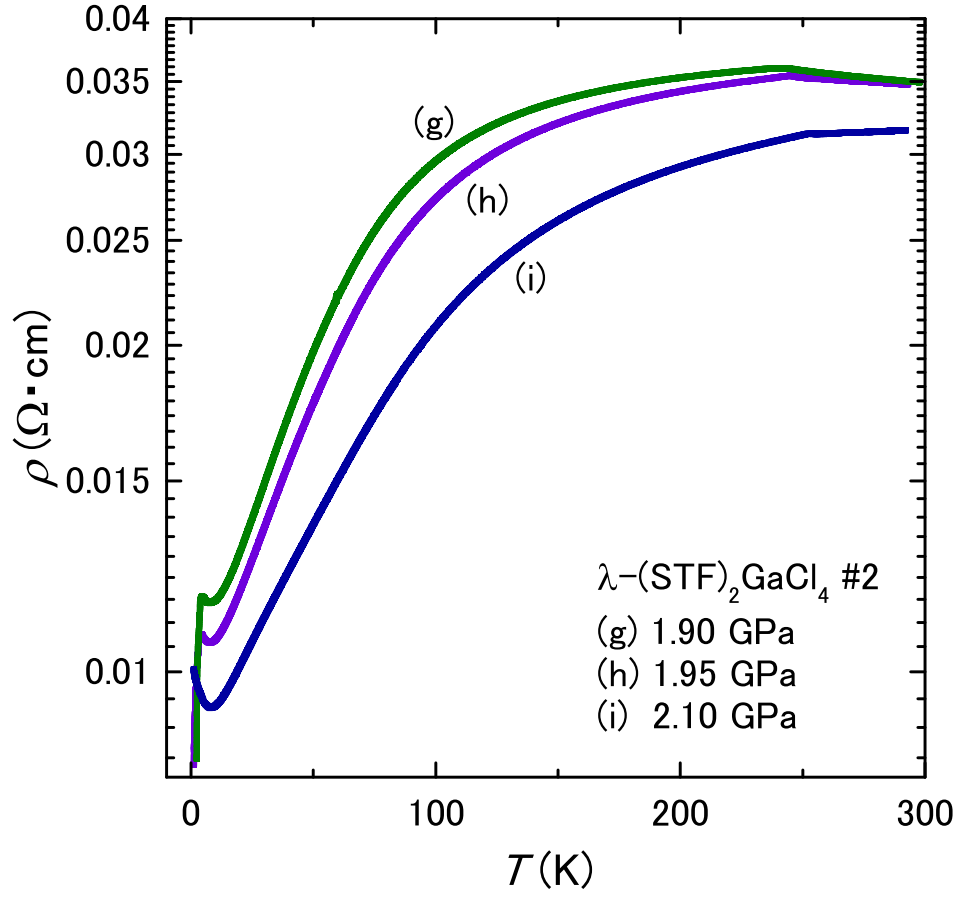


Figure 3.4: Temperature dependence of the electrical resistivity of $\lambda-(\text{BEDT-STF})_2\text{GaCl}_4$ at various pressures: (g) 1.90, (h) 1.95, and (i) 2.10 GPa for sample #2.

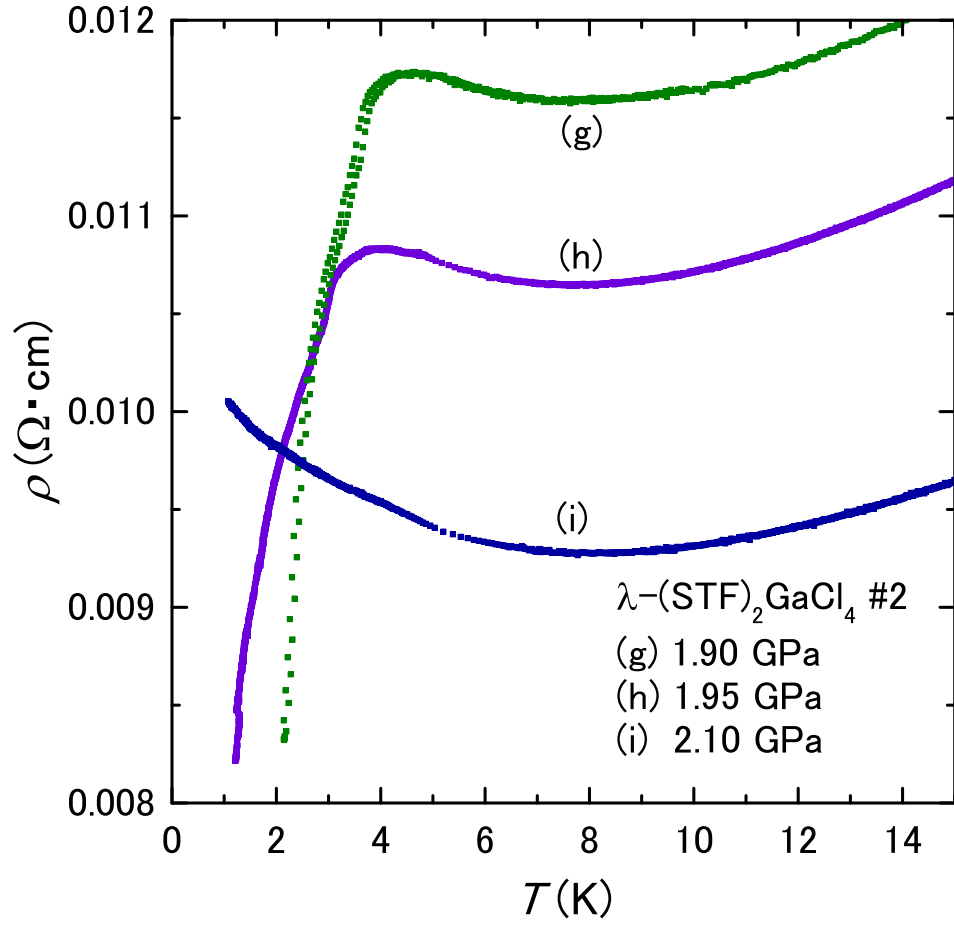


Figure 3.5: Enlarged view of the Fig. 3.4 for the low temperature region.

1.35, and 1.60 GPa, which is reminiscent the SC transition. The onset temperature of the resistivity drop increased in the range from 1.22 GPa to 1.35 GPa and then gradually decreased above 1.35 GPa. Cooperatively with resistivity drop, the double shoulder-shaped anomalies are observed, which can be attributed to inhomogeneities in the pressure due to the solidified pressure medium. However, it is not clear and needs more investigation for sample dependence.

Figure 3.4 shows the temperature dependence of the electrical resistivity for sample #2 at the higher pressure region. Over the whole temperature range, the resistivity in sample B at 1.90 GPa ((g) in Fig. 3.4), is larger than that in sample #1 at 1.60 GPa ((f) in Fig. 3.1). This is probably due to micro-cracks in sample #2. In addition, the resistivity ratio $\rho_{300\text{K}}/\rho_{6\text{K}} \sim 3$ in sample B at 1.90 GPa was much less than $\rho_{300\text{K}}/\rho_{6\text{K}} \sim 40$ in sample A at 1.60 GPa. We deduce that the sample #1 has much better quality than sample #2.

The extended figure for the low temperature region is shown in Fig. 3.5. The onset temperatures of the sharp drops in the resistivity are 3.8 K and 3.1K at 1.90 GPa and 1.95 GPa respectively. The shoulder type anomaly appears with the resistivity drop also in the sample #2. The resistivity drop is suppressed above 2.10 GPa down to 1.1 K. In the sample #2, its resistivity shows a minimum at 8 K and it increases with decreasing temperature down to the lowest temperature. The upturn of the resistivity just above the SC transition is observed only in sample #2 and it is probably caused by the localization effect due to the disorder.

To elucidate the electrical state at low temperatures, we measured resis-

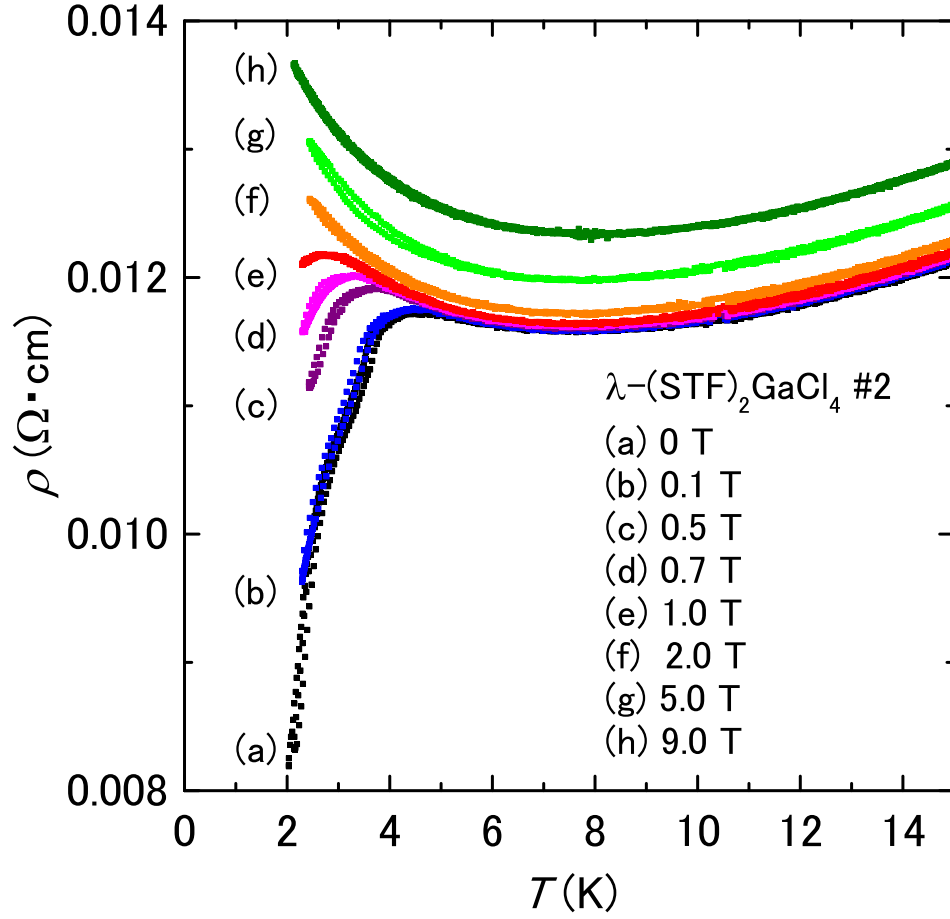


Figure 3.6: Temperature dependence of the resistivity at 1.90 GPa of sample B for various magnetic fields: (a) 0, (b) 0.1, (c) 0.5, (d) 0.7, (e) 1.0, (f) 2.0, (g) 5.0, and (h) 9.0 T were applied perpendicular to the c -axis. The resistivity curves at 0 T and 0.1 T show almost same behavior; thus, their curves overlap.

tivity while applying a magnetic field for sample #2. Fig. 3.6 shows the temperature dependence of the resistivity for various magnetic fields at 1.90 GPa in the temperature range of 2-30 K. The magnetic fields were applied perpendicular to the c -axis. The resistivity curves at 0 T and 0.1 T almost overlap. The resistivity drop at 0 T below 3.8 K was completely suppressed above 2 T. From this behavior, we can confirm the superconductivity below 3.8 K. This is the first observation of an SC phase in the λ -(STF)₂GaCl₄ salt. Above 5 K, magnetoresistance was proportional to the magnetic field B . The insulating behavior below 8 K continue at low temperatures above 2 T in sample #2.

3.1.2 Pressure-temperature phase diagram

We obtained the SC transition temperature T_c from the onset of the resistivity drop, as it is difficult to determine T_c from the midpoint of the transition due to the double shoulder structure in the resistivity curve. We present the hydrostatic pressure-temperature (P - T) phase diagram in Fig. 3.7 together with the insulator-metal boundary temperature T_{IM} . In the figure, the open and solid symbols correspond to samples A and B, respectively. Above 1.22 GPa, the SC phase appears abruptly. With increasing pressure, T_c increases gradually, and the pressure 1.35 GPa gives the highest $T_c = 5.95$ K. Above 1.35 GPa, T_c decreases. The metallic phase is observed above SC phase. The temperature region of metallic phase becomes wider with increasing pressure and above 1.60 GPa, it appears up to the room temperature.

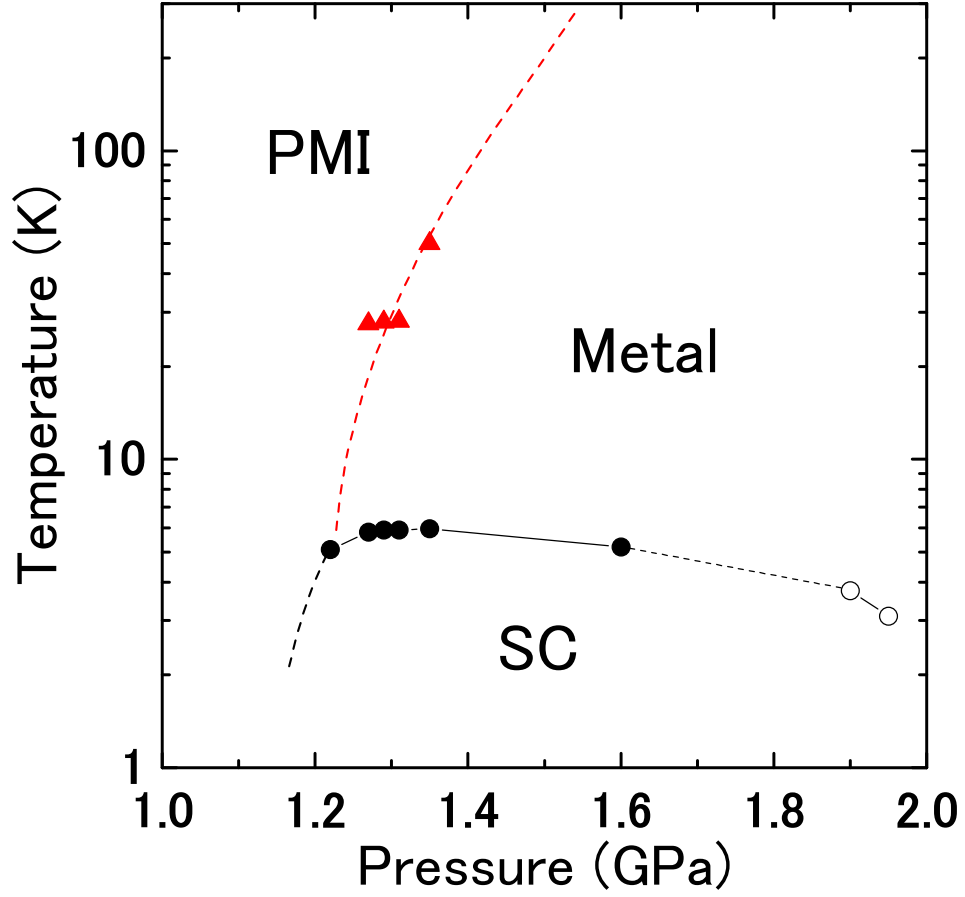


Figure 3.7: P - T phase diagram for λ -(STF)₂GaCl₄ salt. Open and solid circles represent the onset superconducting temperature T_c obtained from samples A and B, respectively. Solid triangles are the insulator-metal boundary obtained from the local maximum in resistivity.

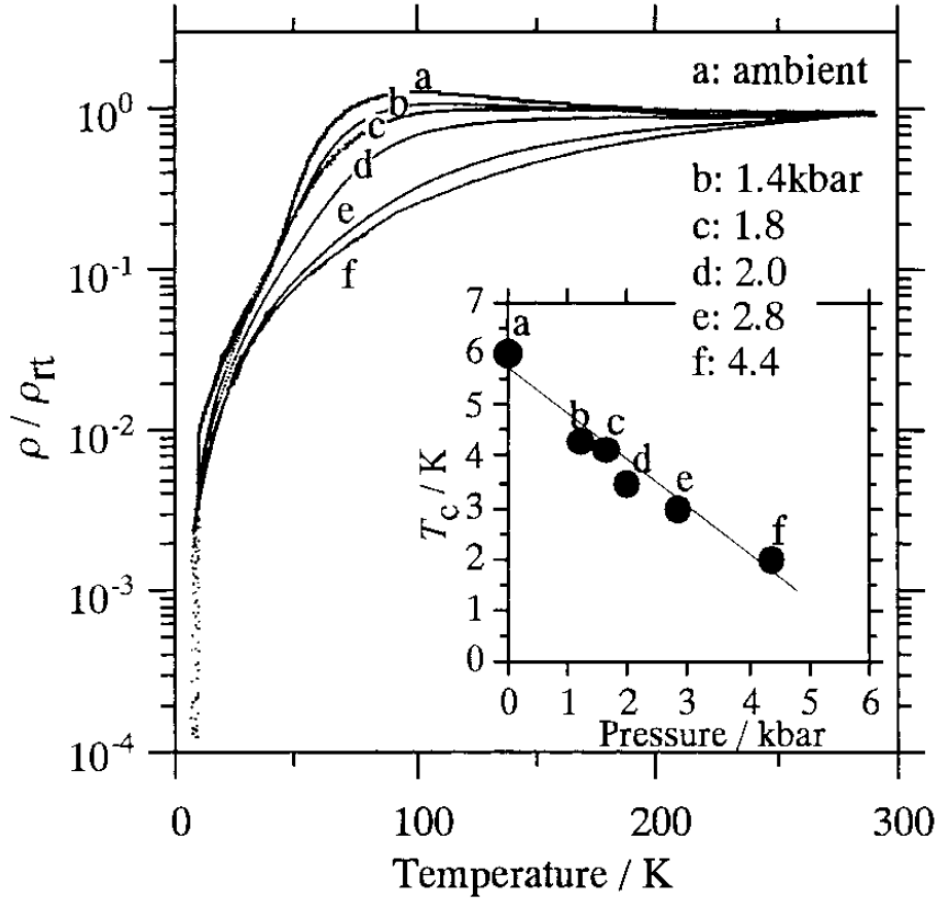


Figure 3.8: Pressure dependence of electrical resistivity for λ -(BETS) $_2$ GaCl $_4$ ((a) ambient pressure, (b) 0.14 , (c) 0.18, (d) 0.20, (e) 0.28, (f) 0.44 GPa). [13]

3.1.3 Phase diagram of λ -D $_2$ GaCl $_4$

We now compare the present results for λ -(STF) $_2$ GaCl $_4$ with λ -(ET) $_2$ GaCl $_4$ and λ -(BETS) $_2$ GaCl $_4$. As shown in the previous section, we found the SC phase in the STF salt above 1.22 GPa for the first time. The λ -STF salt above 1.35 GPa corresponds to the λ -BETS salt at ambient pressure (Fig. 3.8)[13]. The $T_c = 5.5$ K in the λ -(BETS) $_2$ GaCl $_4$ [11], which is obtained from the mid-point of the resistivity drop, is close to that of λ -(STF) $_2$ GaCl $_4$ at 1.35 GPa. Accordingly, this superconductivity is the same as that in λ -(BETS) $_2$ GaCl $_4$

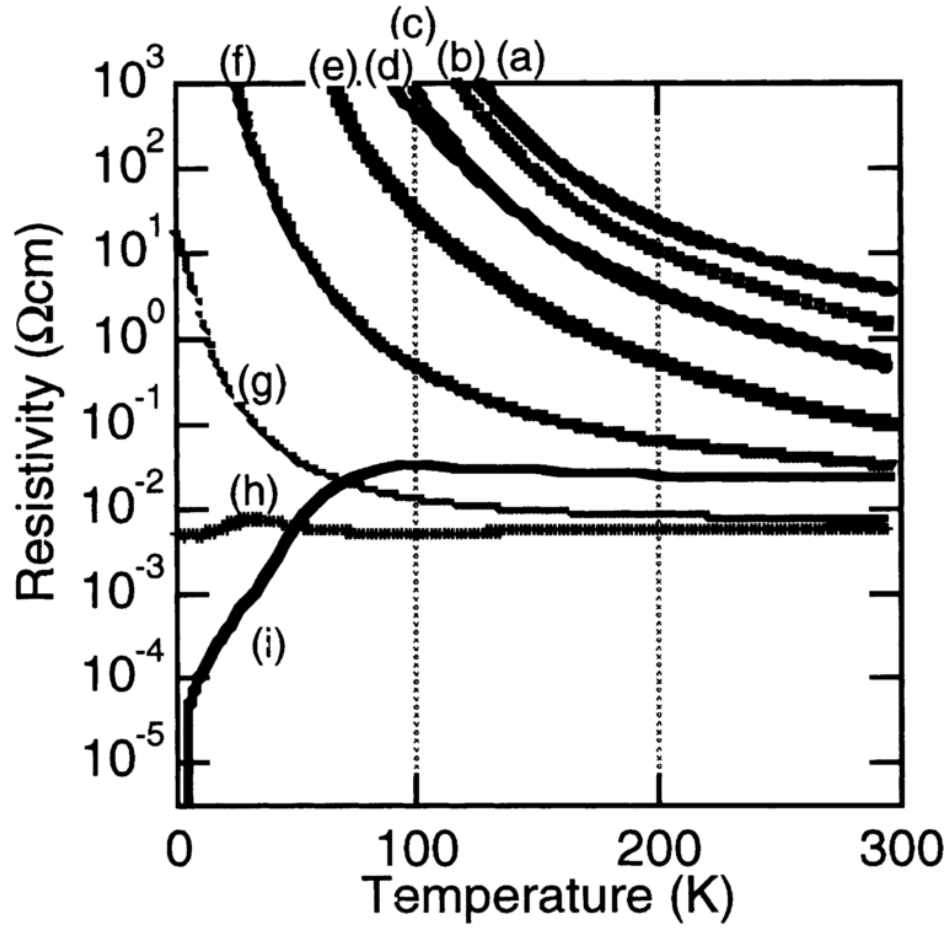


Figure 3.9: Pressure dependence of electrical resistivity for λ -(ET) $_2$ GaCl $_4$ ((a) 1 bar, (b) 4.5 kbar, (c) 16.5 kbar), λ -(STF) $_2$ GaCl $_4$ ((d) 1 bar, (e) 4.5 kbar, (f) 13.5 kbar, (g) 17.3 kbar, (h) 18 kbar), and λ -(BETS) $_2$ GaCl $_4$ ((i) 1 bar). [10]

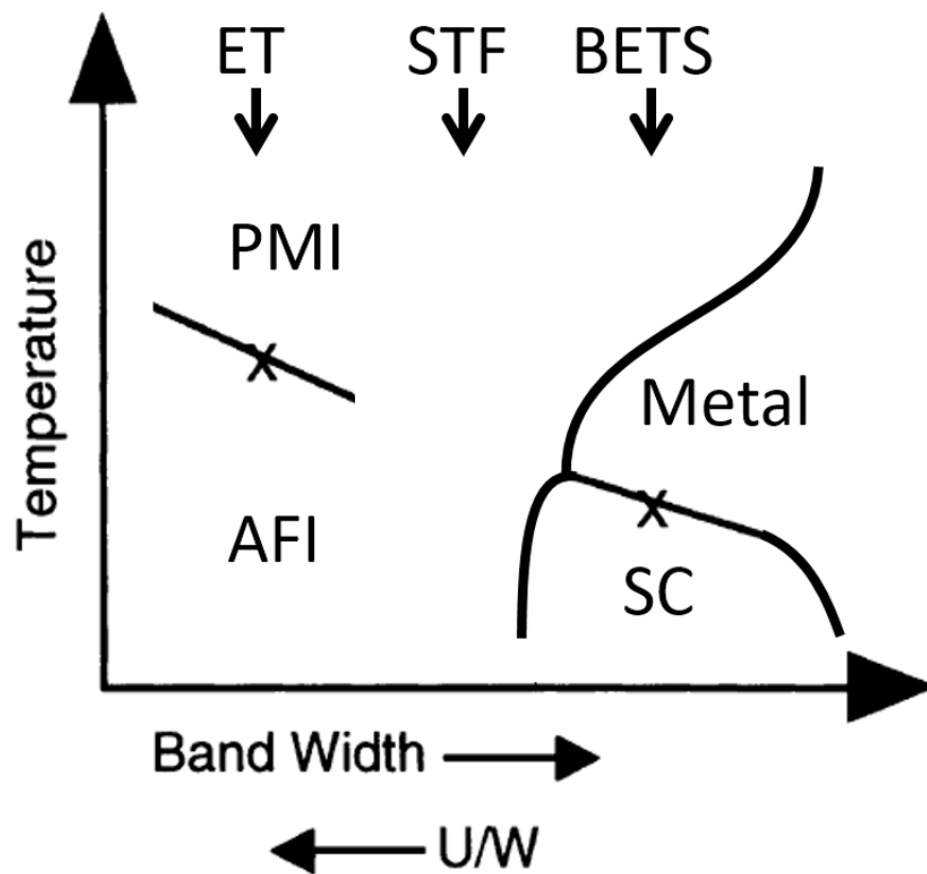


Figure 3.10: Universal phase diagram for λ - D_2 GaCl₄.

at ambient pressure.

As shown in Fig. 3.9, the resistivity in the λ -ET salt at ambient pressure showed insulating behavior over all temperature range and the resistivity in the λ -ET salt under 1.65 GPa shows almost the same behavior to that in the λ -STF salt at ambient pressure[10]. This suggests that the hydrostatic pressure of 1.65 GPa for λ -(ET)₂GaCl₄ plays the same role to the chemical pressure induced by the changing of the donor molecules from the ET to the STF. However, obvious SC transition was not observed in the λ -STF salt up to 1.80 GPa in their report. This should be caused by the quality of the crystal because the resistivity ratio $\rho_{300\text{K}}/\rho_{6\text{K}}$ in their report ~ 1 is smaller than our results $\rho_{300\text{K}}/\rho_{6\text{K}} \sim 40$ and 3 for sample #1 and #2, respectively. From these results, we deduced that the all of the λ -D₂GaCl₄ family can be placed on the universal phase diagram shown in Fig. 3.10.

3.1.4 Static Susceptibility

Figure 3.11 shows the temperature dependence of the static spin susceptibility χ_s measured for the powdered λ -(STF)₂GaCl₄ of 10.8 mg. The measurement was performed at ambient pressure under an external magnetic field of 1.0 T. The background signal of the sample holder was separately measured and subtracted from the result of the sample measurements. To subtract the component of the core diamagnetisms, we measured the susceptibility for the powdered STF, TBA-GaCl₄, and TBA-Br monocrystals and obtained $\chi_{\text{STF}} = -1.65 \times 10^{-4}$, $\chi_{\text{TBA-GaCl}_4} = -1.90 \times 10^{-4}$, and $\chi_{\text{TBA-Br}} = -1.75 \times 10^{-4}$ emu/mole. The core diamagnetisms of $\chi_{\text{Br}} = -0.35 \times 10^{-4}$

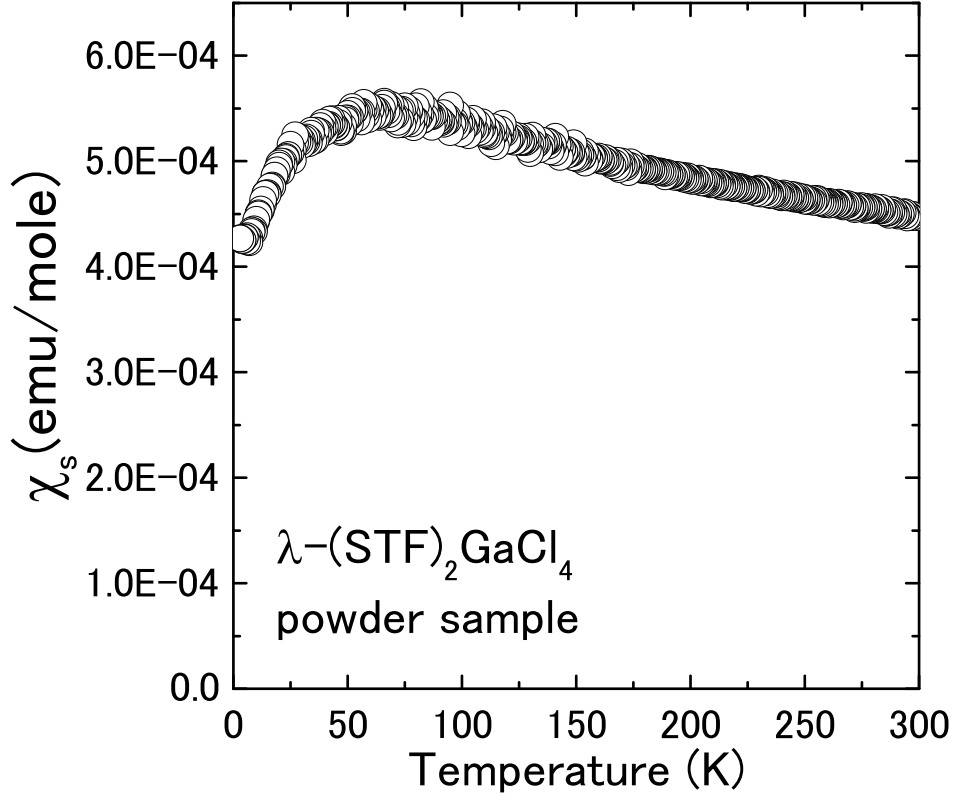


Figure 3.11: Temperature dependence of the static spin susceptibility in λ -(STF)₂GaCl₄ measured on a powdered sample of 10.8 mg. The external magnetic field of 1 T is applied. Open circles represent the measurements. Core diamagnetisms was -3.80×10^{-4} emu/mole and Curie components were subtracted from the original data.

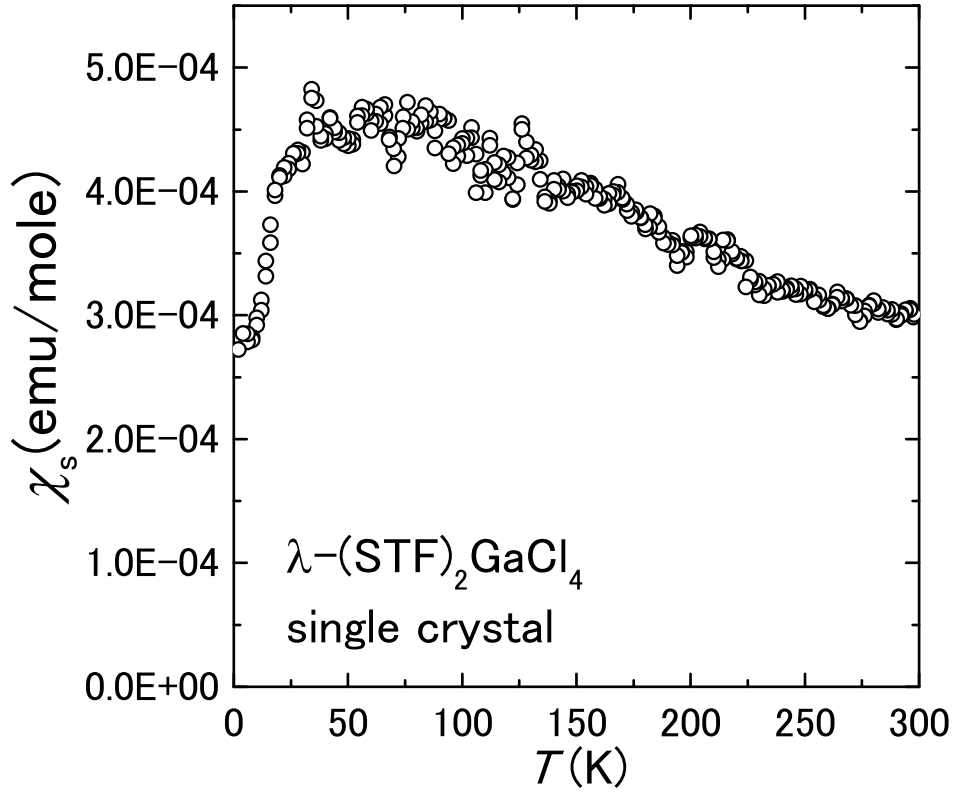


Figure 3.12: Temperature dependence of the static spin susceptibility in λ -(STF) $_2$ GaCl $_4$ measured on a single crystal of approximately 1 mg. The external magnetic field of 1 T is applied parallel to c -axis. Core diamagnetisms was -3.80×10^{-4} emu/mole and Curie components were subtracted from the original data.

emu/mole, was obtained from the previous report[24]. Accordingly, we estimated the core diamagnetisms of sample salt as -3.80×10^{-4} emu/mole from $2\chi_{\text{STF}} + (\chi_{\text{TBA-GaCl}_4} - \chi_{\text{TBA-Br}} + \chi_{\text{Br}})$. The component of Curie-tail was estimated from the low temperature region of observed susceptibility and subtracted. The results for a single crystal of $\approx 1\text{mg}$, are shown in Fig. 3.12. The external magnetic field of 1 T is applied parallel to the c -axis. Since the static susceptibility for the powder and single crystal show the same temperature dependence, χ_s is isotropic against the direction of the magnetic field. The value of χ_s increases with decreasing temperature down to 65 K. At low temperatures below 25 K, χ_s displayed a gradual decrease. Down to 2 K, there is no anomaly such as a sharp drop, which corresponds to the transition to the magnetic ordered phase.

3.1.5 Proton nuclear magnetic resonance

NMR spectrum

To elucidate the magnetic state of λ -(STF) $_2$ FeCl $_4$ at ambient pressure, we carried out the nuclear magnetic resonance measurements for proton sites (^1H -NMR). Figure 3.13 shows NMR spectrum for various temperature of λ -(STF) $_2$ GaCl $_4$. The measurements are conducted for a single crystal and the magnetic field of 2.37 T is applied parallel to the c -axis, which is the needle axis of the sample. All spectrum can be fitted by a single Lorentz peak and we estimated the line width and shift from this analysis. The temperature dependence of the line width and NMR shift from the $\nu_0 = 100.73$ MHz, which is the resonance frequency of the free proton in the external field of

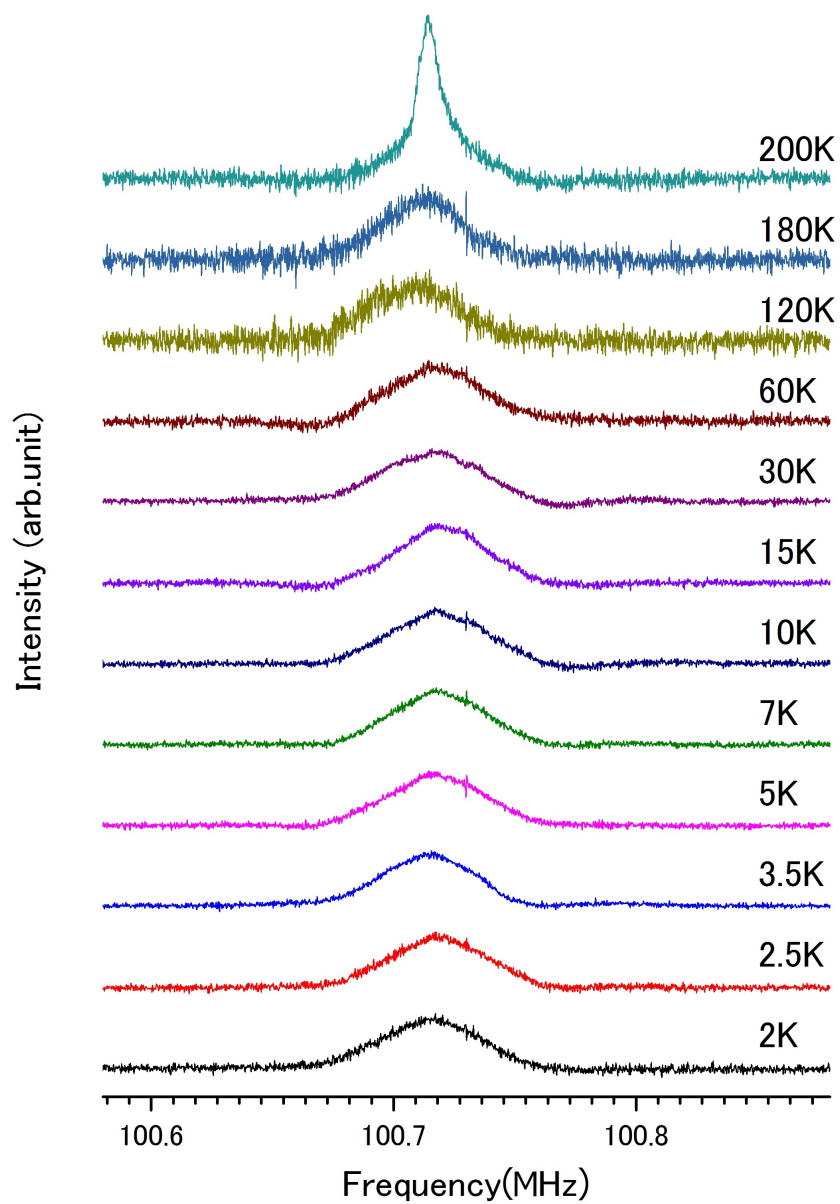


Figure 3.13: ^1H -NMR spectrum for various temperature for $\lambda\text{-(STF)}_2\text{GaCl}_4$.

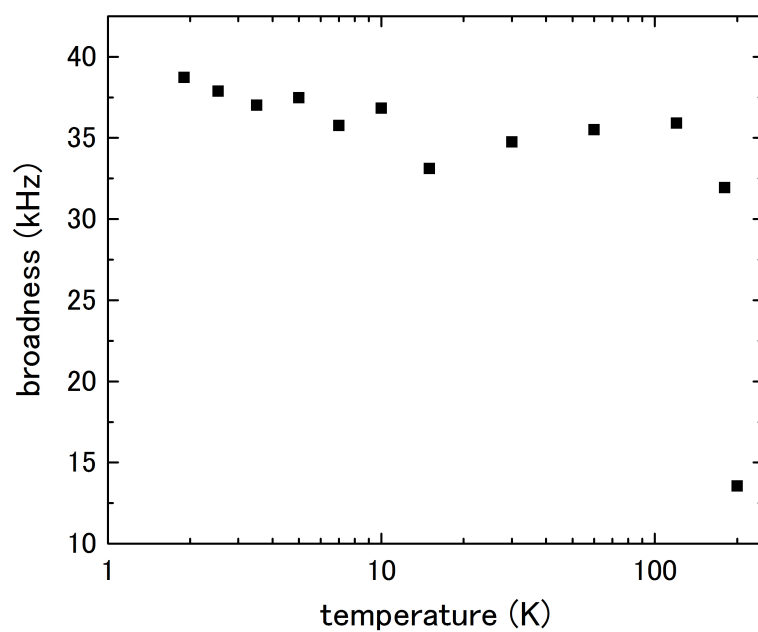


Figure 3.14: Temperature dependence of the line width of λ -(STF)₂GaCl₄.

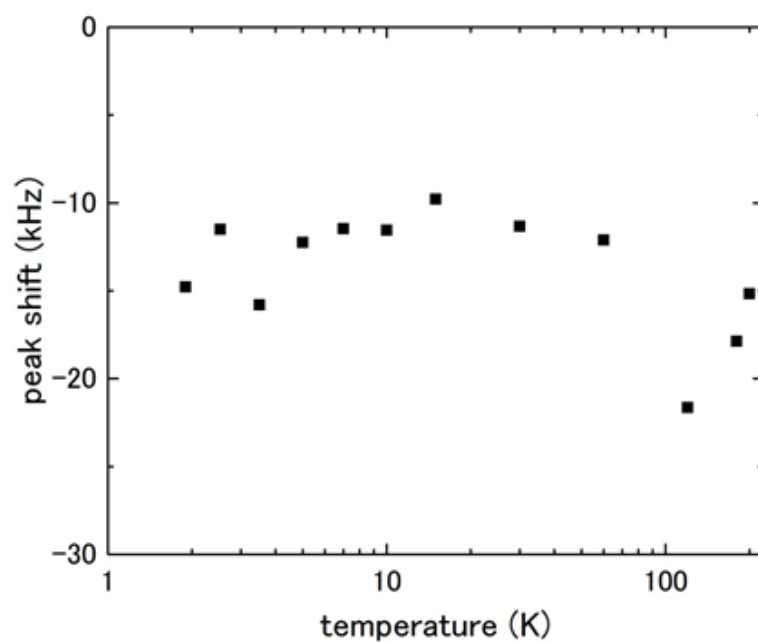


Figure 3.15: Temperature dependence of the NMR shift of λ -(STF)₂GaCl₄.

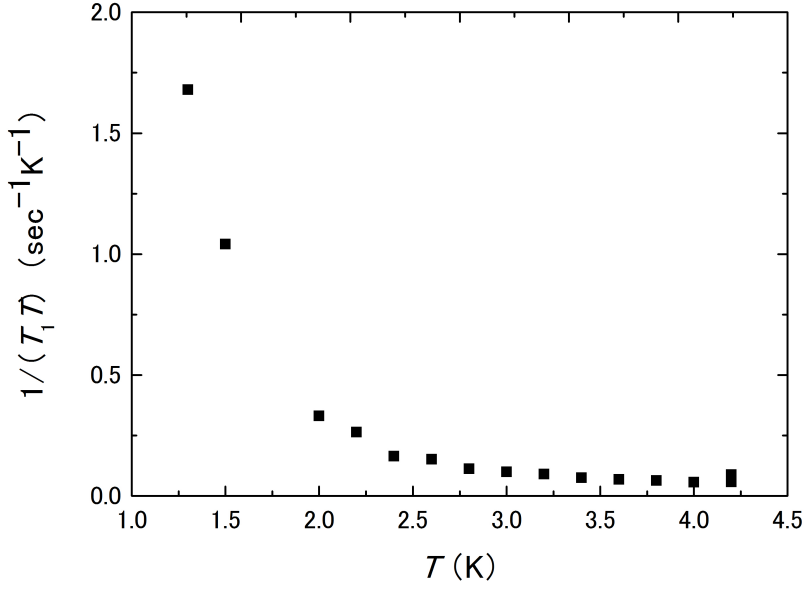


Figure 3.16: Temperature dependence of the $1/T_1T$ of λ -(STF)₂GaCl₄.

2.37 T, is shown in Fig. 3.14 and Fig. 3.15 respectively. Below 200 K, the broadening of the peak was observed. This behavior can be explained by the slowing of ethylene-motion, which is typically seen in the ET, STF, and BETS salts. With decreasing temperature, the line width and peak frequency do not change down to 2.5 K and it indicates that there is no appearance of the internal field.

Spin-lattice relaxation rate (T_1^{-1})

We also conducted the measurements for spin-lattice relaxation rate (T_1^{-1}) for the powder sample of λ -(STF)₂GaCl₄. Figure 3.16 shows the temperature dependence of $(T_1T)^{-1}$ in the temperature range from 4.2 K down to 1.3 K. In this temperature region, $(T_1T)^{-1}$ increase with decreasing temperature, which corresponds to the increasing of the critical slowing down due to the

	t'/t	J'/J
$\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$	1.06	1.12
$\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$	0.75	0.56
$\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$	0.68	0.46
$\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$	0.92	0.85

Table 3.1: t'/t of $\kappa\text{-(ET)}_2X$ for various anions X and $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$. [25, 26]

increasing of AF magnetic fluctuation. However, the peak structure, which reflects the AF transition, does not observed down to 1.3 K. This $(T_1T)^{-1}$ behavior without AF order, at least down to 1.3 K, is consistent to the result of the spin susceptibility, which does not shows the obvious step down due to the AF transition down to 2 K.

3.1.6 Discussion for the magnetic property in the insulating phase

Here, we discussed the magnetic properties in the ground state of $\lambda\text{-(STF)}_2\text{GaCl}_4$ at ambient pressure, which shows the insulating behavior. We found that the $\lambda\text{-(STF)}_2\text{GaCl}_4$ does not shows the obvious AF transition down to 1.5 K from our magnetic measurements. The broad hump structure of the temperature dependence of its spin susceptibility is reminiscent that of the $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$ or $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ as shown in Fig. 3.17 and Fig. 3.18, which are proposed to be the spin-frustration systems[47, 28]. $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$ undergoes an insulator-superconductor transition with increasing pressure 0.36 GPa[29] and its insulating state does not shows AF magnetic order at least down to 32 mK[47] unlike a $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$. This paramagnetic state is expected to be mainly caused by the spin-frustration in the triangular lattice structure. As shown in Fig. 3.19(a), in the regular triangle lattice network

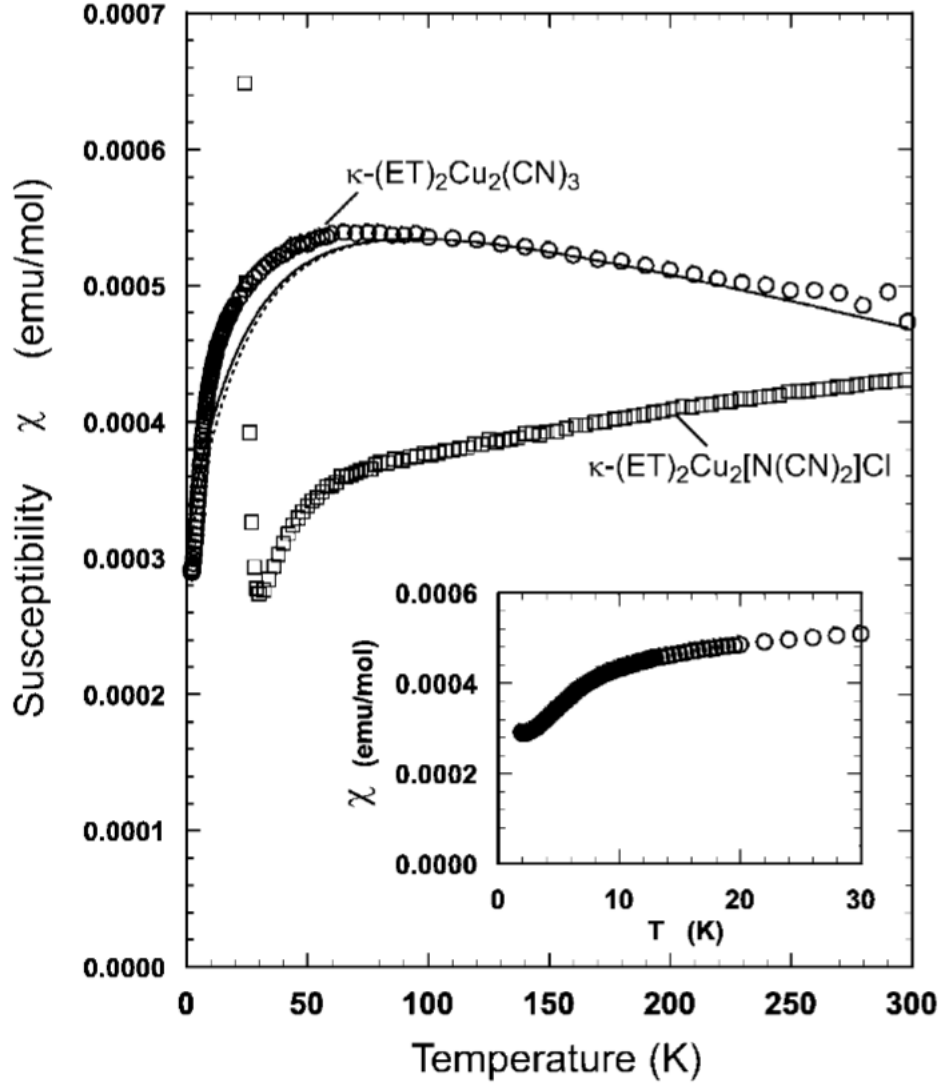


Figure 3.17: Temperature dependence of the static susceptibility of the powdered samples of $\kappa\text{-(ET)}_2\text{Cu}_2\text{(CN)}_3$ and $\kappa\text{-(ET)}_2\text{Cu}_2\text{[N(CN)}_2\text{]Cl}$. The solid and dotted curves represent the result of the series expansion of the triangular-lattice Heisenberg model using [6/6] and [7/7] Padé approximants with $J = 250$ K.[47]

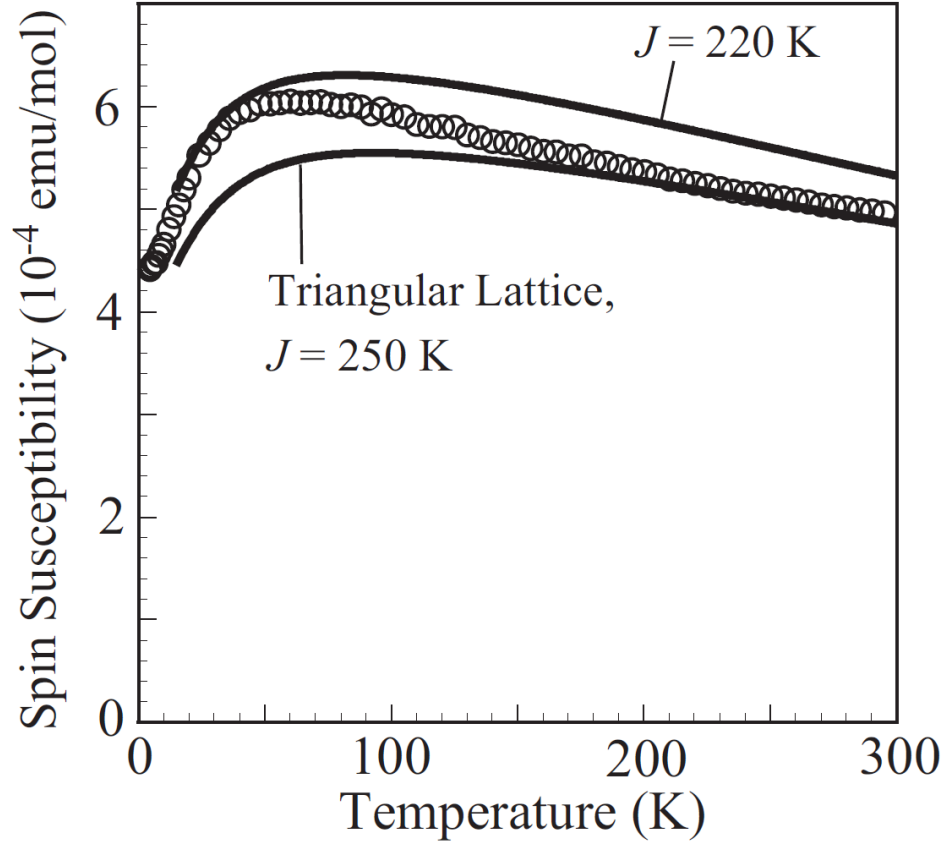


Figure 3.18: Temperature dependence of the static susceptibility of powdered samples of $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$. Solid curves show the result of the [7/7] Padé approximants for the high temperature expansion of the triangular-lattice Heisenberg model with $J = 220$ and 250 K.[28]

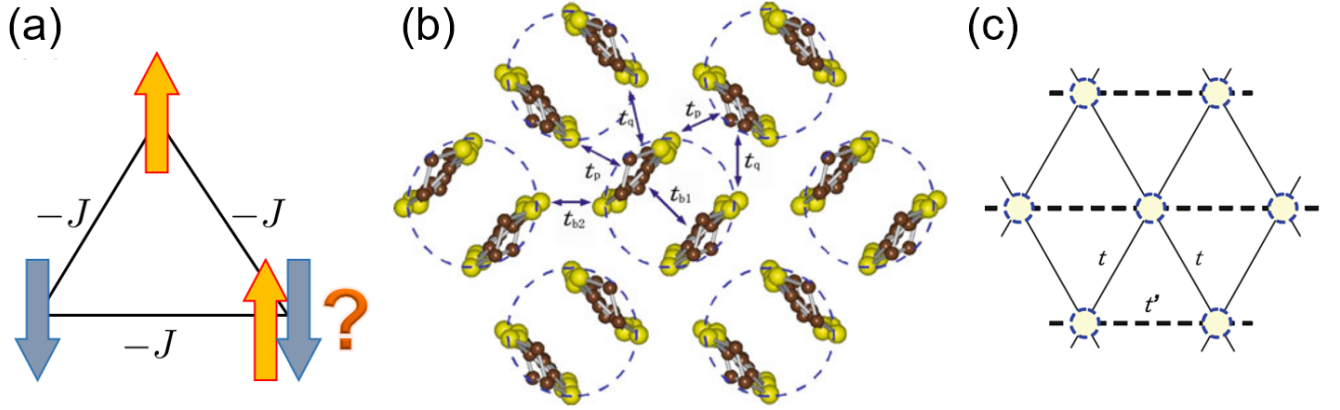


Figure 3.19: (a) Schematic drawing of the spin-frustration. (b) Arrangement of ET layer of κ -(ET) $_2X$, viewed along the long axes of ET molecules. Also shown are the transfer integrals between ET molecules, (c) Schematic representation of the two-dimensional ET layer obtained by regarding the face-to-face BEDT-TTF dimer pair as a single unit.[33]

of the exchange interaction J ($\propto t^2$), since the exchange field at one spin site is canceled out, and the AF long-range order is suppressed. The arrangement of ET molecules layer in κ -(ET) $_2X$ is shown in Fig. 3.19(b). In the κ -type structure, “face-to-face” pair of ET molecules is considered as a dimer unit and dimer units form a triangular lattice, as shown in Fig. 3.19(c), which is a simplified picture introduced by Kino and Fukuyama[30]. The effective transfer integrals between the dimer units can be estimated as $t = |t_p| + |t_q|/2$ and $t' = t_{b2}/2$, where t_p , t_q , and t_{b2} are defined in Fig. 3.19(c)[47]. The parameter of regularity of the triangular lattice, t'/t , in κ -(ET) $_2X$ and EtMe $_3$ Sb[Pd(dmit) $_2$] $_2$ are listed in Table 3.1. κ -(ET) $_2$ Cu $_2$ (CN) $_3$ and EtMe $_3$ Sb[Pd(dmit) $_2$] $_2$ have very regular triangle lattice.

A number of calculation for the spin behavior in the $S = 1/2$ two-dimensional Heisenberg AF system in a regular triangular lattice have been conducted. Elstner *et al.* calculate the temperature dependence of the susceptibility started

from the Hamiltonian, which is defined as the summation of $J\mathbf{S}_i \cdot \mathbf{S}_j$ over all nearest neighbor spin pairs (i, j),

$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \quad (3.1)$$

with adopting the [7/7] Padé approximant as a method for extrapolation to low temperature[31]. The calculated susceptibility expressed as

$$\chi = \frac{Ck_B}{J} \frac{4x(1 + b_1x + \cdots + b_6x^6)}{(1 + c_1x + \cdots + c_7x^7)} \quad (3.2)$$

where $C = N_A g^2 \mu_B^2 / 4k_B$, $x = J/4k_B T$, k_B is a Boltzmann constant, g is a g-factor, and μ_B is a Bohr magneton, with the coefficients $b_1 = 13.1382922$, $b_2 = 38.2639722$, $b_3 = 214.744540$, $b_4 = 260.983171$, $b_5 = 622.734802$, $b_6 = 186.114208$, and $c_1 = 19.1382922$, $c_2 = 129.093725$, $c_3 = 597.987880$, $c_4 = 1902.06491$, $c_5 = 3943.84464$, $c_6 = 5164.99740$, $c_7 = 3452.67229$ [32].

The spin susceptibility of κ -(ET)₂Cu₂(CN)₃ and EtMe₃Sb[Pd(dmit)₂]₂ are represented by this calculation with $J = 250, 220$ K at the low temperature region, respectively, as shown in the solid curves in Fig. 3.17 and Fig. 3.18. The present result for λ -(STF)₂FeCl₄ also can be well represented by this analysis. As shown in the solid curve in Fig. 3.20, below 150 K, the observed susceptibility and calculated line with $J = 165$ K are almost completely overlap. In the temperature range above 150 K, the data deviate from the fitted curve. This deviation can be caused by the thermal expansion effect typically seen in organic crystals. For example in TMTTF salts, it is known that the observed spin susceptibility, which is assumed to be a constant pressure susceptibility,

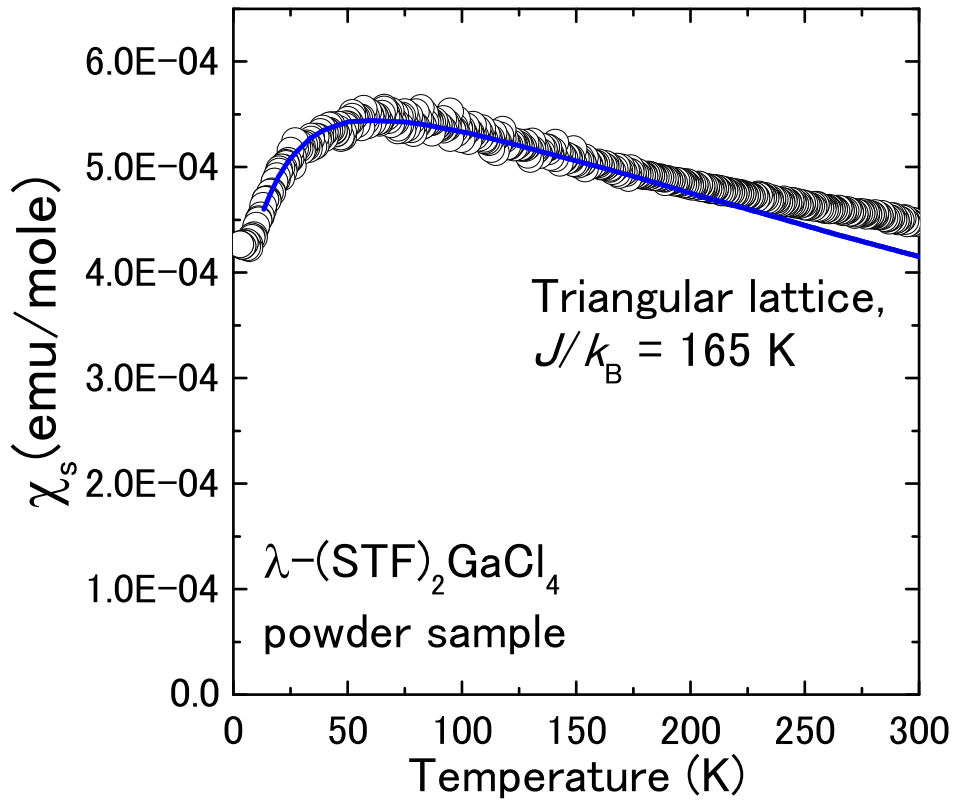


Figure 3.20: Temperature dependence of the static spin susceptibility in λ -(STF)₂GaCl₄ measured on a powdered sample of 10.8 mg, shown in Fig. 3.11. Solid line is the susceptibility curve calculated for the $S = 1/2$ Heisenberg AF model in a triangular lattice[31] with an exchange coupling constant $J = 165$ K.

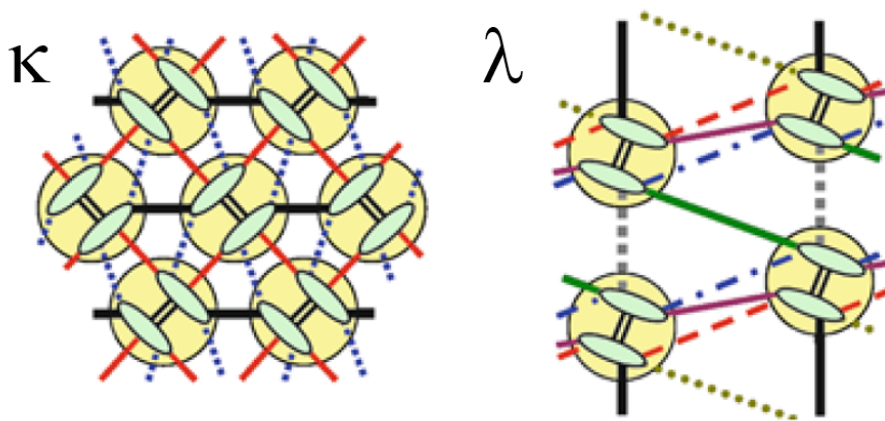


Figure 3.21: Geometry of donor layer in the organic conductor κ - and λ -(ET)₂X.[33]

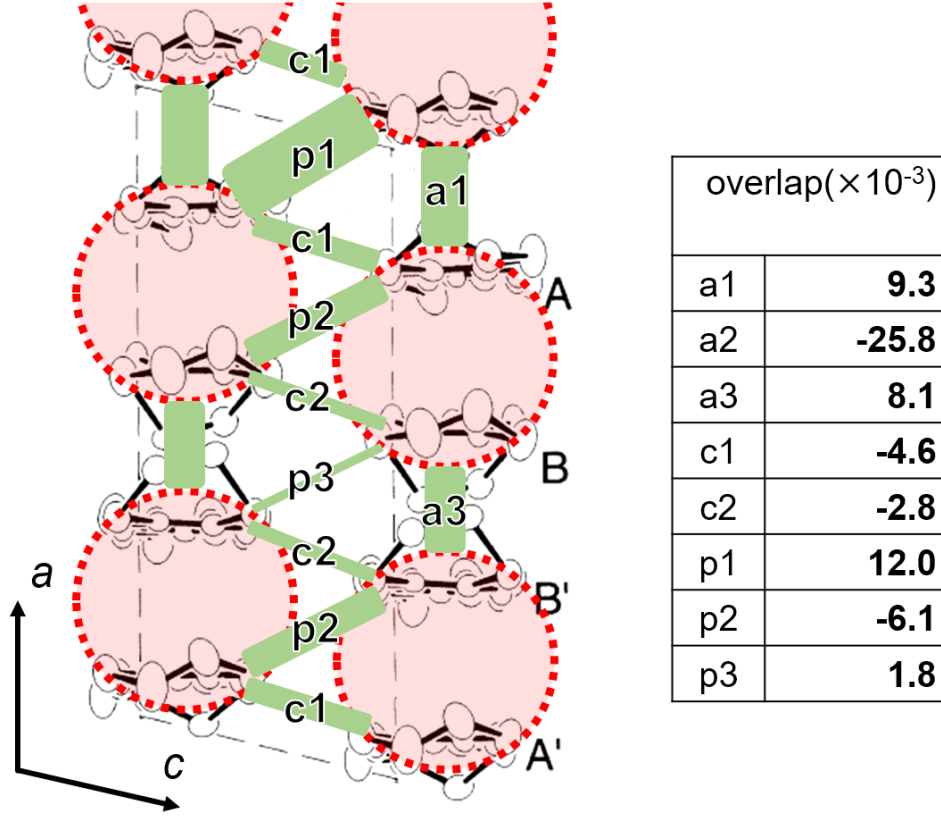


Figure 3.22: Schematic drawing of the explanation for triangle geometry of the transfer integrals[10] in λ -(ET) $_2$ X with polarization of charge density.

deviates from a constant volume susceptibility[34].

Since the susceptibility shows good agreement to the calculation of regular triangular model, the non-ordering state in λ -(STF) $_2$ GaCl $_4$ is thought to be caused by the spin-frustration mechanism like the κ -(ET) $_2$ Cu $_2$ (CN) $_3$ or EtMe $_3$ Sb[Pd(dmit) $_2$] $_2$. However, it is not yet clear whether spin frustration plays an important role in this phase because the geometry of the transfer integrals differs from the regular triangle as shown in Fig. 3.21[10]. Seo *et al.* calculated the transfer energies for λ -(BETS) $_2$ GaBr $_x$ Cl $_{4-x}$ from atomic coordinates and found that spin frustration in the AF Heisenberg system is not strong.[35]

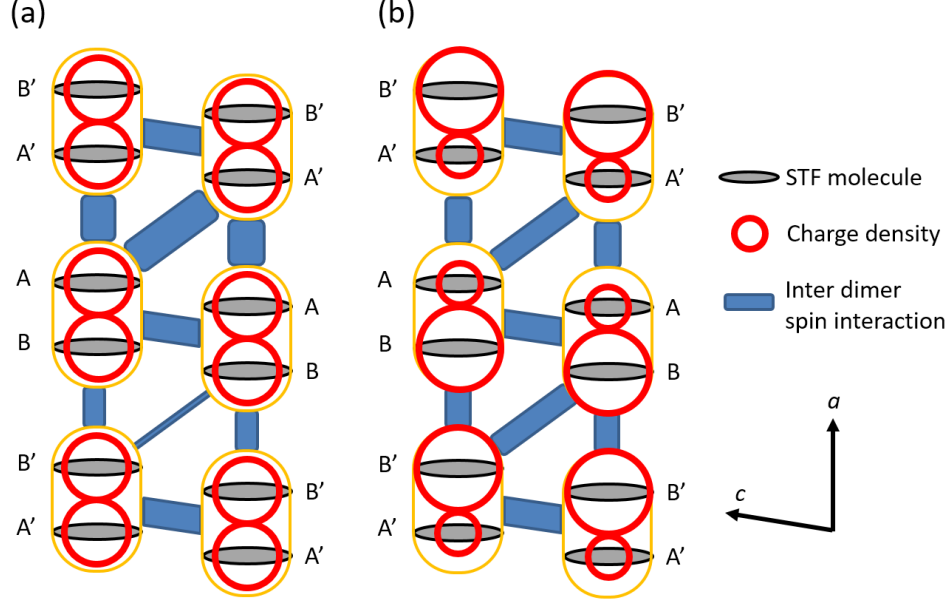


Figure 3.23: Schematic drawing of the explanation for triangle geometry of the transfer integrals in λ -(ET) $_2$ X with polarization of charge density.

As a possible scenario, we considered the freedom of the charge density. Fig. 3.22 shows the overlap integrals of λ -(BETS) $_2$ GaCl $_4$ calculated by Mori *et al*[10]. The red circles denote the dimer of BETS molecules and the thickness of the green lines are proportional to the magnitude of the inter dimer overlap integrals. Note that the inter-chain overlap integral between A and A' such as $p1(= 12.0 \times 10^{-3})$ and $c1(= -4.6 \times 10^{-3})$ is larger than that between B and B' such as $p3(= 1.8 \times 10^{-3})$ and $c2(= -2.8 \times 10^{-3})$. The schematic drawing of the inter-dimer overlap is shown in Fig. 3.22. Here, we consider the charge polarization in the dimers. As shown in in Fig. 3.23, if the charge density is concentrated at B and B' site, i.e. there is a o-O-O-o charge ordering in the stacking chain, where O (o) is charge rich (poor) site, the uniformity of the overlap integral improves and the geometry of the network of the exchange interactions reach to the regular triangle. The existence of the charge distri-

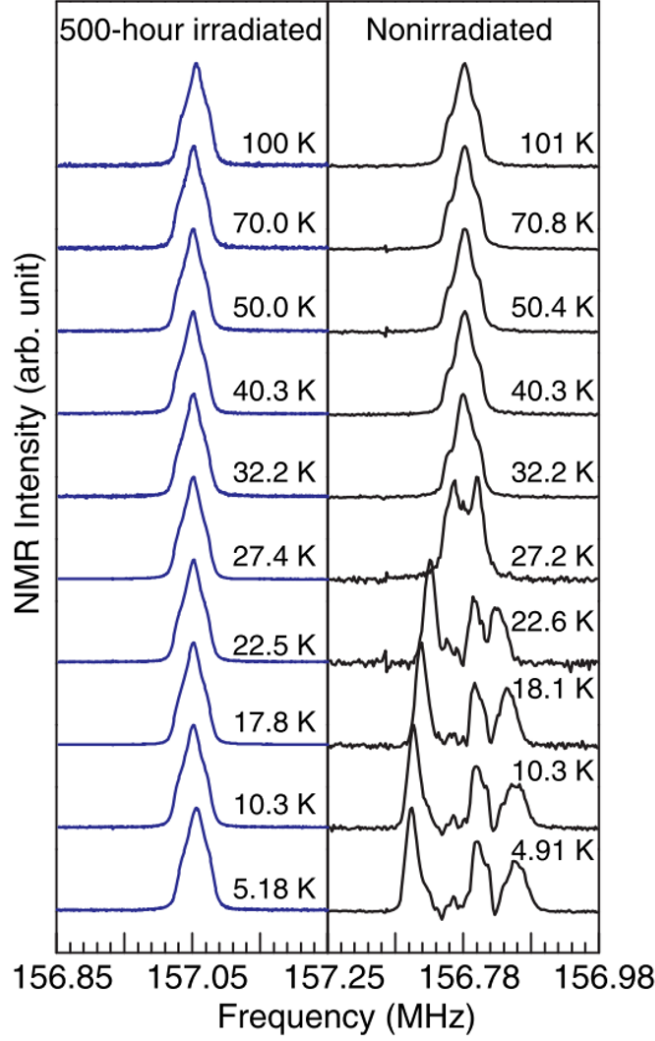


Figure 3.24: The temperature dependence of ^1H -NMR spectra of the 500 hours x-ray irradiated and non-irradiated κ -(ET) $_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ crystals. [37]

bution was reported in λ -(BETS) $_2\text{GaCl}_4$ by the ^{77}Se -NMR study[36]. The angular dependence of the Knight shift and the line width suggests that the charge distribution is $+0.5 \pm 0.15$ considering the neutral valence of BETS is $+0.5$. Therefore, the spin-liquid-like behavior of the susceptibility in λ -(STF) $_2\text{GaCl}_4$, which has the same crystal structure to λ -(BETS) $_2\text{GaCl}_4$ can be explained by the charge polarization.

As another explanation, disordering of donor molecules due to the asym-

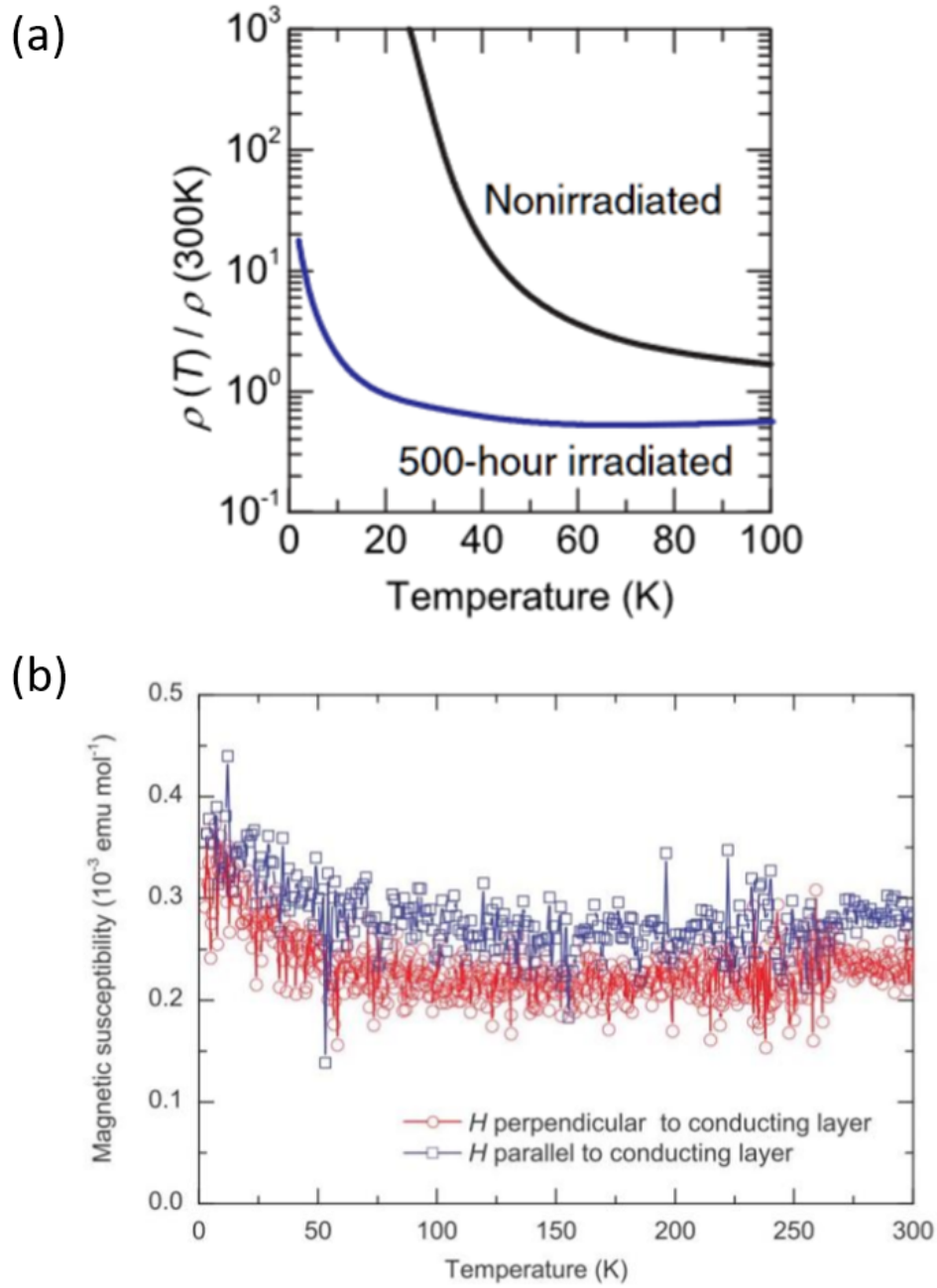


Figure 3.25: (a) Temperature dependence of resistivity of the 500 hours x-ray irradiated and non-irradiated κ -(ET)₂Cu[N(CN)₂]Cl crystals. (b) Temperature dependence of susceptibility of the 500 hours x-ray irradiated κ -(ET)₂Cu[N(CN)₂]Cl. [37]

metric donor structure disturbs the ordering of the AF spin system, so the paramagnetic insulating (PMI) phase becomes favored. As shown in Fig. 3.24, in the recent report for κ -(ET)₂Cu[N(CN)₂]Cl, which goes to AFI phase below 30 K[8], the 500 hours of X-ray irradiation suppress the AF magnetic order at least down to 340 mK[37]. However, the degree of the disorder in this X-ray irradiation research thought to be very large. In the irradiated κ -(ET)₂Cu[N(CN)₂]Cl, the insulating behavior of the clean sample is strongly suppressed and the susceptibility shows an almost temperature independent behavior (Fig. 3.25(a) and (b)). The electronic state seems to be quite changed by the X-ray irradiation. In contrast, the resistivity ratio of the λ -(STF)₂GaCl₄ under the pressure, $\rho_{300\text{K}}/\rho_{6\text{K}} \sim 3 - 40$, is comparable to that of the λ -(BETS)₂GaCl₄ and both of them shows the SC state. Therefore, the disorder effect in λ -(STF)₂GaCl₄ is much smaller than that of the irradiated κ -(ET)₂Cu[N(CN)₂]Cl. Further investigation is needed to determine which scenario is preferred.

We found that the ground state of the λ -STF salt at ambient pressure is the insulating phase without any magnetic ordering. Accordingly, as shown in Fig. 3.26, the phase neighboring the SC phase is the not-AF-ordered paramagnetic insulating (PMI) phase in λ -type salts. We deduce that the AFI phase seen in λ -ET salts disappears with increasing pressure and that it enters the PMI phase. After that, the SC phase appears with some additional pressure, although the possibility of another magnetic phase cannot be completely excluded just below the critical pressure. This behavior is somewhat different from that in κ -ET salts, where the SC phase appears adjacent to the

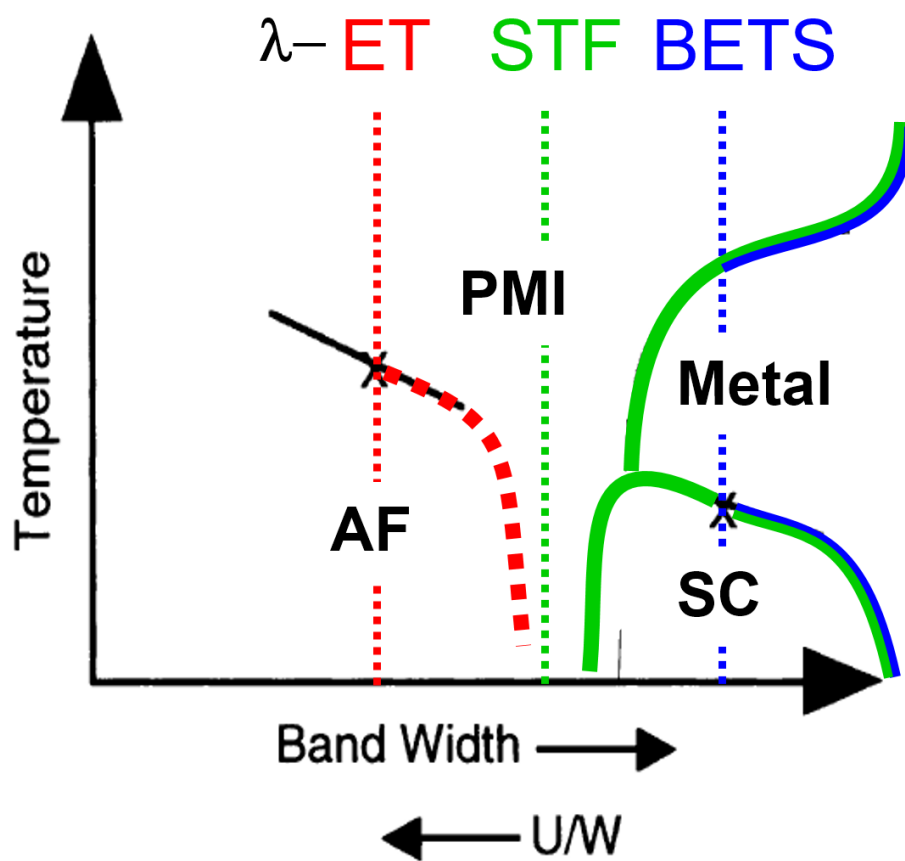


Figure 3.26: Phase diagram of λ - D_2GaCl_4 deduced from present result.

AFI phase. Therefore, some different mechanisms expected for the origins of superconductivity between the κ -type and λ -type salts.

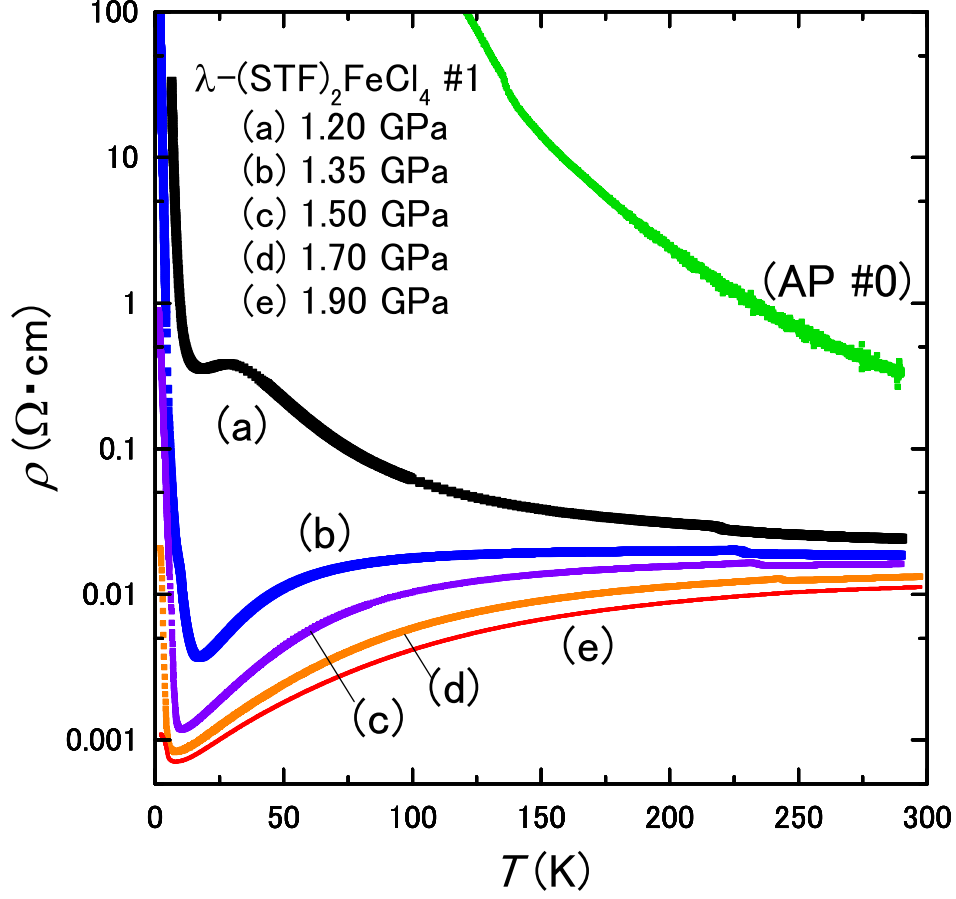


Figure 3.27: Temperature dependence of the electrical resistivity of λ -(BEDT-STF) $_2$ FeCl $_4$ at various pressures: ambient pressure for sample #0, (a) 1.20, (b) 1.35, (c) 1.50, (d) 1.70, (e) 1.90 GPa for sample #1.

3.2 λ -(STF) $_2$ FeCl $_4$

3.2.1 Electrical resistivity

Figure 3.27 shows the temperature dependence of the electrical resistivity in λ -(STF) $_2$ FeCl $_4$ for sample #0 and #1 at various pressures. Below 1.20 GPa, in the high temperature region, the resistivity increases with decreasing temperature. At 30 K, it has a local maximum and then decreases down to 20 K. Below 20 K, it shows a sharp divergence. Above 1.35 GPa, the insulating behavior

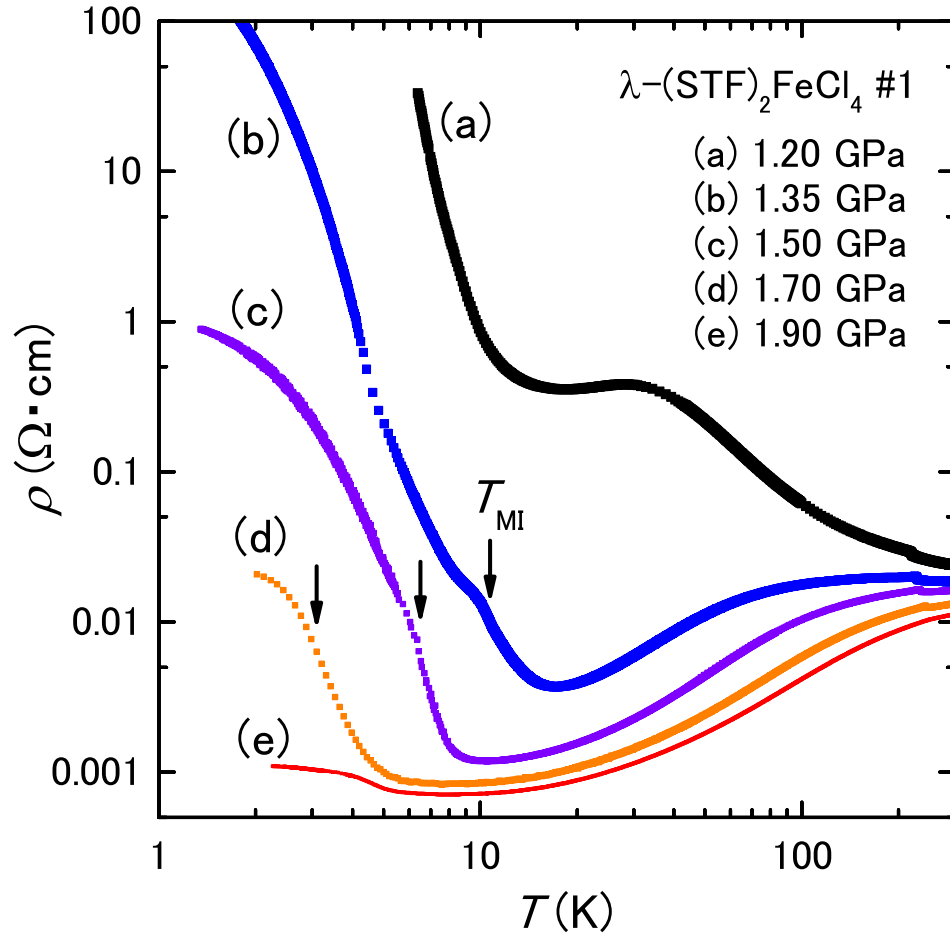


Figure 3.28: Logarithmic plot for horizontal axis of Fig. 3.27.

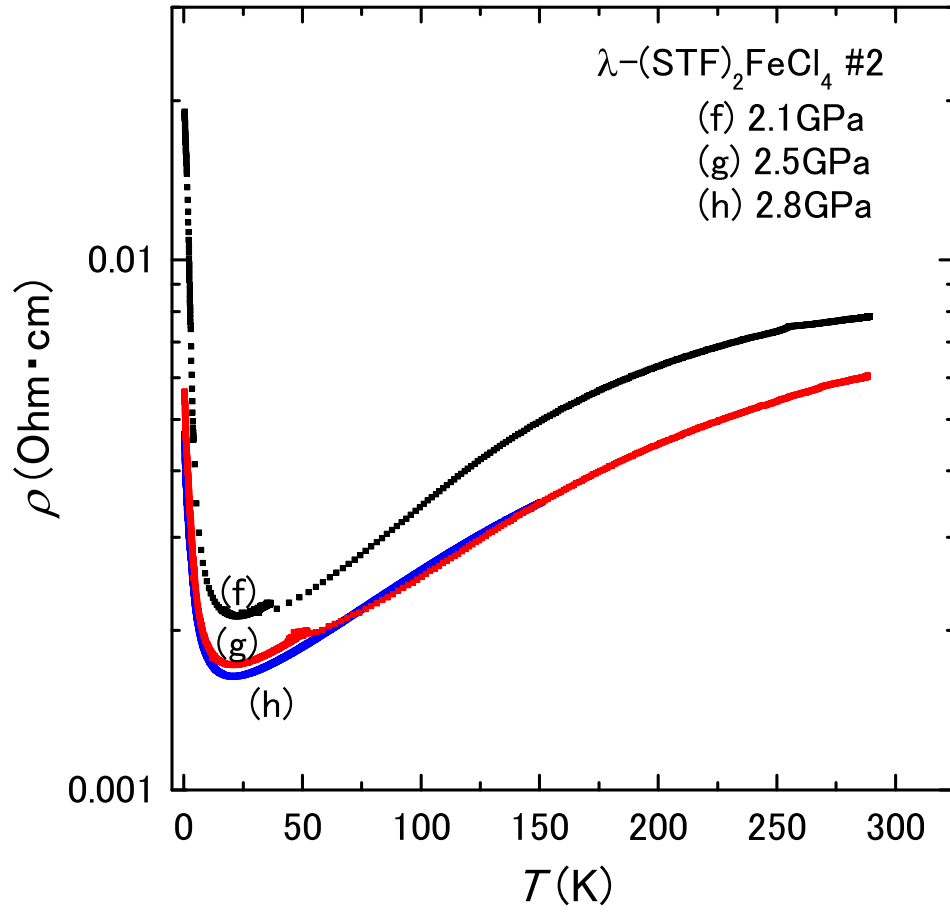


Figure 3.29: Temperature dependence of the electrical resistivity of $\lambda\text{-(BEDT-STF)}_2\text{FeCl}_4$ at various pressures: (f) 2.10, (g) 2.50, (c) 2.80 GPa for sample #2.

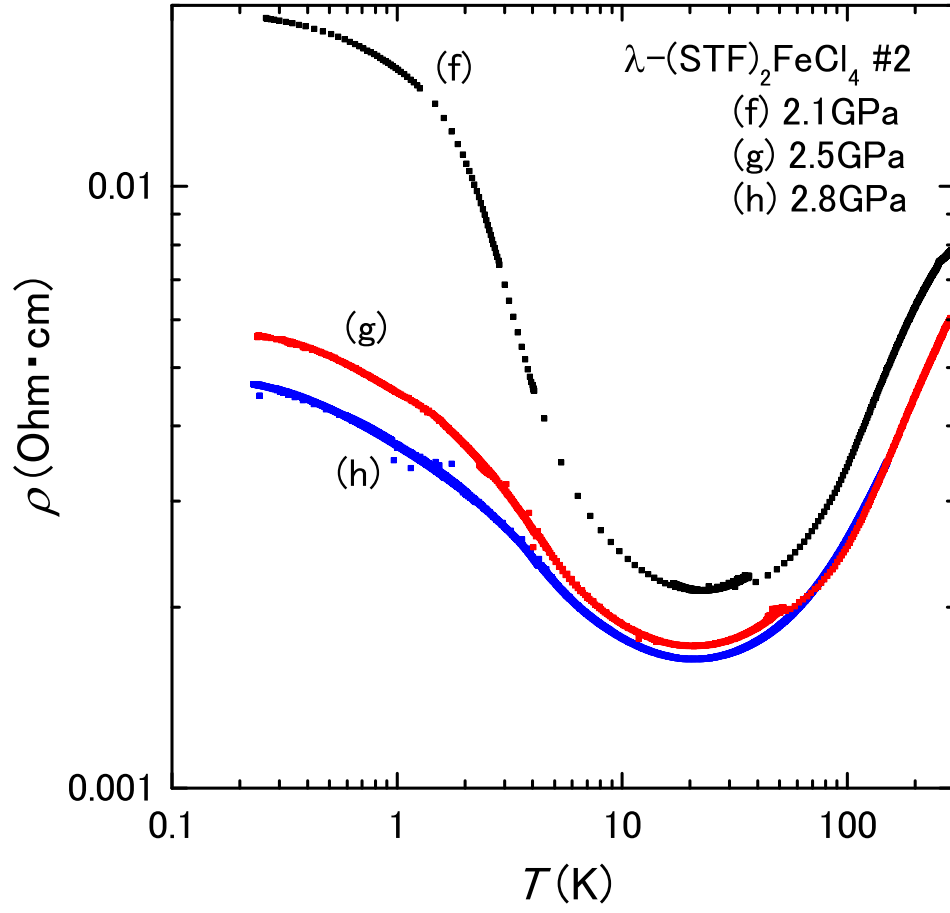


Figure 3.30: Logarithmic plot for horizontal axis of Fig. 3.29.

in the high temperature region is suppressed by pressure and the resistivity curves shows a minimum indicating the presence of the metal-insulator (MI) transition. As shown in Fig. 3.28, although the slightly increasing of the resistivity at low temperature is observed up to 1.90 GPa, the MI transition is suppressed at 1.90 GPa. We determine the MI transition temperature T_{MI} as 9.0 K, 6.5 K and 3.0 K for 1.35 GPa, 1.50 GPa and 1.70 GPa, respectively, from the peak in the derivative in the logarithm of the resistivity with $1/T$. Figure 3.29 and Fig. 3.30 shows the temperature dependence of the electrical resistivity for sample #2 at the higher pressure region and we cannot find the SC transition down to 0.3 K. Although the residual resistivity at lowest temperature shows a sample dependence, the resistance minimum appears in the both samples.

Fig. 3.31 shows the P - T phase diagram obtained from the T_{MI} and T_{min} , which is defined as a local minimum of the temperature dependence of the resistivity, of the sample #1. Open circles and squares represent T_{MI} and T_{min} respectively. T_{MI} decreases with increasing pressure. In the previous report shown in Fig. 3.32, the resistivity in λ -(BETS) $_2$ FeCl $_4$ at ambient pressure shows a weak insulating behavior at high temperature region, a broad IM transition around 100 K, which is similar to that of the λ -(BETS) $_2$ GaCl $_4$, and a very sharp increasing due to the AF transition at 8.3 K. With increasing pressure, the insulating behavior in high temperature region is suppressed and it goes to SC phase above 0.3 GPa as shown in Fig. 3.33 and Fig. 3.34.

The temperature dependence of λ -(STF) $_2$ FeCl $_4$ around 1.50 GPa is similar to that of λ -(BETS) $_2$ FeCl $_4$ at ambient pressure. The λ -(STF) $_2$ FeCl $_4$ does not

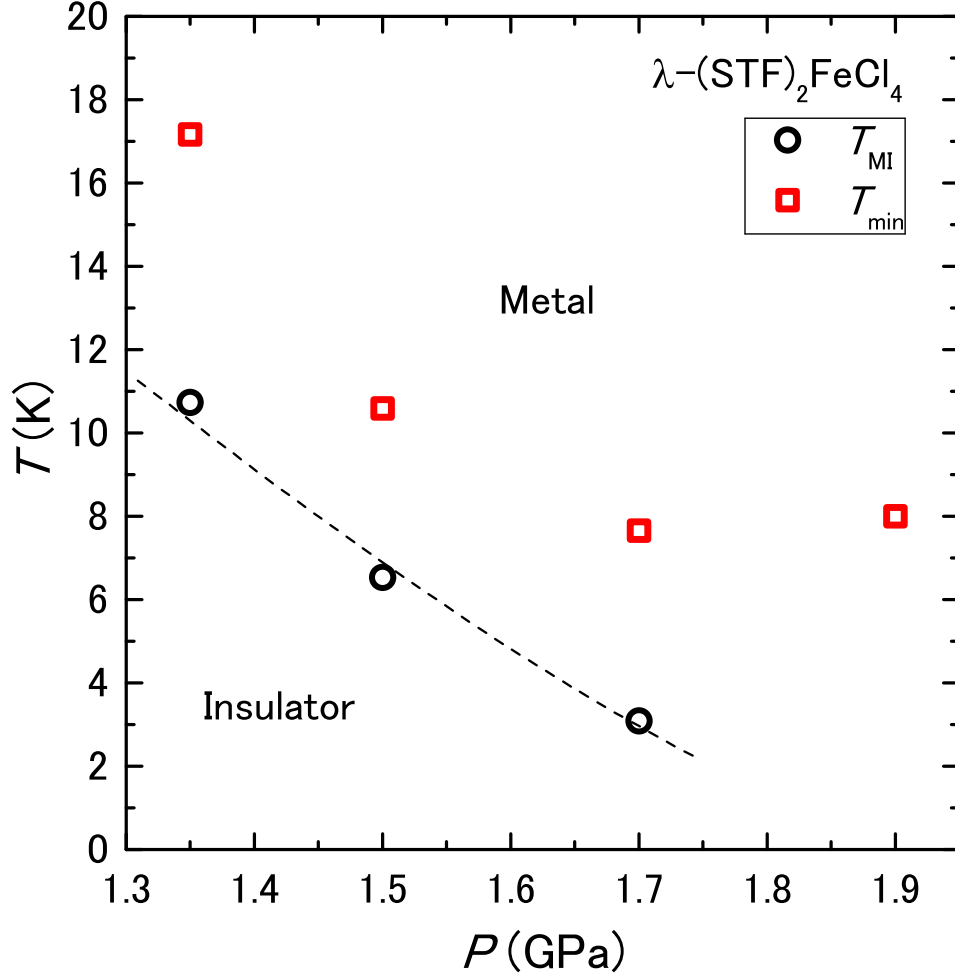


Figure 3.31: P - T phase diagram for λ -(STF) $_2$ FeCl $_4$ salt. Open circles and squares represent the T_{MI} and T_{min} respectively. T_{MI} is the temperature where $\frac{\partial \ln \rho}{\partial (1/T)}$ shows a maximum. T_{min} is defined as a local minimum of the temperature dependence of the resistivity.

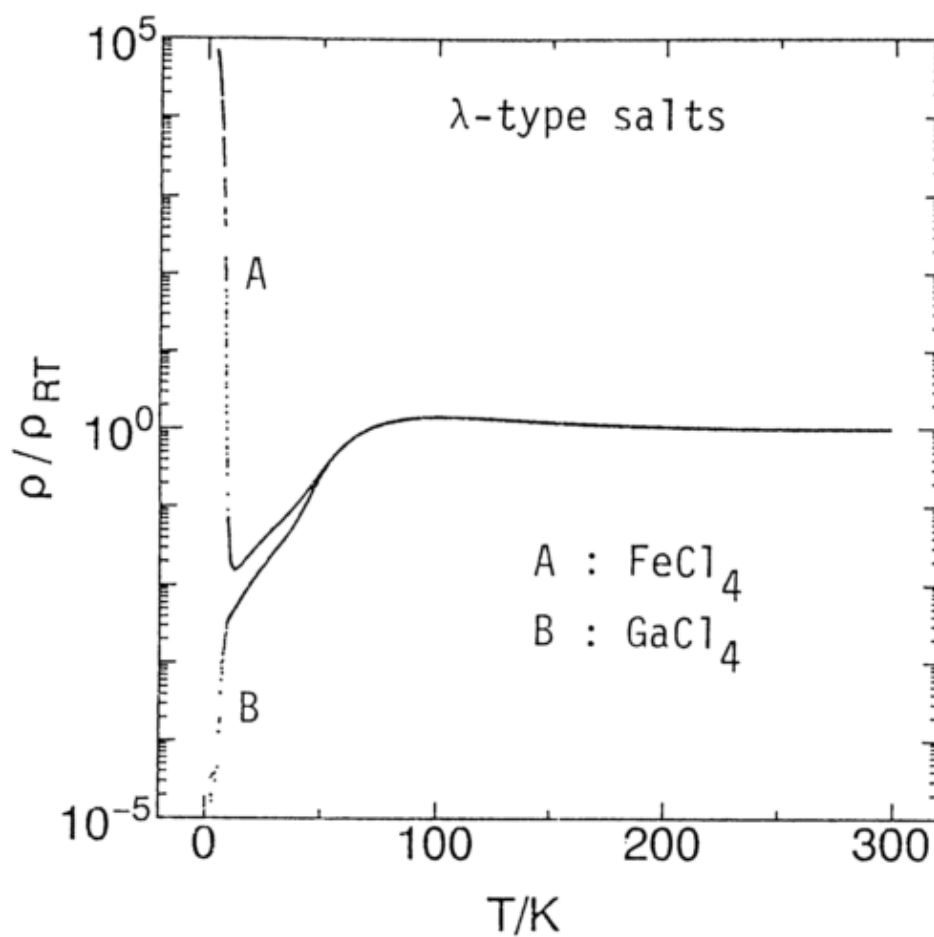


Figure 3.32: Temperature dependence of the resistivity normalized by the value at room temperature of λ -(BETS) $_2$ GaCl $_4$ and λ -(BETS) $_2$ FeCl $_4$. [11]

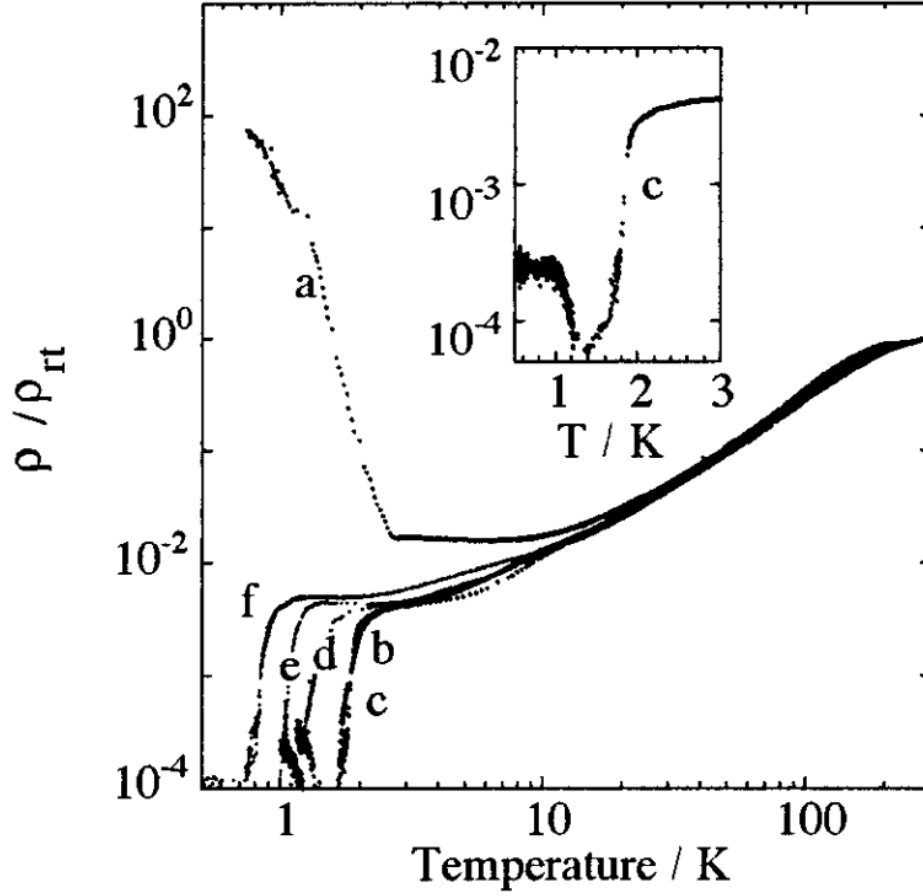


Figure 3.33: The resistivity of λ -(BETS)₂FeCl₄ at (a) 2.5, (b) 3.0, (c) 3.2, (d) 4.0, (e) 4.5, and (f) 5.0 kbar. The inset shows the anomalous resistivity behavior observed at 3.2 kbar.[38]

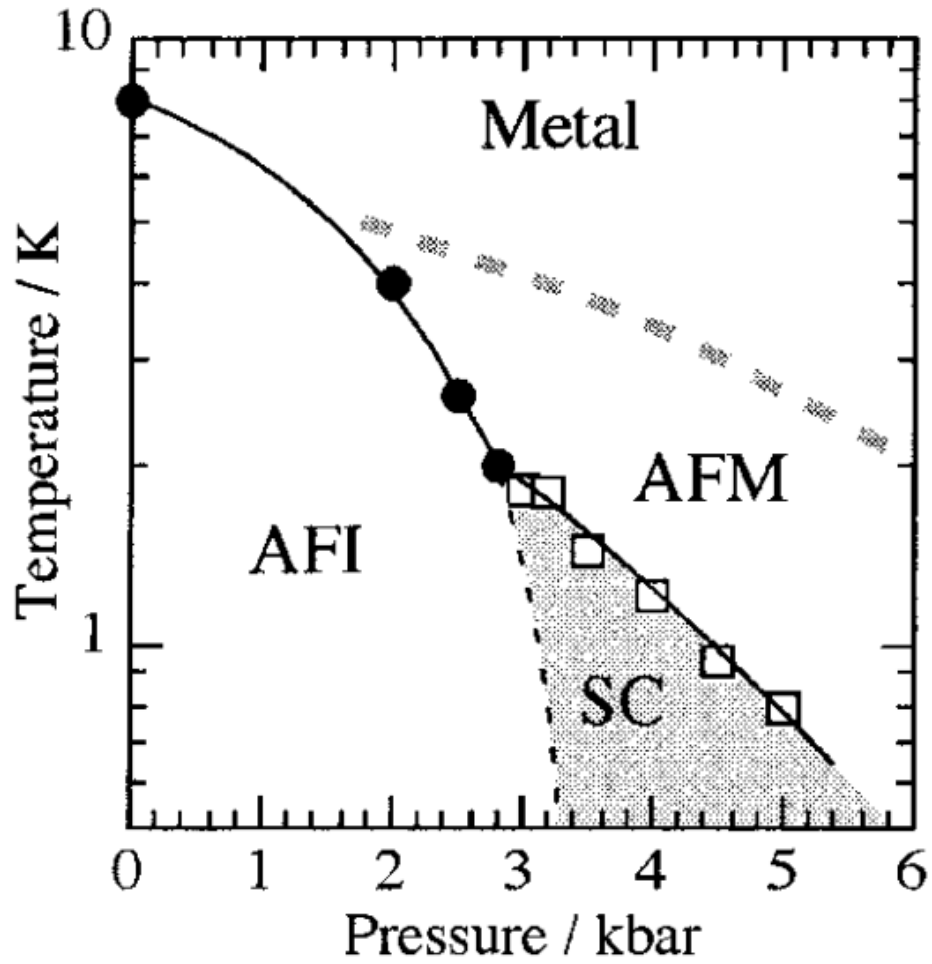


Figure 3.34: The phase diagram of λ -(BETS)₂FeCl₄. The bold broken line shows the pressure dependence of the peak temperature of the susceptibility. AFM = antiferromagnetic metal phase.[38]

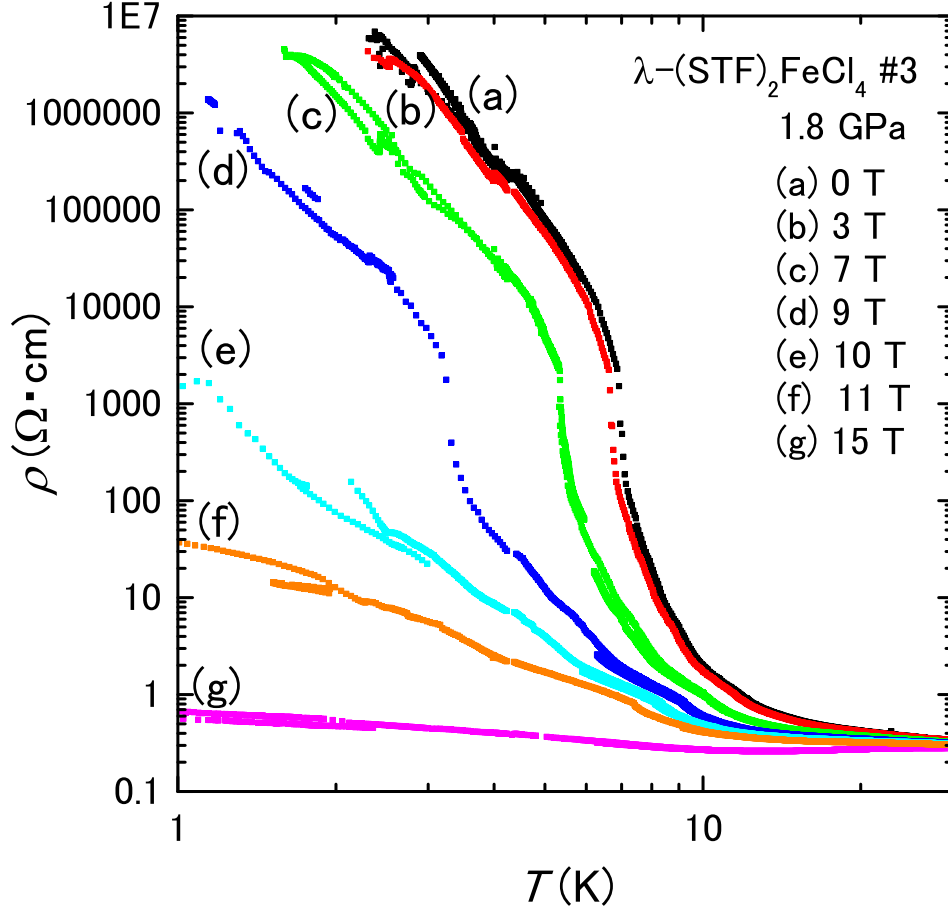


Figure 3.35: Temperature dependence of the electrical resistivity of λ -(BEDT-STF) $_2$ FeCl $_4$ at 1.5 GPa under various magnetic field : (a) 0, (b) 3, (c) 7, (d) 9, (e) 10, (f) 11, (g) 15 T for sample #3.

show the SC transition up to 2.8 GPa down to 0.3 K. The absence of the SC phase in λ -(STF) $_2$ FeCl $_4$ may be caused by the effect of the disorder.

Electrical resistivity under magnetic field

We have measured the resistivity of λ -(STF) $_2$ FeCl $_4$ for sample C with a magnetic field to check the electrical state at low temperatures at 1.5 GPa as shown Fig. 3.35. The magnetic fields were applied along to the c -axis, which is parallel to the conducting plane. With decreasing temperature, the resistivity

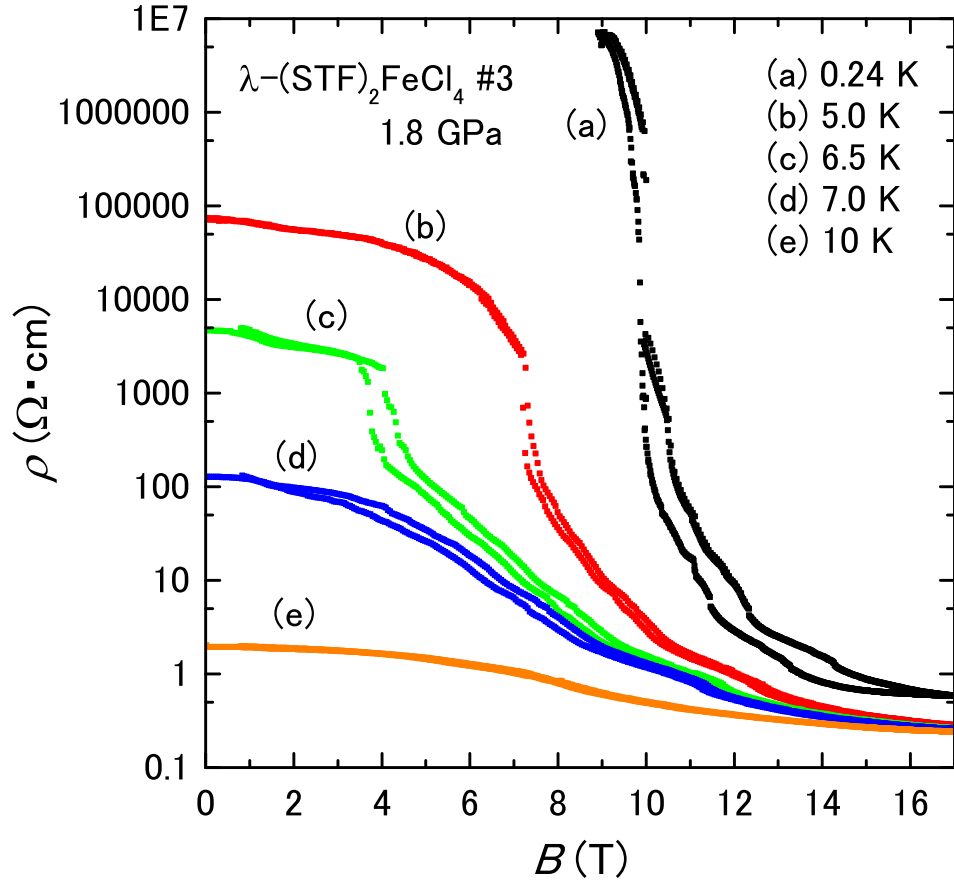


Figure 3.36: Magnetic field dependence of the electrical resistivity of $\lambda\text{-(BEDT-STF)}_2\text{FeCl}_4$ at 1.5 GPa under various temperature : (a) 0.24, (b) 5.0, (c) 6.5, (d) 7.0, (e) 10.0 K for sample #3.

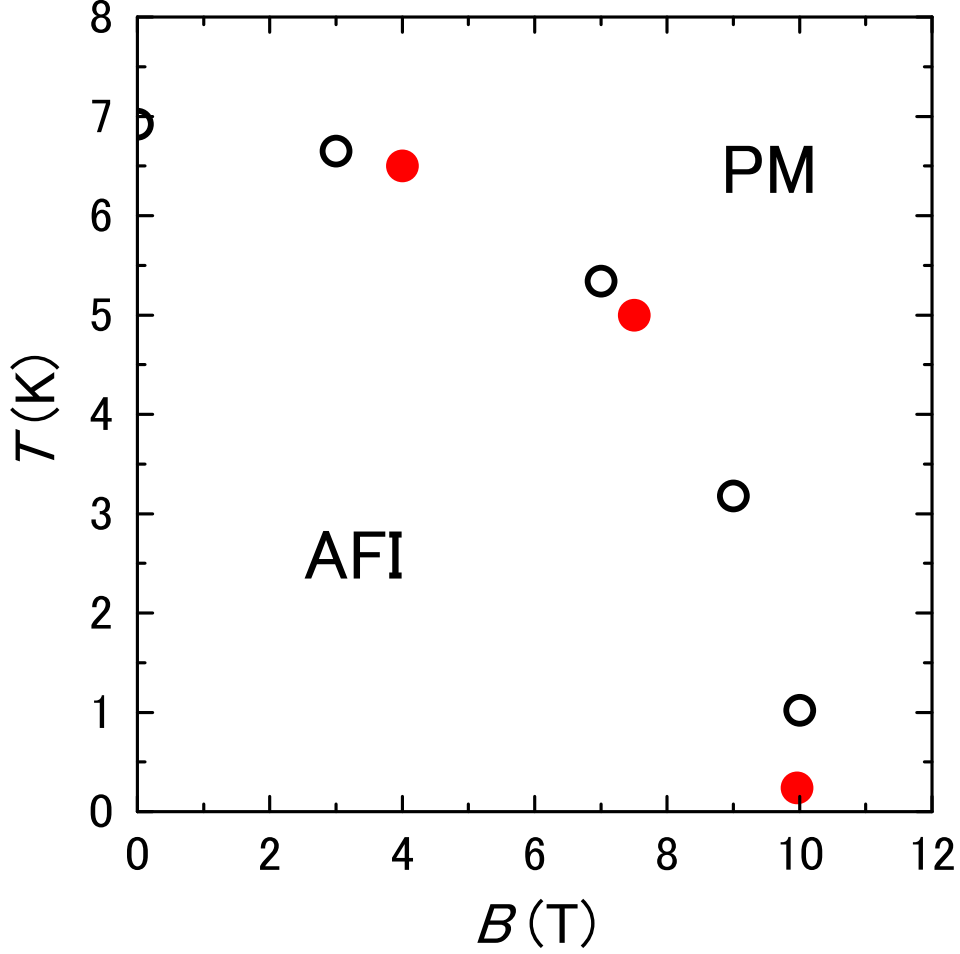


Figure 3.37: B - T phase diagram for λ -(STF) $_2$ FeCl $_4$ salt at 1.5 GPa. Closed and open circles are obtained from temperature and field sweep measurements.

shows a rapid increase at 0 T below 7.0 K and the rapid increase of resistivity completely suppressed above 10 T. Fig. 3.36 shows the magnetoresistivity for various temperature. With increasing magnetic field, the magnetoresistivity decreases with a sharp drop at 4, 7.5, 10 T for 6.5, 5.0, 0.24 K, respectively.

From these results, we determined the magnetic field - temperature (B - T) phase diagram for λ -(STF) $_2$ FeCl $_4$ at 1.5 GPa as shown in Fig. 3.37. We determine T_{MI} from the peak in the derivative of the logarithm of the resistance with $1/T$, as shown by open circles in Fig. 3.37. We also determine T_{MI} from

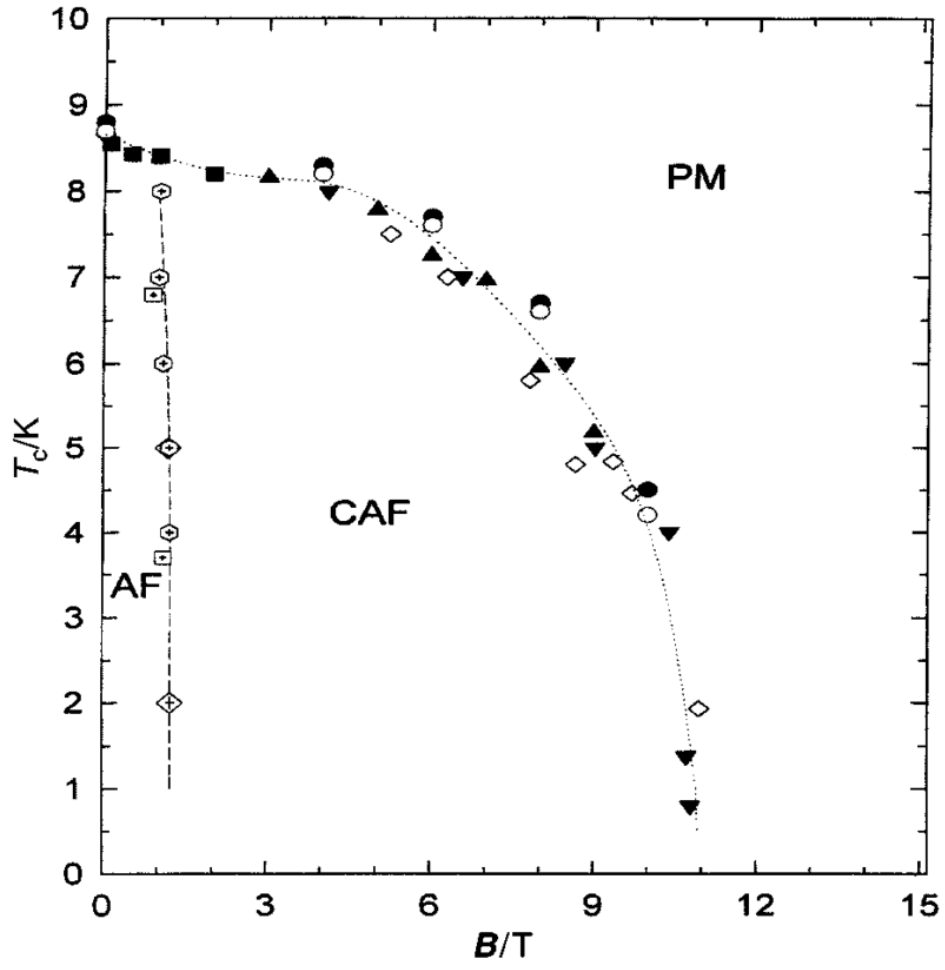


Figure 3.38: B - T phase diagram for λ -(BETS)₂FeCl₄ salt at ambient pressure.[11]

the peak in the derivative of the logarithm of the resistance with B , shown by filled circles. Based on the analogy of λ -(BETS) $_2$ FeCl $_4$ at ambient pressure (see Fig. 3.38), we conclude that this MI transition at 1.50 GPa corresponds to the AF transition and λ -(STF) $_2$ FeCl $_4$ at ambient pressure is located at a lower pressure region of the phase diagram compared to λ -(BETS) $_2$ FeCl $_4$ at ambient pressure.

3.2.2 Proton nuclear magnetic resonance

To elucidate the spin state of λ -(STF) $_2$ FeCl $_4$ at ambient pressure, we carried out ^1H -NMR measurements. Figure 3.39 and Fig. 3.40 shows the ^1H -NMR spectra at 132.5 MHz for a single crystal of λ -(STF) $_2$ FeCl $_4$ at ambient pressure for the various temperatures below 70 K. The external magnetic field in the range of 3.00 - 3.25 T is perpendicular to the c -axis, which is the long axis of the crystal. A sharp peak was observed at 3.117 T, which corresponds to the signal from the isolated protons. Since the sharp peak at 3.117 T and broad peak in the 3.150 - 3.165 T range, shown as “*”, did not show temperature and field angular dependence (Fig. 3.41), they can be regarded as the signal from the grease or contamination. Above 20 K, there are some signals from the proton sites in 3.10 - 3.15 T range. Since the nearest distance between the Fe spin ($s = 5/2$) and the proton site is 3.44 Å (Fig. 1.25), the expected maximum value of the NMR shift is 0.22 T. As the temperature decreases from 70 K to 16 K, the spectrum is gradually broadened and then shows a drastic splitting below 16 K. At the lowest temperature, we observed many peaks in the wide field range of 3.05 - 3.20 T, which are assigned to the 16 independent sites of

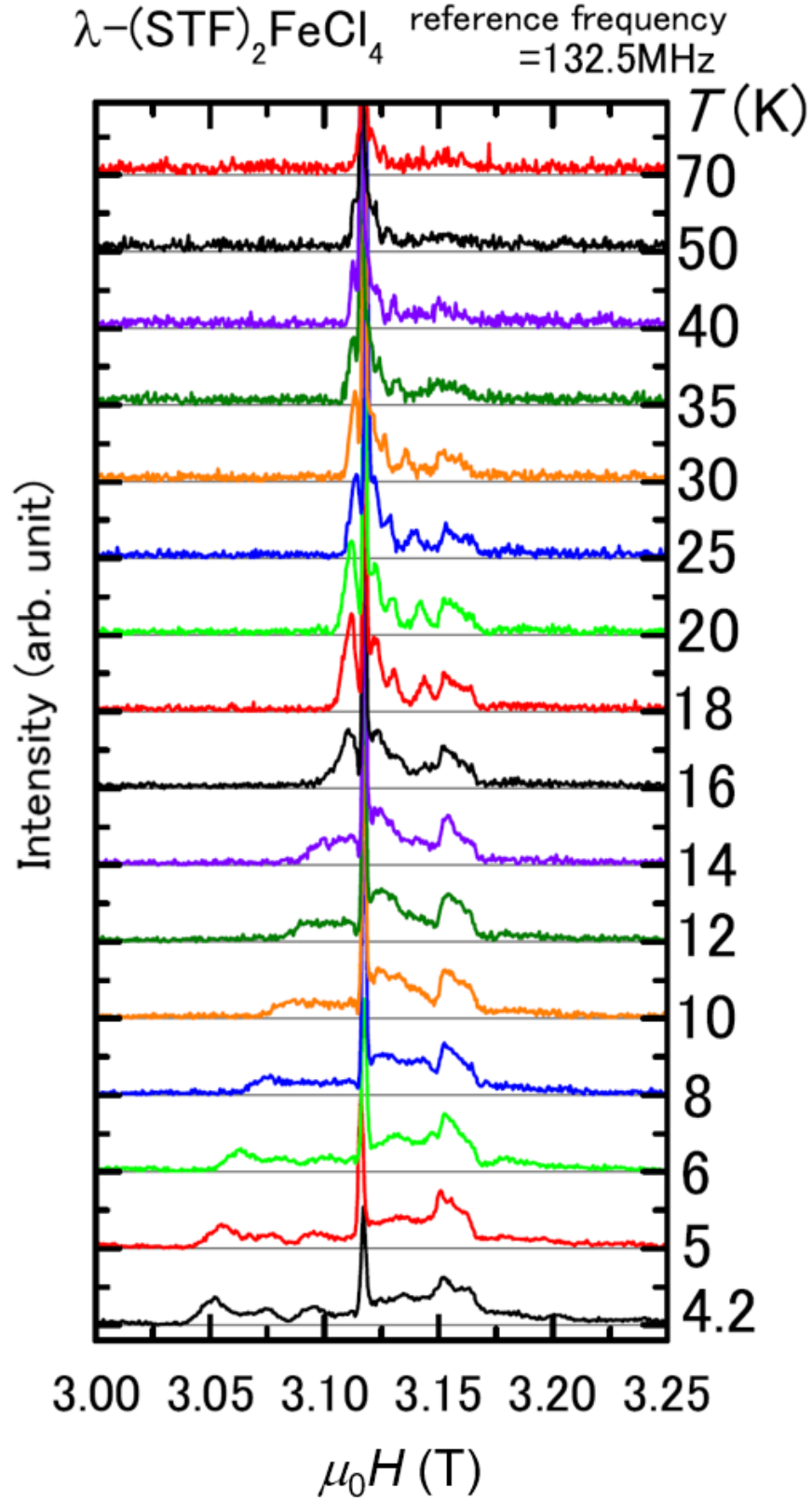


Figure 3.39: Temperature dependence of the ^1H -NMR field-swept spectra at 132.5 MHz for a single crystal of $\lambda-(\text{STF})_2\text{FeCl}_4$ at ambient pressure. External magnetic field was applied perpendicular to the c -axis.

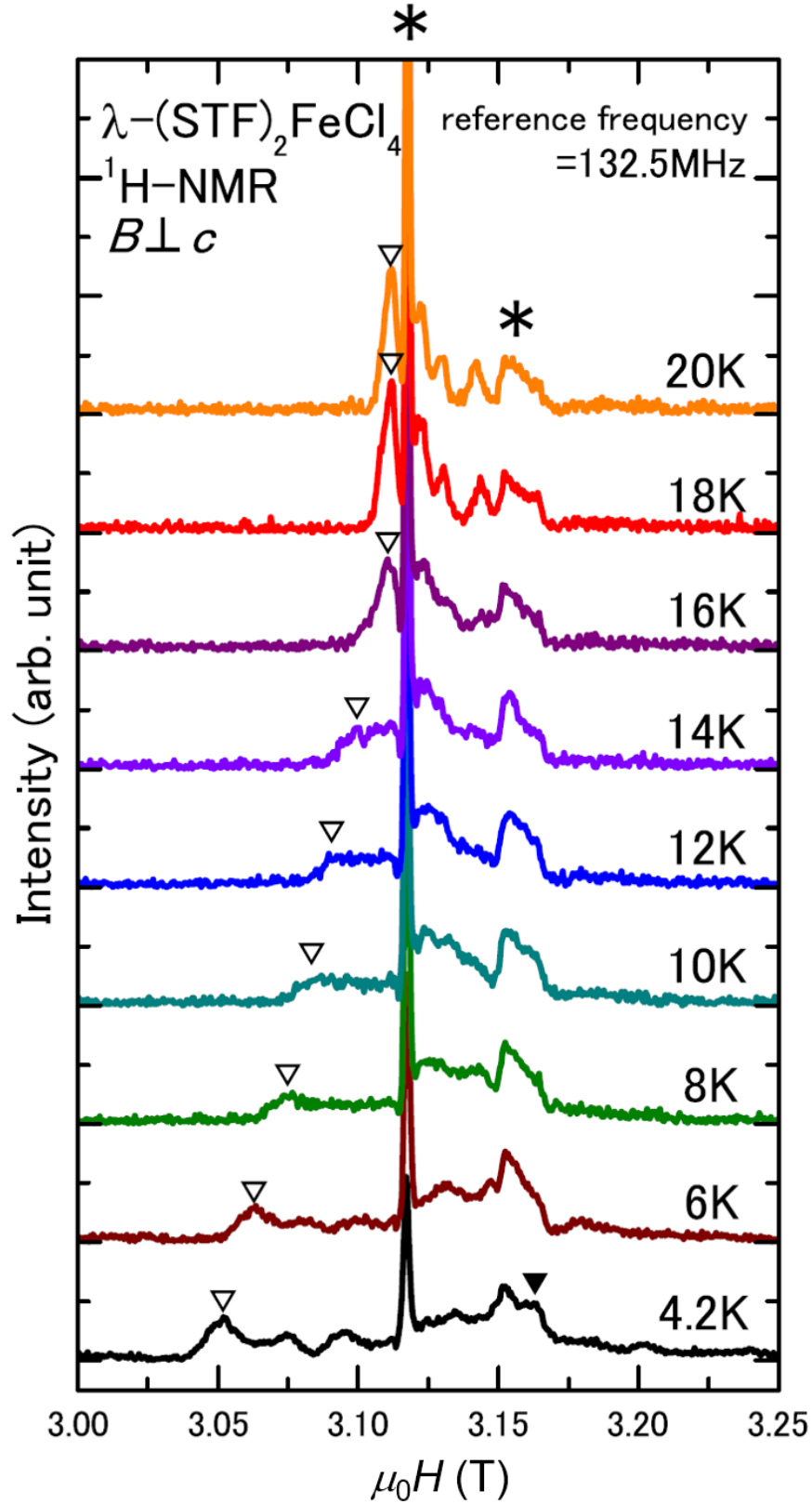


Figure 3.40: Enlarged figure of Fig. 3.39 for the region below 20 K. Central sharp peaks at 3.117 T and broad peak in the range from 3.150 T to 3.165 T, (marked as “*”), which does not have temperature or field-rotation dependence, are thought to be signals from the contamination or the grease.

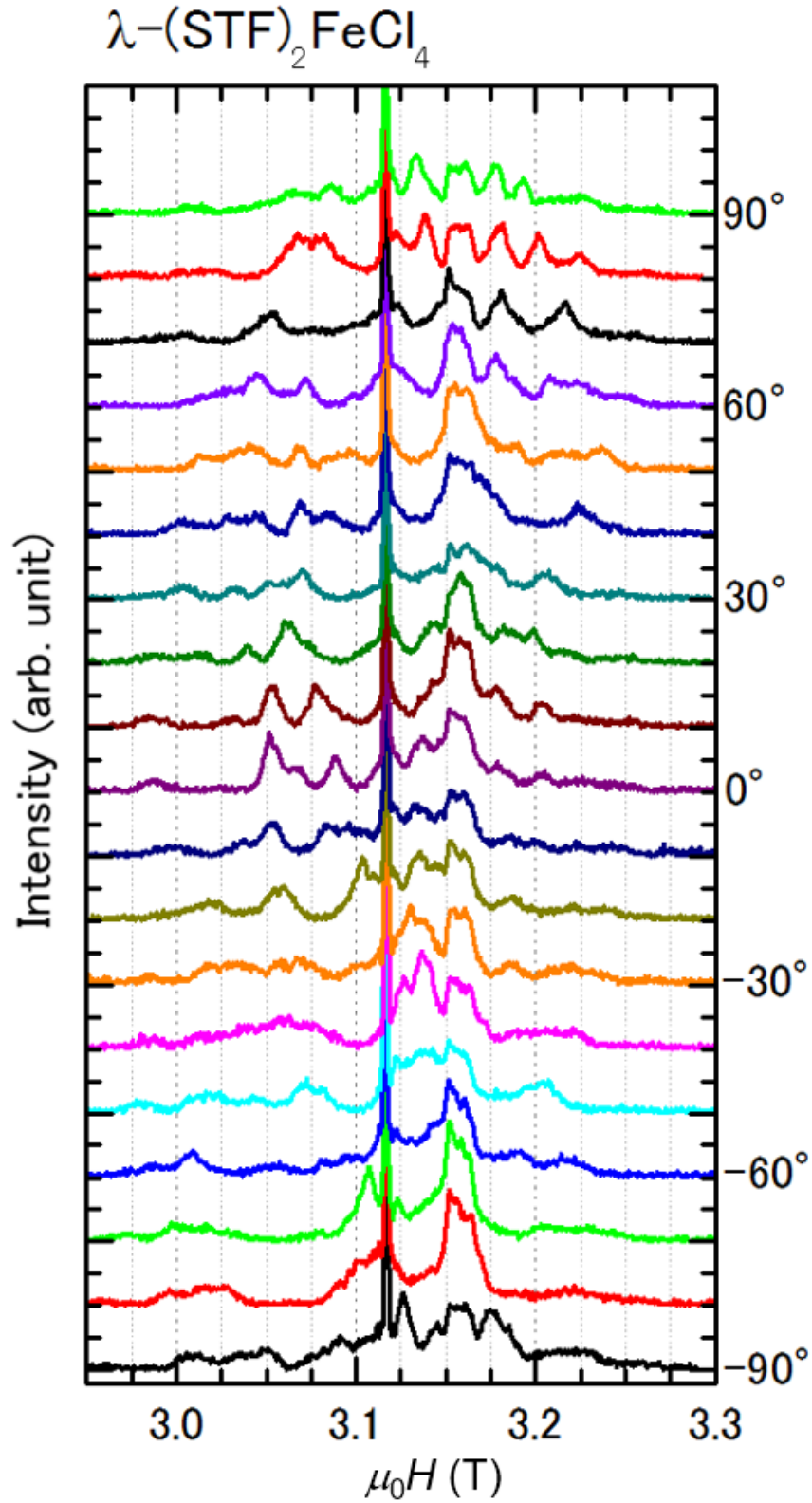


Figure 3.41: Rotation dependence of ^1H -NMR field-swept spectra at 132.5 MHz for a single crystal of $\lambda-(\text{STF})_2\text{FeCl}_4$ at 4.2 K. External magnetic field was applied perpendicular to the c -axis.

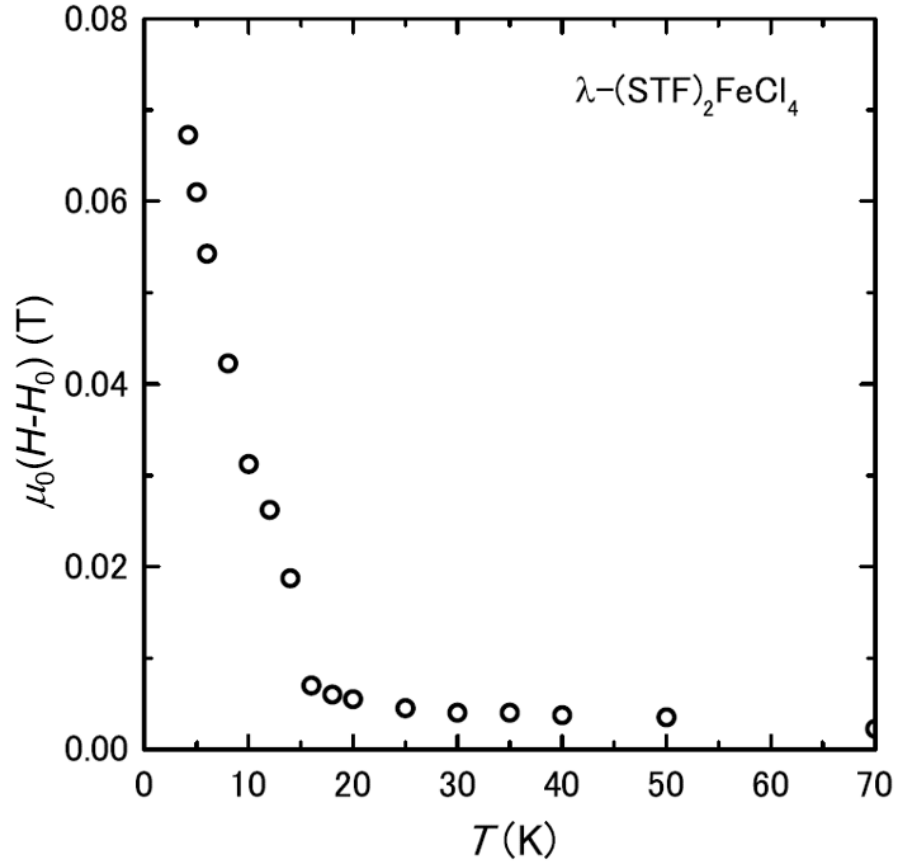


Figure 3.42: Temperature dependence of NMR shift obtained from the peak marked as “ ∇ ” in Fig. 3.40. B_0 equals to 3.117 T, where the sharp central peak observed.

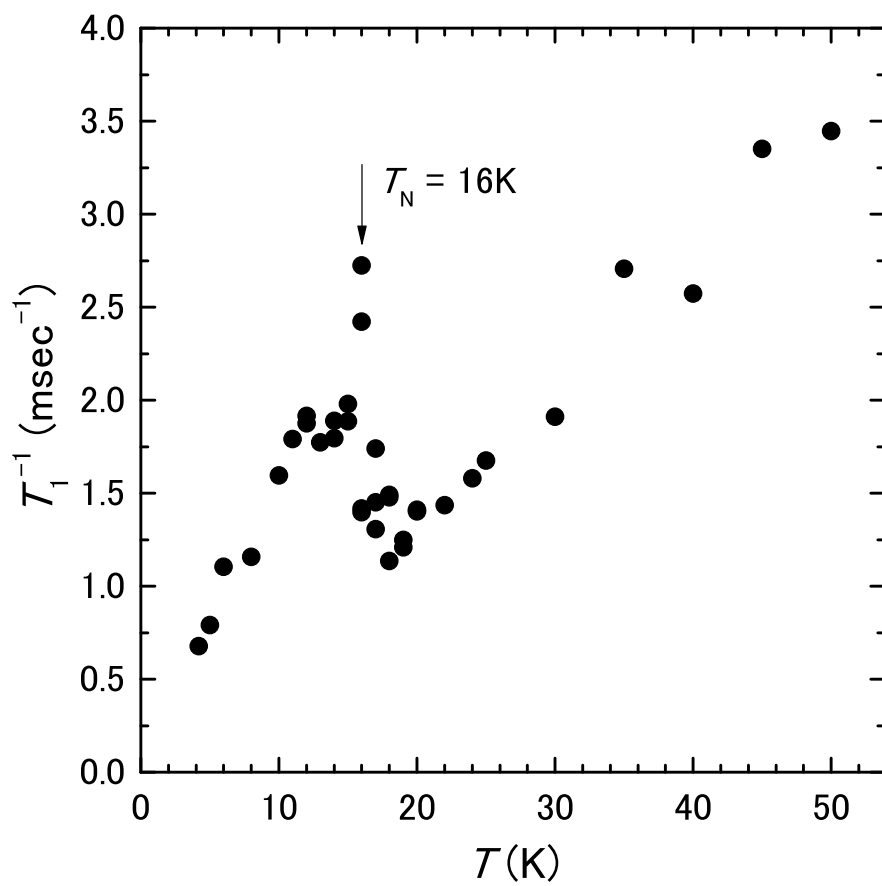


Figure 3.43: Temperature dependence of T_1^{-1} .

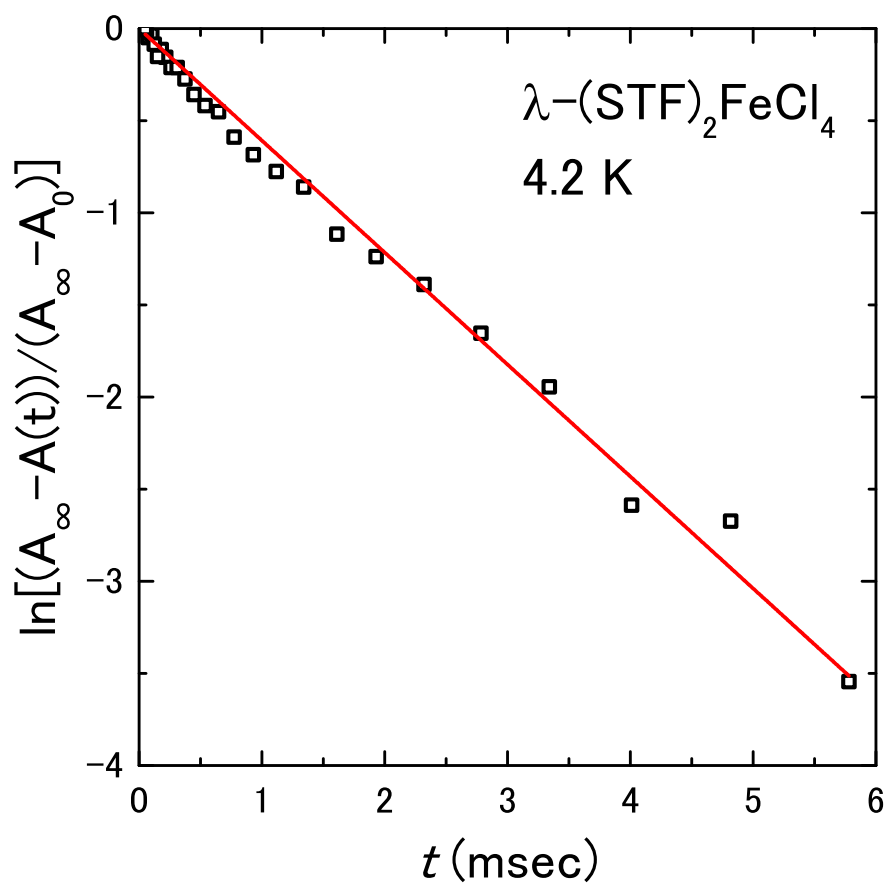


Figure 3.44: ^1H -NMR relaxation curve at 4.2 K.

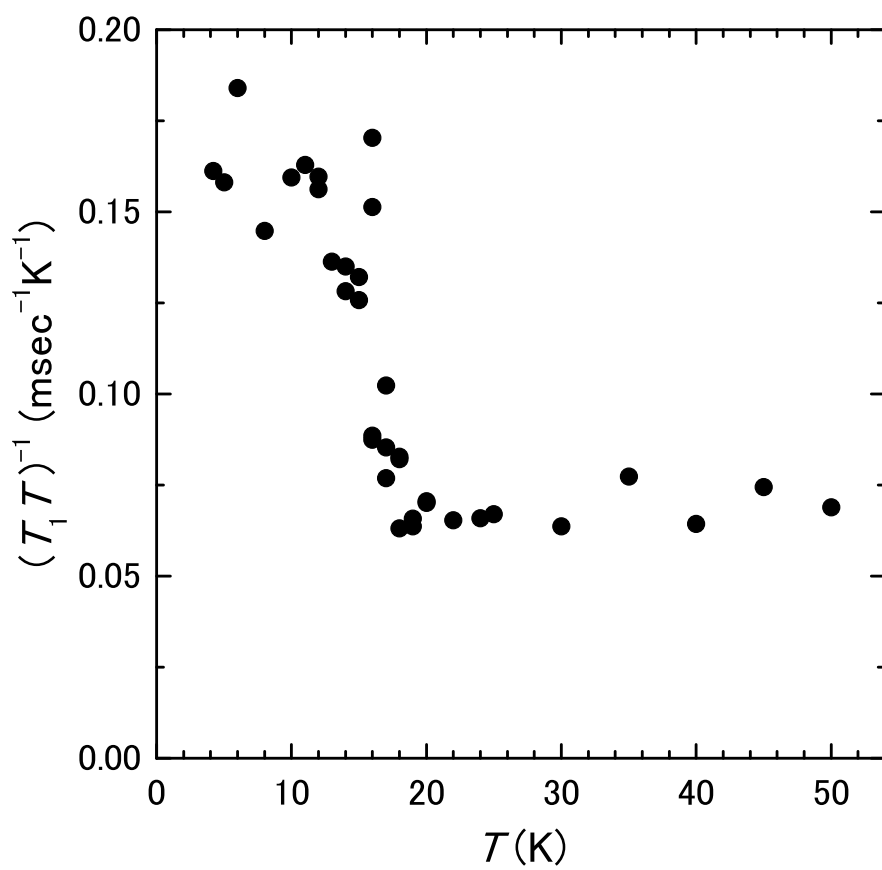


Figure 3.45: Temperature dependence of $(T_1 T)^{-1}$.

the proton group. The local fields on each site are predominantly determined by the dipole magnetic field from the $3d$ spin dipole moments of Fe^{3+} ions. The temperature dependence of the NMR shift at spectrum peak marked as “ ∇ ” in Fig. 3.40 is shown in Fig. 3.42. It is clear that the drastic peak spirting begins at 16 K. The NMR shift increases with decreasing temperature without saturating.

Figure 3.43 shows the temperature dependence of T_1^{-1} at a single spectrum peak marked as “ ∇ ”. For all temperatures, the relaxation curve described by the almost single exponential, for an example, the typical relaxation curve at 4.2 K is shown in Fig. 3.44. The sharp peak anomaly observed at approximately 16 K is associated with the increase of low-frequency fluctuations due to the AF transition at T_{AF} ; the peak temperature corresponds to the drastic broadening temperature in the spectra. The temperature dependence of the $1/T_1T$ is shown in Fig. 3.45. The step like anomaly, which is corresponds to the peak structure in $1/T_1$, appears at 16 K. Below and above 16 K, the value of the $1/T_1T$ is almost constant, which is the behavior typically seen in the metallic phase. However, $\lambda\text{-(STF)}_2\text{FeCl}_4$ at ambient pressure shows insulating behavior in all temperature region up to room temperature. The cause of this behavior is not clear yet and it needs further researches.

3.2.3 Static susceptibility

Figure 3.46 shows the static susceptibility observed under the external fields $B//c$ (needle axis of the crystal) and $B \perp c$ at 0.1 T. The components of the sample holder, the core diamagnetisms and the Curie tail from the magnetic

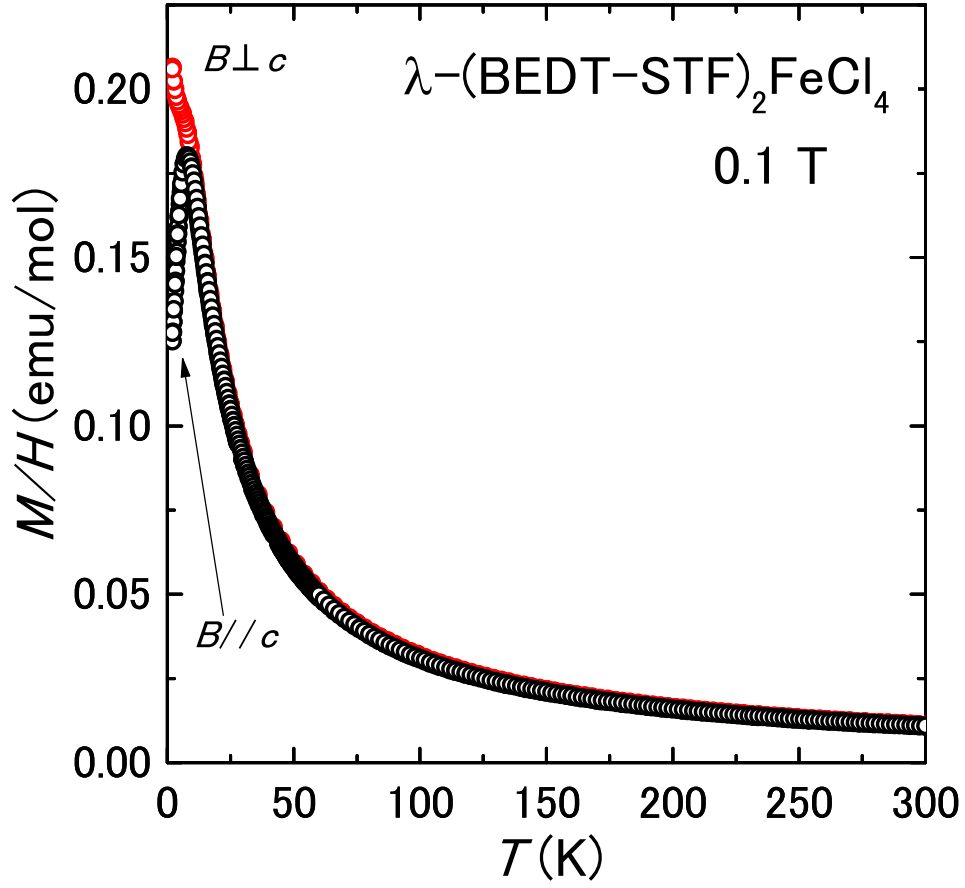


Figure 3.46: Temperature dependence of the static susceptibility in the aggregated sample of $\lambda-(\text{STF})_2\text{FeCl}_4$. Measurements for $B//c$ (needle axis of the crystal) and $B \perp c$ were carried out for the same sample.

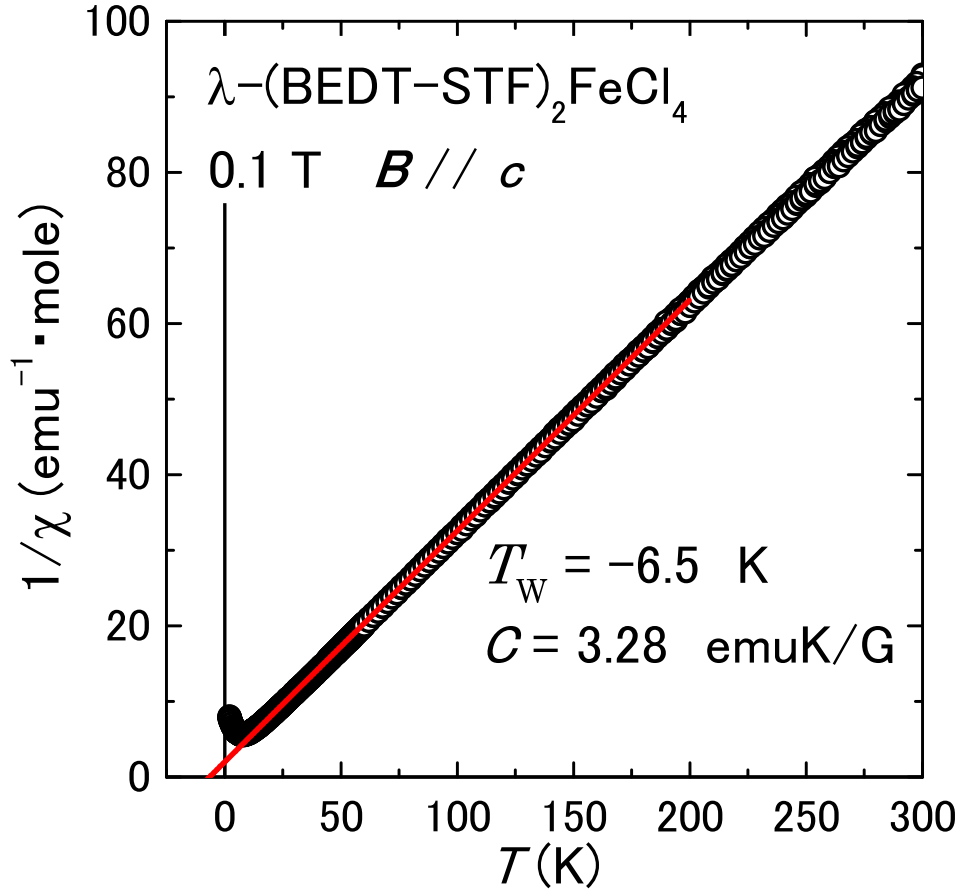


Figure 3.47: Curie-Weiss plot of the static susceptibility of $\lambda\text{-(STF)}_2\text{FeCl}_4$ measured in $B//c$. The solid red line is the linear fitting in the temperature range of 50-150 K. Weiss temperature is determined as -6.49 K.

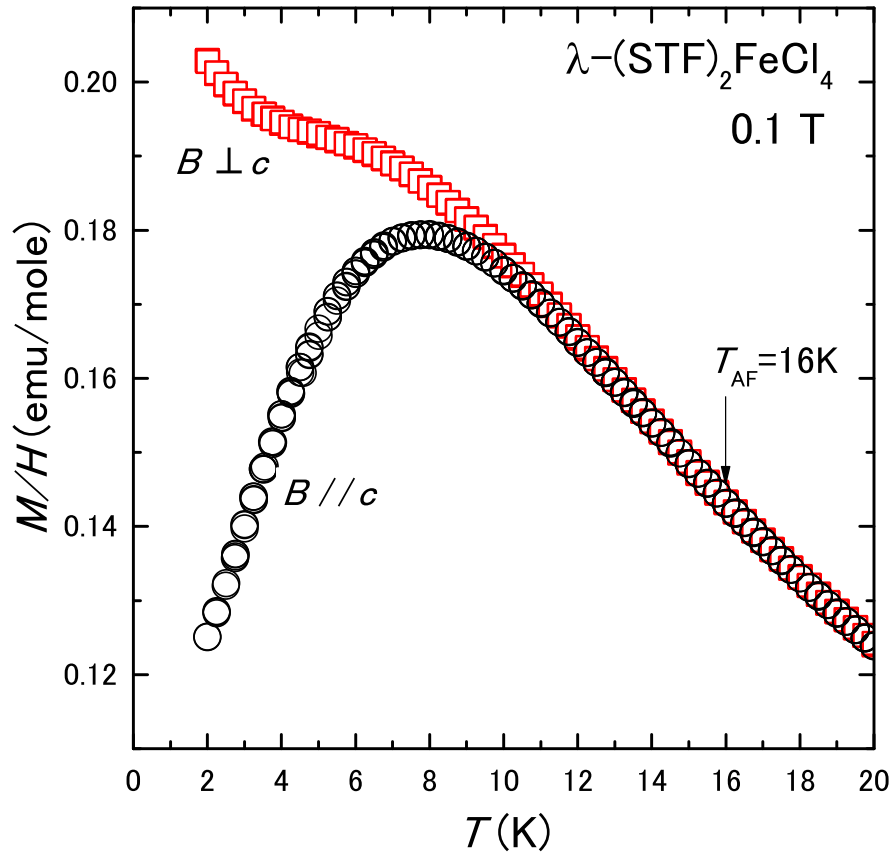


Figure 3.48: Temperature dependence of the static susceptibility in $\lambda\text{-(STF)}_2\text{FeCl}_4$ measured for $B//c$ and $B \perp c$ of 0.1 T.

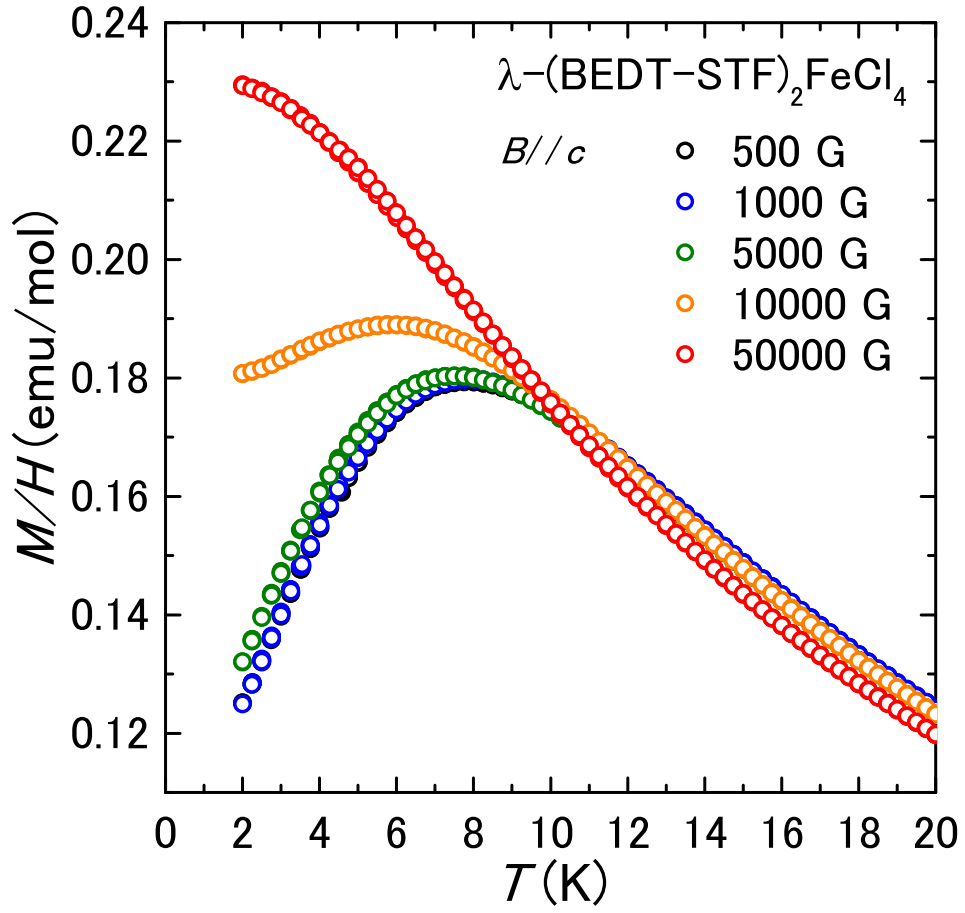


Figure 3.49: Temperature dependence of the static susceptibility in $\lambda-(\text{STF})_2\text{FeCl}_4$ measured for $B//c$ for various field.

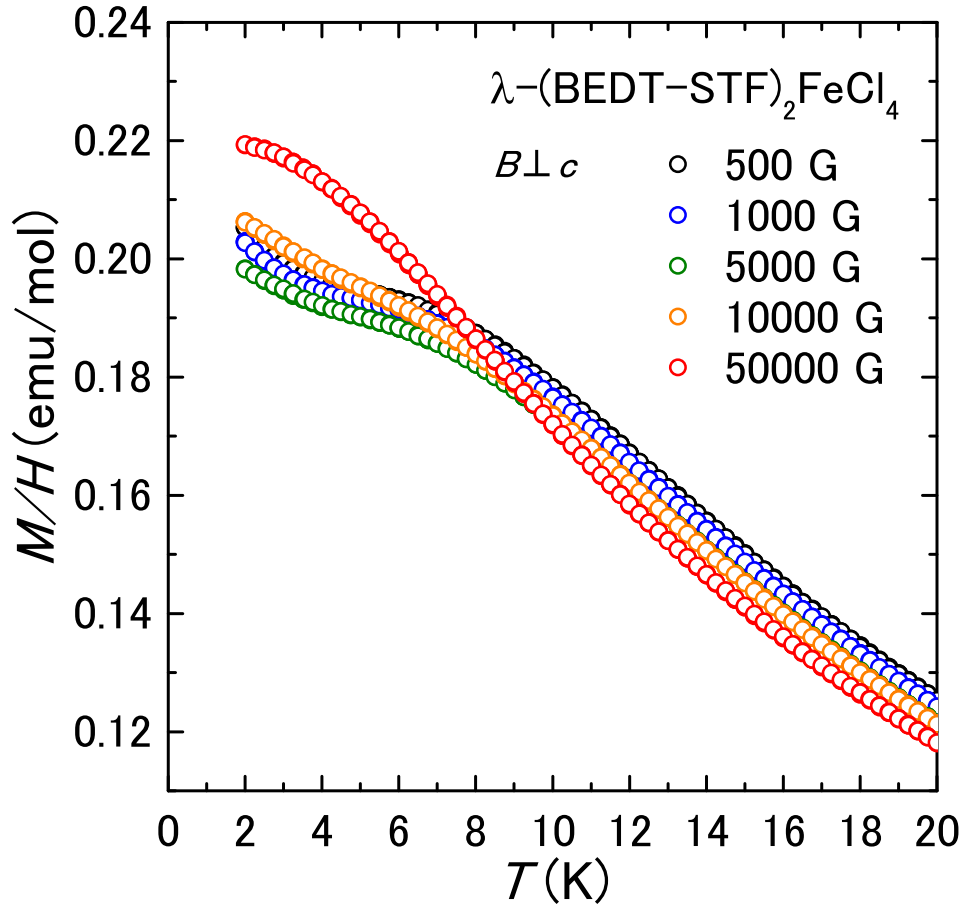


Figure 3.50: Temperature dependence of the static susceptibility in $\lambda\text{-(STF)}_2\text{FeCl}_4$ measured for $B \perp c$ for various field.

impurity were ignored since the spin contribution of the sample is a thousand times larger than such signals. The observed static susceptibility mainly reflects the parallel component to the external field of the $3d$ -spin moments. As shown in Fig. 3.47, above 20 K, the magnetic susceptibility in both direction shows Curie-Weiss-type behavior for the $S = 5/2$ high-spin state with the Weiss temperature $T_W = 6.5$ K.

To compare the results in both field-direction and discuss the magnetic behavior around T_{AF} , the enlarged figure for the low temperature region is shown in Fig. 3.48. Note that the magnetic susceptibility does not show any anomalies at T_{AF} , which is determined from the NMR studies, and the anisotropy in magnetic susceptibility gradually appears below T_{AF} . In the field direction $B//c$, the magnetic susceptibility shows a broad hump structure at low temperature with a peak at 8 K. On the contrary, the magnetic susceptibility for the field perpendicular to the c direction continues to increase with decreasing temperature.

The static susceptibility for $B//c$ and $B \perp c$ for various field up to 5T is shown in Fig. 3.50 and Fig. 3.50, respectively. The hump structure in $B//c$ disappears with increasing magnetic field in the range of 1-5 T and the temperature dependence of susceptibility in both of $B//c$ and $B \perp c$ case is almost overlap at 5 T. This disappearance of the anisotropy by the magnetic field reminiscent the spin-flop of AF ordered moments with the easy axis, which corresponds to the c -axis.

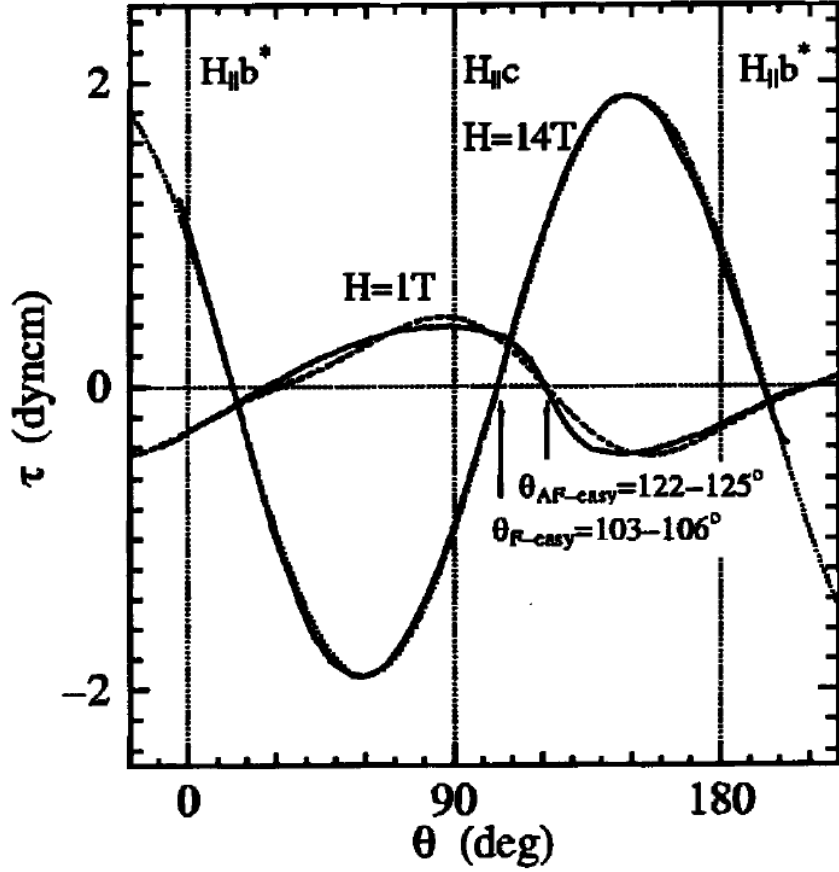


Figure 3.51: Angle θ dependence of the magnetic torque in λ -(BETS) $_2$ FeCl $_4$ with magnetic fields of 1 T and 14 T are applied. Broken and dotted curves are the fitting result. [39]

3.2.4 Discussion for magnetic property

Analysis of magnetic properties in “ π -ordering model”

In the previous report shown in Fig. 1.24, the magnetic susceptibility of λ -(BETS) $_2$ FeCl $_4$ at ambient pressure with $B//c$ shows a sharp drop at $T_{AF} = 8.3$ K and a decrease with a shoulder-shaped anomaly with decreasing temperature below $T_{AF} = 8.3$ K[18]. About this AF phase of λ -(BETS) $_2$ FeCl $_4$, Akiba *et al.* pointed out that the π spin system shows AF magnetic ordering and $3d$ spin system keeps the freedom of rotation in the internal field[21]. They

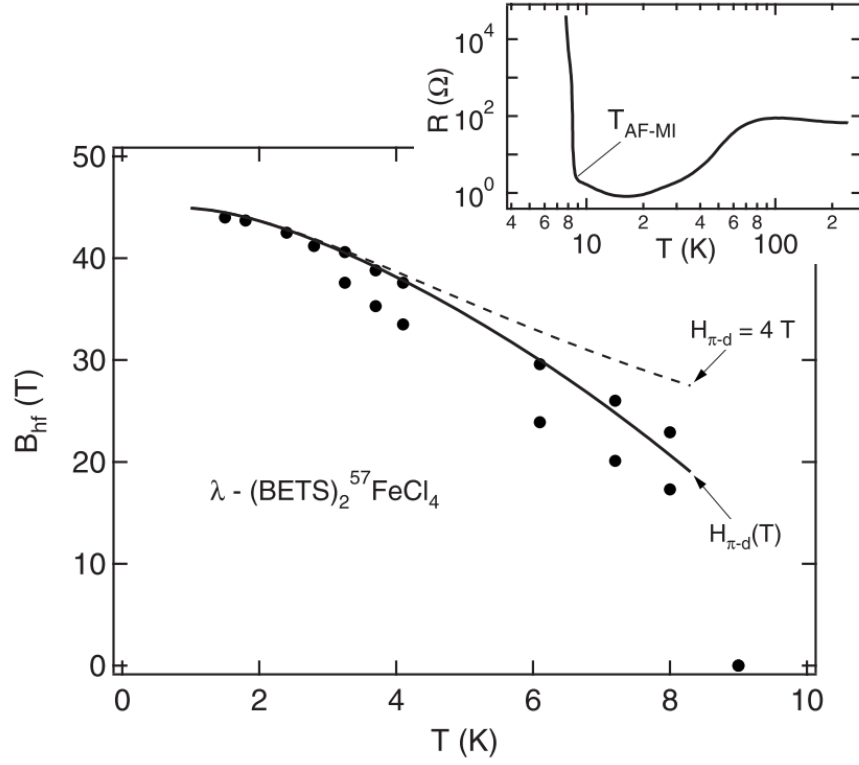


Figure 3.52: Temperature dependence of the hyperfine fields on Fe sites B_{hf} in λ -(BETS)₂FeCl₄ obtained by the Mössbauer spectroscopy method. Solid and dashed curves are the calculated B_{hf} using temperature dependent and independent internal fields on Fe site, respectively. [40]

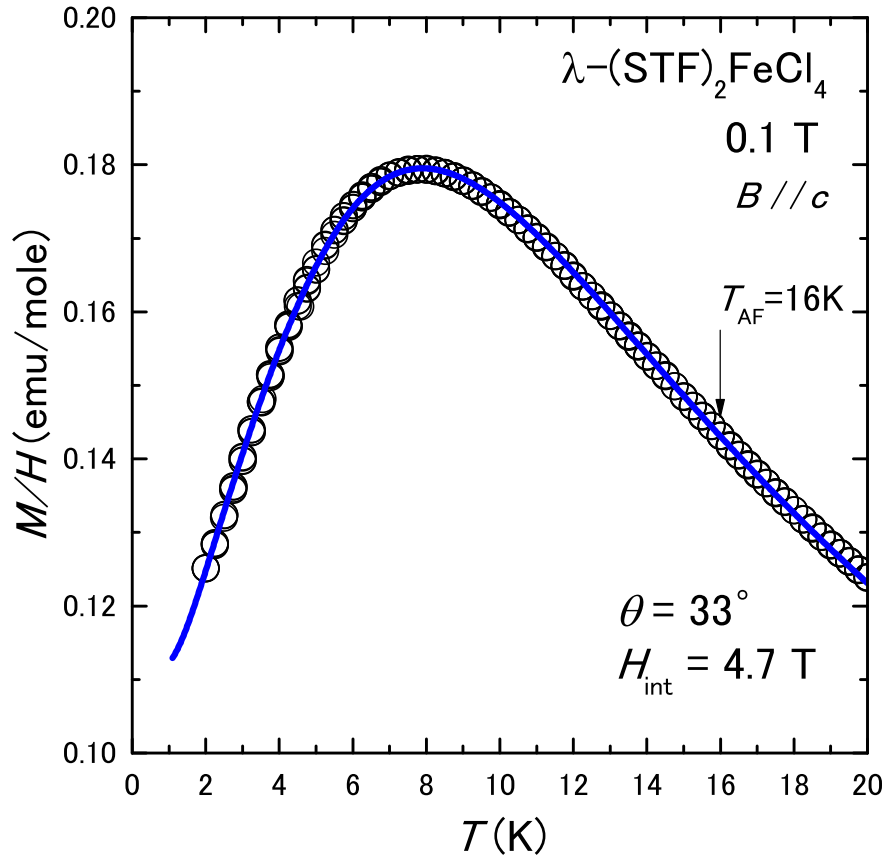


Figure 3.53: Temperature dependence of the static susceptibility in $\lambda-(\text{STF})_2\text{FeCl}_4$ measured for $B//c$ of 0.1 T. Solid curve is the calculated magnetic susceptibility using “ π -ordering model”.

explained the broad shoulder anomaly of the spin susceptibility by the free $3d$ spin in the internal field $\mu_0 H_{\text{int}} = 4$ T arising from the AF ordered π spins via the π - d interaction[22]. Here, we call this model “ π -ordering model” and the detail of this model is shown in the Appendix. Since the internal field on the $3d$ spin changes its direction alternately at each Fe site, the magnetization of the $3d$ spins are canceled out and gradually decrease with decreasing temperature in the AF phase. They have successfully reproduced the characteristic shoulder behavior in the spin susceptibility on the basis of this spin model using the parameters of the angle between the external and internal field $\theta = 25^\circ$, and $\mu_0 H_{\text{int}} = 4$ T. According to the torque measurement, the tilt angle θ is estimated as 30° to the c -axis in the c - b^* plane[39] (Fig. 3.51) and sextet Fe Mössbauer signals generated by an internal magnetic field of about 4 T was observed (Fig. 3.52)[40]. These values are in good agreement with that estimated from the Schottky specific heat[21].

The solid line in Fig. 3.53 shows the calculated magnetic susceptibility using the “ π -ordering model” for λ -(STF) $_2$ FeCl $_4$ with the parameters of $\theta = 33^\circ$ and $\mu_0 H_{\text{int}} = 4.7$ T. These values are close to these of λ -(BETS) $_2$ FeCl $_4$. In the AF phase, the temperature dependence of the magnetic susceptibility is well explained by this model. The observed magnetic susceptibility does not show any anomaly at T_{AF} . It can be considered that the Zeeman splitting energy of the $3d$ spin ($S = 5/2$) in $\mu_0 H_{\text{int}} = 4$ T is much smaller than the thermal energy $k_{\text{B}} T_{\text{AF}}$ because of the high T_{AF} in λ -(STF) $_2$ FeCl $_4$. Therefore, the “ π -ordering model” explains both of the STF and BETS salts consistently.

The static susceptibility in λ -(STF) $_2$ FeCl $_4$ can be well explained by the “ π -

$$H_{\text{loc,A}} = A_{\text{hf}} M_{\text{A}}$$

A_{hf} : Hyperfine coupling tensor

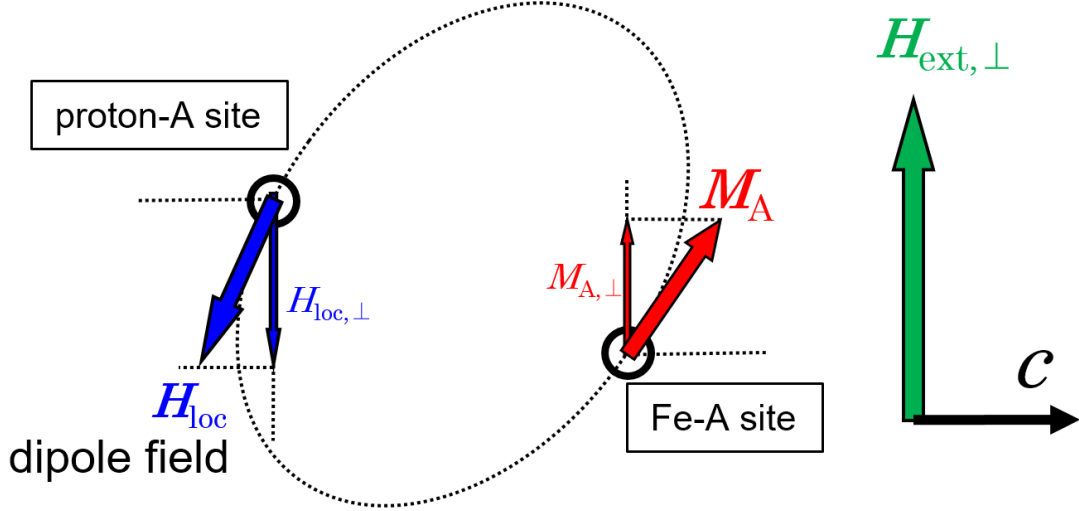


Figure 3.54: Guide for the explanation of δ - χ relation in the present system. Green arrow is the external magnetic field, which is applied perpendicular to the c -axis. Red arrow is the magnetic moment M_{A} of $3d$ spin in the sublattice A. Blue arrow is the internal field at one proton site in the sublattice A, which is due to the dipole interaction from M_{A} .

ordering model” in the entire temperature range. In λ -(BETS) $_2$ FeCl $_4$, since the AF transition of π -spin system occur at 8.3 K, it is difficult to examine the accuracy of the “ π -ordering model” in the wide temperature region. In contrast, in λ -(STF) $_2$ FeCl $_4$, since $T_{\text{AF}} \sim 16$ K is much higher than the energy scale of internal field ~ 4.7 T. We can deduce that the at least π -spin system orders at 16 K and the d -spin system remains the degree of freedom of rotation.

“ π -ordering model” extended with the d - d interaction

Here, we discuss the δ - χ relation, where δ is the NMR shift at one spectrum peak marked as “ ∇ ” in Fig. 3.40 and χ is the static susceptibility with $B \perp c$

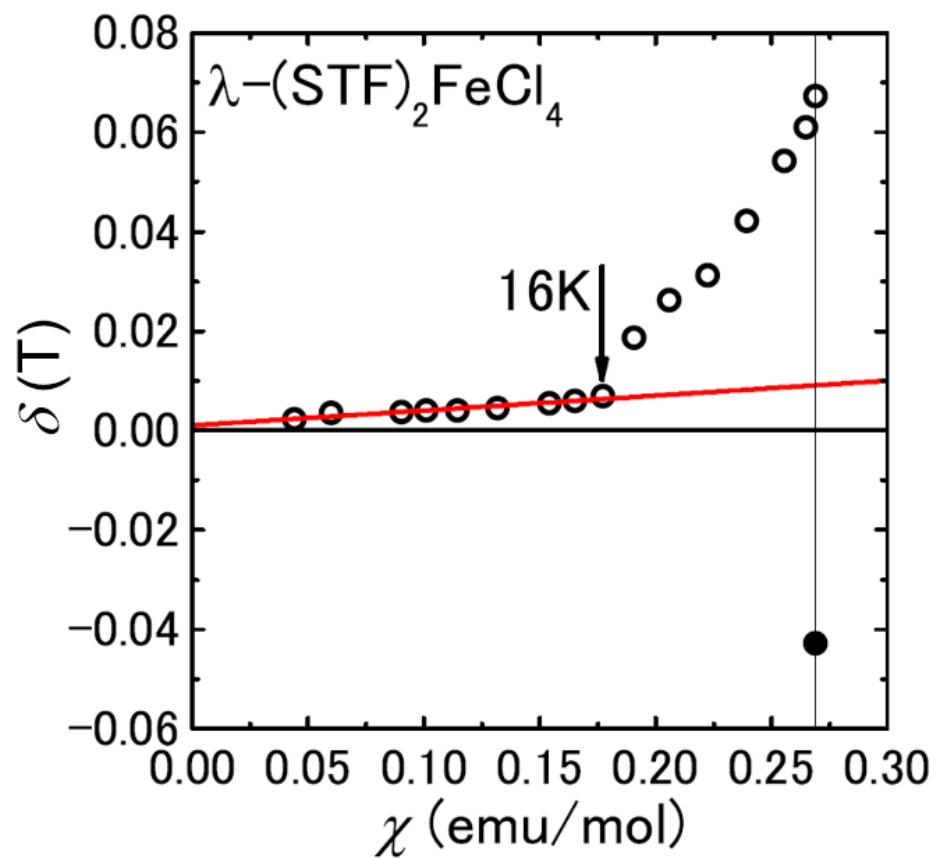


Figure 3.55: δ - χ relation of λ -(STF)₂FeCl₄ obtained from the peaks marked as ∇ and $\blacktriangledown$ in Fig. 3.40.

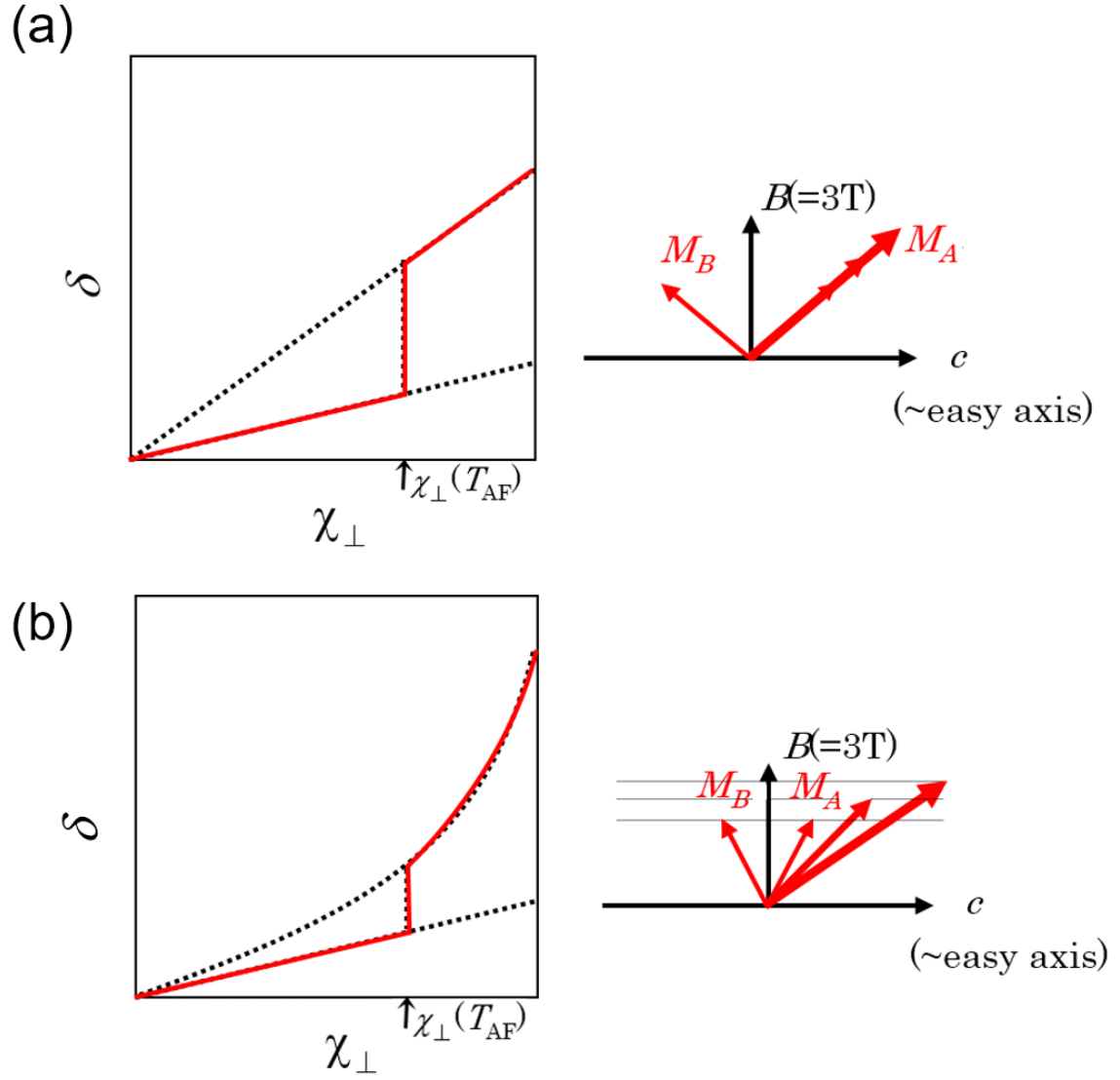


Figure 3.56: Schematic drawing of the δ - χ relation and behaviors of the d -spin magnetizations in sublattice A and B considering the models, which take into account (a) the only π - d , or (b) the π - d and d - d interaction as a source of the internal field.

at 3 T for the single crystal. The δ - χ relation is usually used to obtain the hyperfine coupling constant in the paramagnetic state. The schematic drawing is shown in Fig. 3.54, The obtained χ , using the SQUID magnetometer, reflects the c -perpendicular component of the $3d$ -spin moments $M_{A(B),\perp}$ and δ denotes the c -perpendicular component of the local field $\mathbf{H}_{\text{loc}}$ on the proton site, which is due to the $\mathbf{M}_{A(B)}$ as $\mathbf{H}_{\text{loc}} = A\mathbf{M}_{A(B)}$. In the paramagnetic state (i.e. when $\mathbf{M}_{A(B)}$ is parallel to the direction of the external field.), the slope in δ - χ plot gives a hyperfine coupling constant directly. Generally, in the paramagnetic state, the δ - χ relation follows the formula of $\delta = K + \sigma = A\chi + \sigma$, where K is the Knight shift, A is a hyperfine coupling constant, and σ is the chemical shift.

The δ - χ relation in present study for λ -(STF)₂FeCl₄ is shown in Fig. 3.55. Above 16 K, the observed δ is proportional to χ with negligibly small σ . We evaluated the hyperfine coupling constant as 0.0056 T/ μ_B from the slope of δ - χ plot above 16 K. With decreasing temperature, below 16 K, δ deviates from the proportional line and increases rapidly without saturation. We found a peak marked as “▼” at a symmetrical position to the one marked as “∇” in the spectrum at 4.2 K, although the temperature dependence of the signal marked as “▼” cannot be rigorously traced due to the extrinsic signal. This splitting of the NMR spectrum is caused by the beginning of the AF polarization in the $3d$ spin system. The drastic deviation from the proportional line below 16 K must be caused by the appearance of the c -parallel component of $\mathbf{M}_{A(B)}$ due to the internal magnetic field.

Here, we discuss the δ - χ relation on the “ π -ordering model”. The “ π -

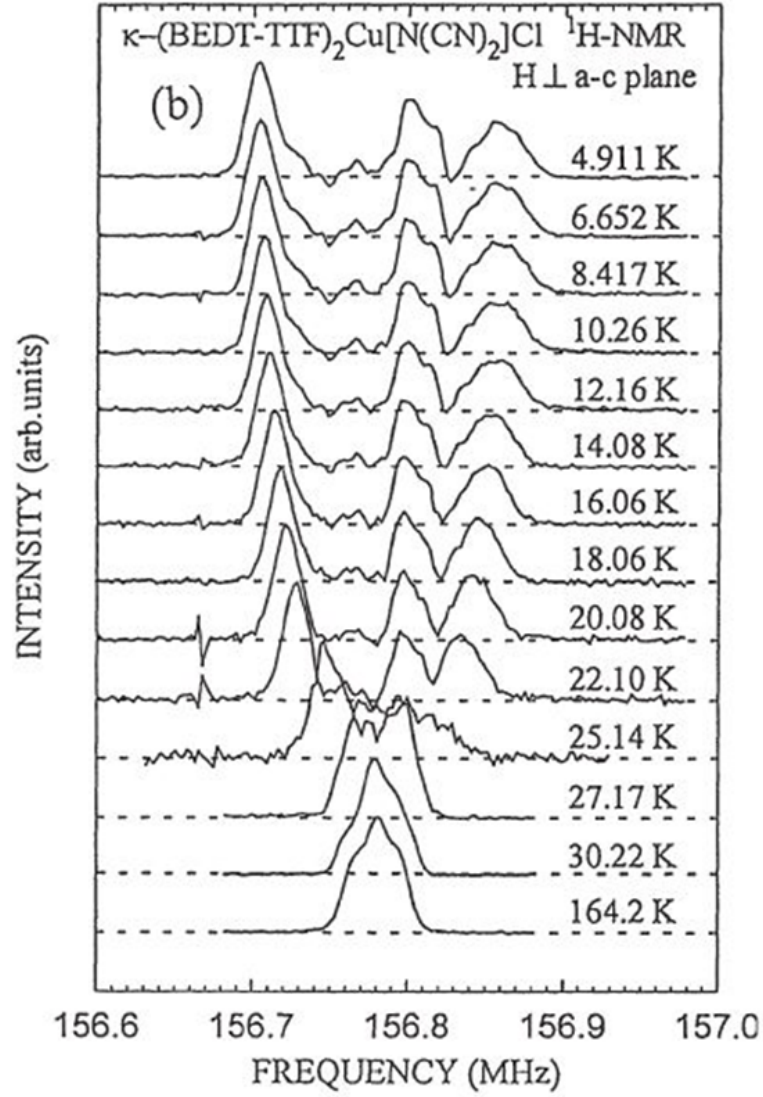


Figure 3.57: $^1\text{H-NMR}$ spectrum of $\kappa\text{-(ET)}_2\text{Cu[N(CN)}_2\text{]Cl}$ for various temperature. Below $T_{\text{AF}}/2 = 13$ K, the split of the spectrum nearly saturates [41].

ordering model” takes into account only the π - d interaction as a source of the internal field on Fe sites[21]. In this model, the $3d$ spins behave as paramagnetic spins placed in the effective field $\mathbf{H}_{\text{eff}} = \mathbf{H}_{\text{ext}} + \mathbf{H}_{\pi-d}$. In this case, since both of δ and χ are proportional to the same Brillouin function, δ must be proportional to χ in the low temperature region below $T_{\text{AF}}/2$, where the π - d exchange field expected to saturate from the mean field theory, although it has a different slope from the metallic phase (see Fig. 3.56(a)). As shown in Fig. 3.57, the temperature dependence of the NMR spectrum in the typical AF magnet, κ -(ET)₂Cu[N(CN)₂]Cl, also suggests that the AF polarization of π -spin system almost saturates below $T_{\text{AF}}/2$ [41]. However, the observed δ - χ relation in AF phase is steeper than the proportional relation and δ continues to increase down to 4.2 K. To explain this behavior, we must extend the “ π -ordering model” and take into account the AF exchange interaction in the d -spin system.

To explain the excess increasing of NMR shift $\Delta\delta$, we stand on the simple model taking into account $\mathbf{H}_{\text{ext}}$, $\mathbf{H}_{\pi-d}$ and $\mathbf{H}_{d-d}$ as shown in Fig. 3.58. For simplicity, we assume the $\mathbf{H}_{\text{ext}}$ is applied perpendicular to the easy axis of the AF ordered π -spin system. As mentioned above, the magnetizations of each sublattices in the AF ordered π -spin system would almost saturate and $\mathbf{H}_{\pi-d}$ is constant below $T_{\text{AF}}/2$. $\mathbf{H}_{d-d}$ is the exchange field from the neighbor d -spin. In the AF phase, each sublattice of ordered π -spin system makes $\mathbf{H}_{d-d,A}$ and $\mathbf{H}_{d-d,B}$ with opposite directions on d -spin sites. $\mathbf{H}_{d-d,A}$ in sublattice-A directs anti-parallel to $\langle \mathbf{M}_B \rangle$. With decreasing temperature, $\mathbf{H}_{d-d,A(B)}$ is grown with growing of $\langle \mathbf{M}_{B(A)} \rangle$ in contrast to $\mathbf{H}_{\pi-d}$, which is temperature

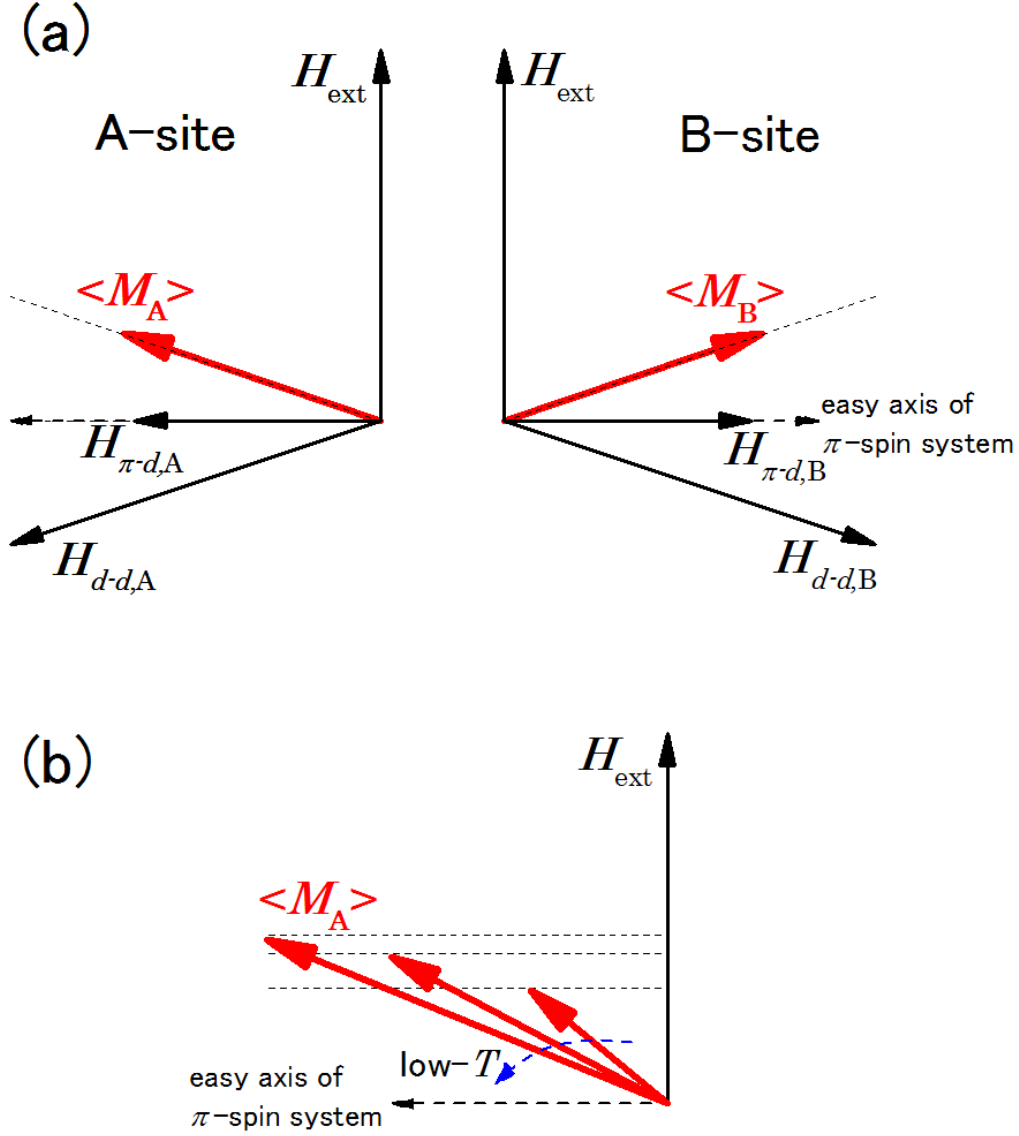


Figure 3.58: (a) Schematic drawing of the magnetic fields and magnetization on each sublattice of the d -spin system. H_{ext} is external field, $H_{\pi-d}$ is the exchange field due to the ordered π -spin system, and $H_{d-dA(B)}$ is the exchange field due to $\langle M_{B(A)} \rangle$. (b) Schematic drawing of the magnetization on d -spin site with changing temperature.

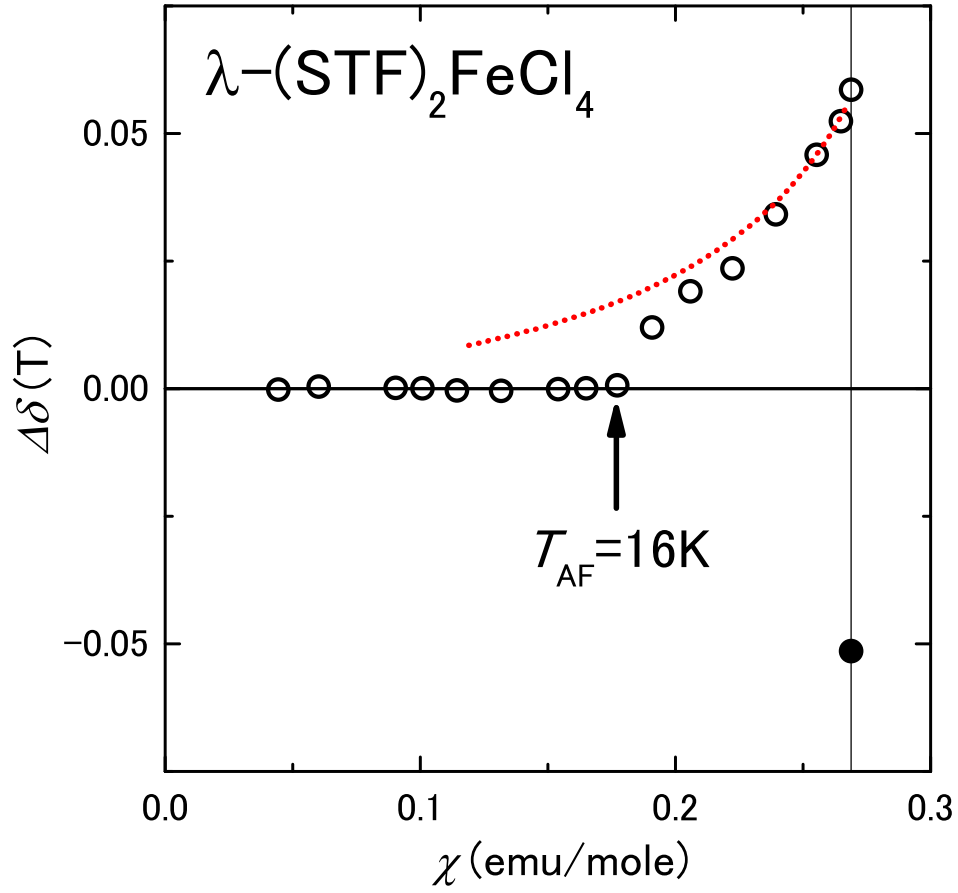


Figure 3.59: δ - χ relation of $\lambda-(\text{STF})_2\text{FeCl}_4$ for the peak, which is marked by ∇ in Fig. 3.40. The contribution from paramagnetic magnetization, solid red line in Fig. 3.55, is already subtracted. Red broken curve is the δ - χ relation calculated by our model with $A_{\text{d-d}} = -2.9$.

independent at low temperature. The changing of ratio between $\mathbf{H}_{\pi-d}$ and $\mathbf{H}_{d-d}$ rotates the moment of d -spin system with decreasing temperature as shown in Fig. 3.58(b). χ is proportional to $\langle \mathbf{M}_A \rangle + \langle \mathbf{M}_B \rangle$. On the other hand, the splitting in δ reflects the amplitude of $\langle \mathbf{M}_A \rangle - \langle \mathbf{M}_B \rangle$. Accordingly, the points of the arrow in Fig. 3.58(b) describes the δ - χ relation. Thus, the observed $\delta - \chi$ relation is well explained by the model considering the rotation of d -spin as shown in Fig. 3.56(b), which predicts that the δ - χ relation shows an increasing of its slope at low temperature.

The dotted line in Fig. 3.59 is the fitting curve for δ - χ relation with our model. The magnetizations in each sublattice A and B in d -spin system is calculated with simple Brillouin function,

$$\langle \mathbf{M}_{A(B)} \rangle = \frac{N}{2} g \mu_B s_d B_S \left(\frac{g \mu_B \mathbf{s}_d \cdot \mathbf{H}_{\text{eff},A(B)}}{k_B T} \right), \quad (3.3)$$

with the effective field $\mathbf{H}_{\text{eff},A(B)} = \mathbf{H}_{\text{ext}} + \mathbf{H}_{\pi-d} + \mathbf{H}_{d-d,A(B)}$. $\mathbf{H}_{d-d,A(B)}$ orients antiparallel to the magnetization of the opposite sublattice and is described as $\mathbf{H}_{d-d,A(B)} = A_{d-d} \langle \mathbf{M}_{B(A)} \rangle$, where $A_{d-d} (< 0)$ is the AF magnetic coupling constant of d - d exchange interaction. Hence, we calculated the χ and $\Delta\delta$ as

$$\chi = (\langle \mathbf{M}_A \rangle + \langle \mathbf{M}_B \rangle) / H_{\text{ext}} \quad (3.4)$$

$$\Delta\delta \propto \langle \mathbf{M}_A \rangle - \langle \mathbf{M}_B \rangle \quad (3.5)$$

using $\mu_0 H_{\text{ext}} = 3$ T with fitting parameters of A_{d-d} and a proportionality constant in Eq. 3.5. We estimated $\mu_0 H_{\pi-d} \sim 2$ T and $\mu_0 H_{d-d} \sim 3.4$ T at 4.2 K from the $\delta - \chi$ curve below 8 K. The obtained $\mu_0 H_{\text{eff}} \sim 5.3$ T is nearly

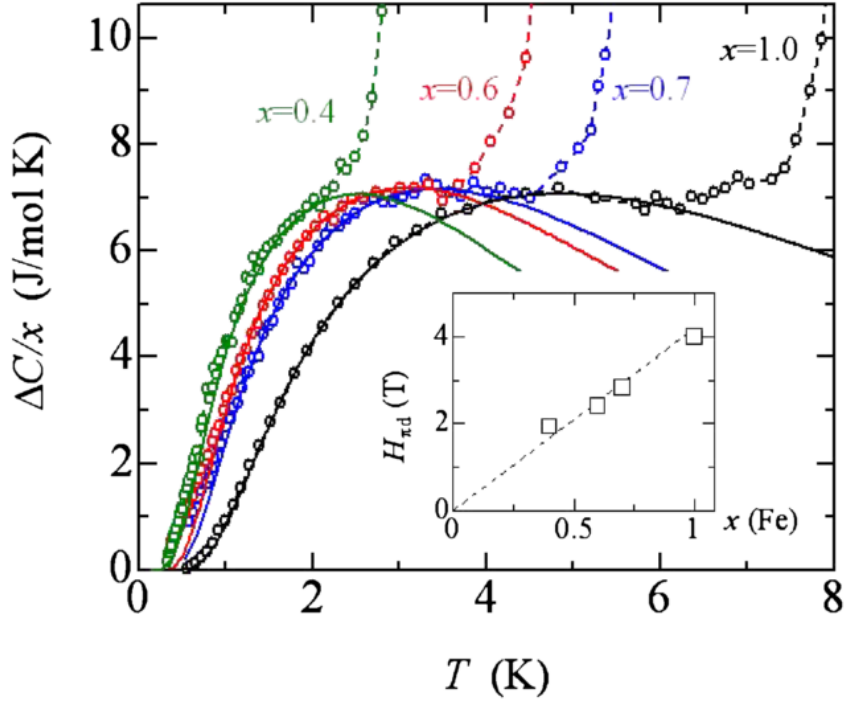


Figure 3.60: Temperature dependences of excess specific heat divided by Fe content $\Delta C/x$. The solid curves show the Schottky specific heats, which are based on the paramagnetic $3d$ spin ($S=5/2$) system under the internal magnetic field $H_{\pi-d}$. The broad maximum of the Schottky specific heat shifts to lower temperatures with decreasing $H_{\pi-d}$. The inset shows the Fe density dependence of $H_{\pi-d}$. [42]

consistent to the obtained value from the temperature dependence of χ with “ π -ordering model”. Although the temperature dependence of the $\mathbf{H}_{d-d}$ modifies the behavior of χ in “ π -ordering model”, the differences are not significant. From these discussion, $d-d$ interaction is thought to assist the stabilization of the AF ordering of the π -spin system.

In the recent report of the specific heat for λ -(BETS) $_2$ Fe $_x$ Ga $_{1-x}$ Cl $_4$, H. Akiba *et al.* pointed out that the $H_{\pi-d}$ is roughly proportional to the Fe spin density x in the range of $x > 0.4$ [42]. They noted this experimental result as a puzzling problem because there is no reason for that high Fe spin density x increases the $H_{\pi-d}$ owing to the saturation magnetization of the AF-ordered

π -spin. However, the internal field on d -spin site they observed contains not only $H_{\pi-d}$ but also H_{d-d} . Therefore, we can solve the puzzling problem by taking into account the contribution of H_{d-d} . The reduction of H_{int} by the decreasing of x can be explained by the reduction of H_{d-d} . Since the number of the neighbor d -spins of the one d -spin site gets reduced with decreasing x , the network of $d-d$ exchange interaction is broken. Accordingly, all of λ -(BETS) $_2\text{Fe}_x\text{Ga}_{1-x}\text{Cl}_4$ and λ -(STF) $_2\text{FeCl}_4$ are well explained by the framework of the “ π -ordering model” extended in d - d exchange coupling.

3.3 Universal phase diagram of the λ -type salts family

λ -(STF) $_2\text{GaCl}_4$ shows the SC phase above 1.2 GPa and it has the same electronic situation to that of λ -(BETS) $_2\text{GaCl}_4$ at approximately 1.5 GPa. The magnetic state of λ -(STF) $_2\text{GaCl}_4$ at ambient pressure, which is the adjacent phase of the SC phase, does not show the AF magnetic order down to 1.3 K, although the increasing of the AF fluctuation, precursory of the AF transition, is observed below 4.2 K. From the behavior of the static susceptibility, this non-AF-ordered state is expected to be a strongly frustrated paramagnetic state.

In the same way, λ -(STF) $_2\text{FeCl}_4$ at 1.5 GPa and λ -(BETS) $_2\text{FeCl}_4$ at ambient pressure are situated at the same electronic state with almost the same T_{AF} and field dependence. As we expected, in λ -(STF) $_2\text{FeCl}_4$ at ambient pressure, we found the AF phase with higher $T_{\text{AF}} = 16$ K than that of the λ -(BETS) $_2\text{FeCl}_4$ at ambient pressure from the ^1H -NMR studies. From the static susceptibility and ^1H -NMR measurements, we found that this AF phase

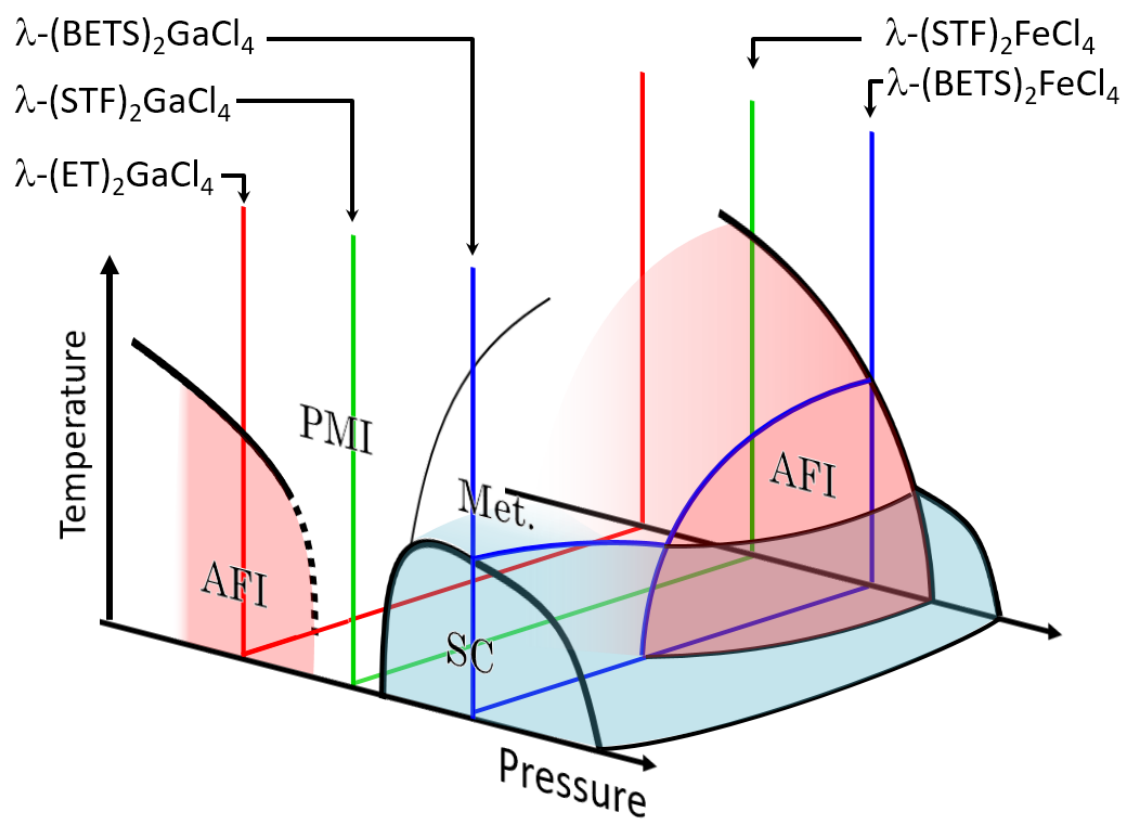


Figure 3.61: Universal phase diagram of λ -type family. A part of λ -(BETS) $_2$ Fe $_x$ Ga $_{1-x}$ Cl $_4$ is investigated by H. Tanaka *et al.*[43]

is stabilized by the same order of the π - d and d - d interactions.

From these experiments for λ -(STF)₂GaCl₄ and λ -(STF)₂FeCl₄, we have concluded that the λ -type salts family, λ - D_2M Cl₄ ($D = \text{ET, STF, BETS, } M=\text{Ga, Fe}$), can be placed on the universal phase diagram with/without $3d$ -spins.

Chapter 4

Conclusion

We have synthesized the single crystals of λ -(STF)₂GaCl₄ and λ -(STF)₂FeCl₄ to investigate the SC phase in λ -type salts family and the π - d interacting system.

We have measured the resistivity under pressure and the static susceptibility at ambient pressure in λ -(STF)₂GaCl₄. We found a superconducting phase in the λ -STF salt above 1.22 GPa. We confirmed the superconductivity by observing pair-breaking under a magnetic field. This is the first observation of superconductivity in λ -STF salts. The superconducting transition temperature T_c increased with increasing pressure in the range below 1.35 GPa and decreased above 1.35 GPa. Above 1.27 GPa, the resistivity curve showed a gradual insulator-metal transition at $T_{IM} \sim 20$ -50 K. Over almost the entire temperature range below room temperature, the metallic state below T_{IM} was broadened with increasing pressure above 1.60 GPa. The temperature dependence of the spin susceptibility at ambient pressure showed paramagnetic behavior over the whole temperature range. This behavior can be described by a spin 1/2 two-dimensional Heisenberg AF system in a triangular lattice

with exchange-coupling constant $J = 165$ K.

We have measured ^1H -NMR and static susceptibility in λ -(STF) $_2\text{FeCl}_4$ to investigate the π - d interacting system. From the temperature dependence of T_1^{-1} observed in ^1H -NMR, we have determined that $T_{\text{AF}} = 16$ K at ambient pressure. The temperature dependence of the spin susceptibility, which shows a broad hump structure without any anomaly at T_{AF} , suggests that the AF transition at 16 K is due to the AF long range ordering in π -spin system. We found the non-negligible effect of the $d-d$ AF interaction to the effective field, which is comparable to that of the $\pi-d$ interaction, from the relation between the ^1H -NMR splitting associated with the AF and the static susceptibility, which is sensitive to the rotation of the local d -spin moment. The AF phases in λ -type salts can be explained by the “ π -ordering model” extended with the large contribution of d - d AF exchange field universally.

In λ - $D_2\text{GaCl}_4$, we deduce that the AF phase is suppressed with increasing pressure and found that the phase adjacent to the SC phase is not a AF phase but the paramagnetic phase. In λ - $D_2\text{FeCl}_4$, we found that the AF phase in the $D = \text{STF}$ salt with the higher transition temperature than that of the $D = \text{BETS}$ salt. From these experiments for λ -(STF) $_2\text{GaCl}_4$ and λ -(STF) $_2\text{FeCl}_4$, we have concluded that the λ -type salts family, λ - $D_2M\text{Cl}_4$ ($D = \text{ET}, \text{STF}, \text{BETS}, M = \text{Ga}, \text{Fe}$), can be placed on the universal phase diagram with/without $3d$ -spins.

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Appendix A

π -ordering model

Specific heat

In a recent study based on thermodynamic properties, H. Akiba *et al.* proposed that π spin state is AF ordered and the $3d$ spin state is in the internal magnetic field arising from the π spin sites [21]. The open circles in Fig. A.1 show the temperature dependence of the excess specific heat ΔC , which is obtained by the subtraction of the specific heat of the GaCl_4 salt from the total one of the FeCl_4 salt. Since both salts are isostructural crystal with almost the same lattice parameters, the specific heat of the GaCl_4 salt can be assumed to be the lattice contribution of that of the FeCl_4 salt. Although GaCl_4 salt shows the SC transition at $T_c = 5.5$ K, the jump of the electronic specific heat at this temperature is negligibly small (~ 0.1 J/mol·K)[44]. Therefore, ΔC denotes the spin contribution. A sharp peak structure was observed at 8.3 K, which cooperative with MI transition and a broad hump structure that appears to be a Schottky-type anomaly was found on a lower temperature. If π and d spin systems cooperatively align antiferromagnetically, the larger peak of ΔC would be observed at T_{AF} , followed by a rapid reduction of the entropy

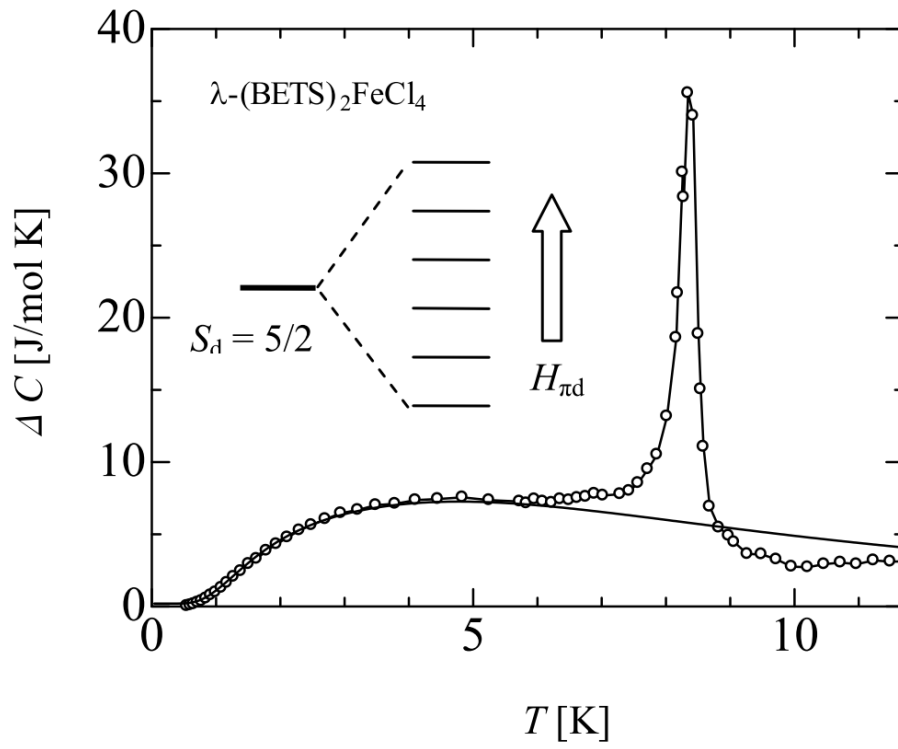


Figure A.1: Temperature dependence of the excess specific heat ΔC of λ -(BETS)₂FeCl₄ obtained by subtracting the lattice and electric specific heats estimated for λ -(BETS)₂GaCl₄. [21]

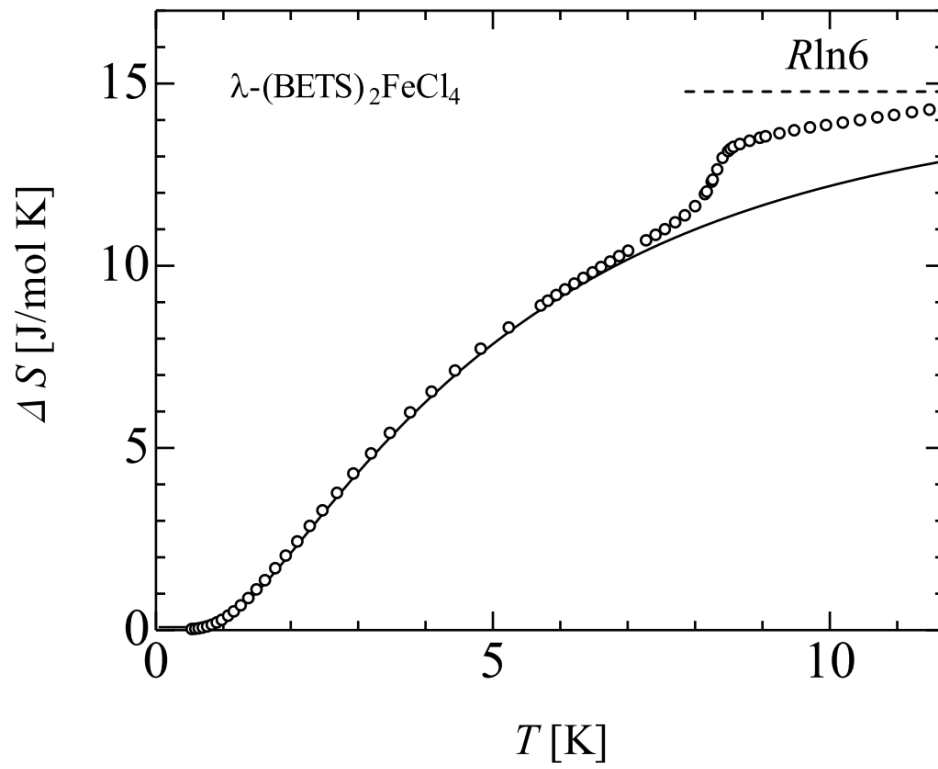


Figure A.2: Temperature dependence of spin entropy of λ -(BETS) $_2$ FeCl $_4$ estimated from ΔC . [21]

without the hump structure. This hump anomaly suggests that the existence of the discrete energy levels due to the Zeeman effect, i.e. the existence of the free spin system in the internal field given by the AF ordered spin system.

The solid curve in Fig. A.1 is the temperature dependence of the spin specific heat for the paramagnetic spin system with $S = 5/2$ split into six levels under an effective magnetic field $\mu_0 H_{\pi-d} \approx 4$ T. The Schottky-type specific heat with six levels is described as

$$\begin{aligned} \Delta C = \frac{Nk_B\Delta^2}{k_B^2T^2} \{ & [\sin(\Delta/k_BT) + 9\sin(3\Delta/k_BT) + 25\sin(5\Delta/k_BT)] \times \\ & [\cosh(\Delta/k_BT) + \cosh(3\Delta/k_BT) + \cosh(5\Delta/k_BT)] - \\ & [\sin(\Delta/k_BT) + 9\sin(3\Delta/k_BT) + 25\sin(5\Delta/k_BT)]^2 / \\ & [\cosh(\Delta/k_BT) + \cosh(3\Delta/k_BT) + \cosh(5\Delta/k_BT)]^2 \}, \end{aligned} \quad (\text{A.1})$$

where N is the number of spins, k_B is the Boltzmann constant, and Δ is a half of the energy gap of the discrete levels. This description supposes that the $3d$ spin system behaves paramagnetically and AF ordered π spin system gives the internal field $H_{\pi-d}$ to the d -spin system. This calculation can reproduce the observed ΔC very well. The entropy $S(T) = \int_0^T dT \Delta C/T$ indicates the information about the degrees of freedom. As shown in Fig. A.2, the resulting entropy shows step down at 8.3 K corresponding to the sharp peak of ΔC and, at high temperature region, reaches to a value of $R \ln 6 = 14.9$ J/mol·K, which corresponds to the spin degrees of freedom for the $3d$ spin.

According to these studies for specific heat of λ -(BETS) $_2$ FeCl $_4$, the authors proposed that the AF phase of this salt below 8.3 K occurs by the ordering of π -spin system and the degree of freedom in d -spin system is remained. Here

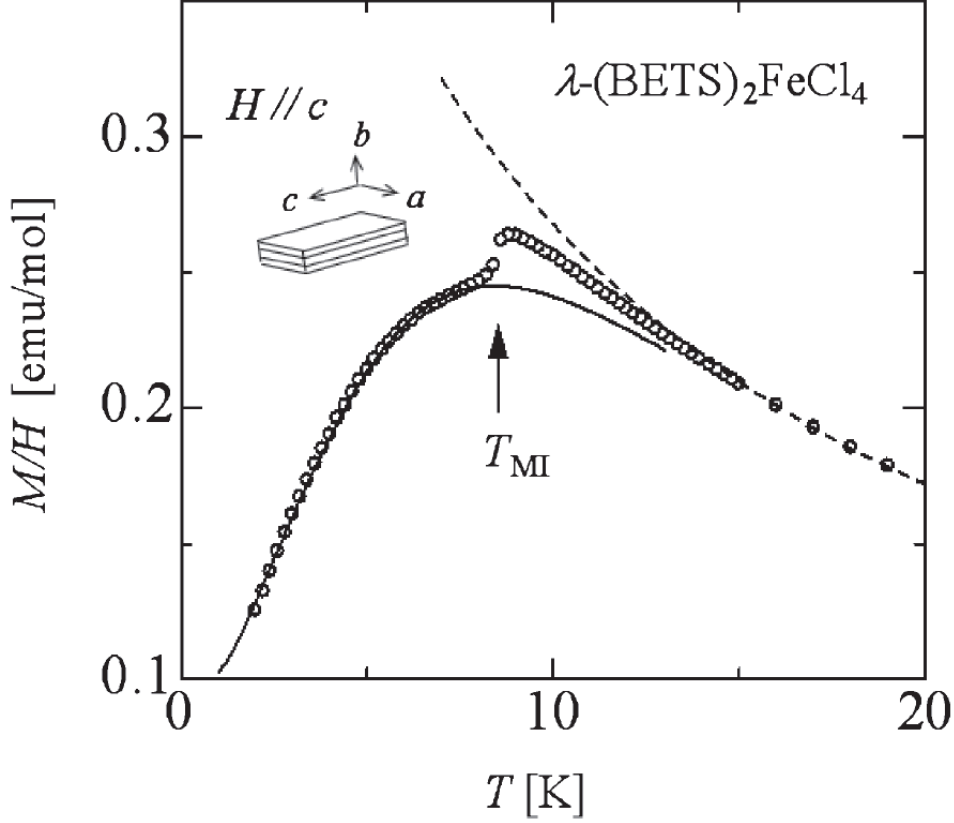
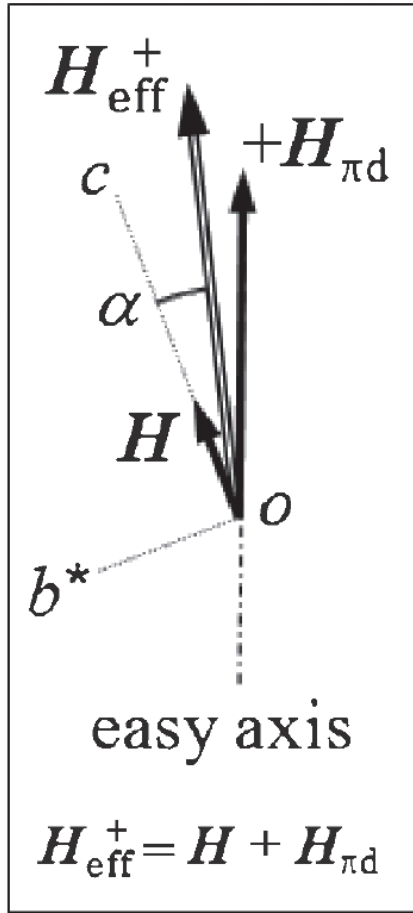


Figure A.3: Temperature dependence of the magnetic susceptibility M/H of λ -(BETS) $_2$ FeCl $_4$ under external magnetic field parallel to the c -axis.[22]

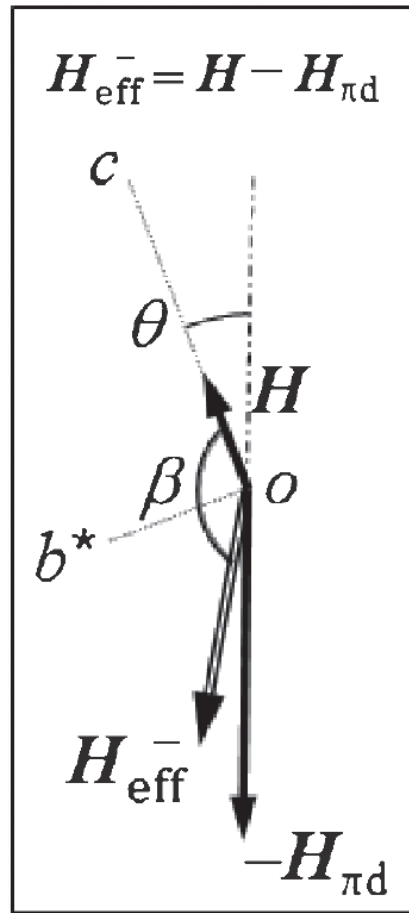
after, this description is called “ π -ordering model” in this paper.

Magnetic susceptibility

“ π -ordering model” also describes the temperature dependence of the magnetic susceptibility[22]. Figure A.3 shows the magnetic susceptibility of the FeCl $_4$ salt observed under the application of an external field $\mu_0 H_{\text{ext}} = 0.1$ T parallel to the c -axis. Above $T_{\text{AF}} = 8.3$ K, the magnetic susceptibility shows Curie-Weiss-type behavior for the $3d$ spin ($S = 5/2$). With decreasing temperature, it shows a sharp step down at T_{AF} , and the characteristic shoulder type anomaly, which corresponds to the region where the Schottky-type specific



A site



B site

Figure A.4: Effective magnetic fields H_{eff}^+ (H_{eff}^-) at the Fe A (B) site with external field H parallel to the c -axis and internal field $+H_{\pi-d}$ ($-H_{\pi-d}$). [22]

heat is observed.

As mentioned above, Schottky-type specific heat can be explained by the Zeeman splitting of the paramagnetic $3d$ -spin system under the internal field $H_{\pi-d}$, which is given by the exchange interaction $J_{\pi-d}$ with AF-ordered π -spin system. According to this description, as shown in Fig. A.4, the spin susceptibility of the paramagnetic $3d$ -spin system assuming the internal field from nearest-neighbor π -spin, which is alternately oriented in the opposite direction. Since the alternating internal field aligns the $3d$ spins, the magnetization of the $3d$ -spin system would be canceled out and gradually decrease with decreasing temperature in the AF phase. The authors calculated the magnetizations M_d^+ and M_d^- at sites A and B using the Brillouin function B_S as

$$M_d^\pm = \frac{N}{2} g\mu_B S_d B_S \left(\frac{g\mu_B \mathbf{S}_d \cdot \mathbf{H}_{\text{eff}}^\pm}{k_B T} \right). \quad (\text{A.2})$$

The external field is applied along the c -axis. Considering the tilt angle between the easy axis and the c -axis, the magnetization component M_d parallel to H can be obtained as

$$M_d = M_d^+ \cos(\alpha) + M_d^- \cos(\beta) \quad (\text{A.3})$$

where the α (β) is the angle between $\mathbf{H}$ and $\mathbf{H}_{\text{eff}}^{+(-)}$, which is determined from θ , $\mathbf{H}_{\pi-d}$ and $\mathbf{H}$.

Appendix B

Properties of the organic spin-liquid materials

Specific heat

The thermodynamics studies were conducted for the organic spin-liquid materials $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ and $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$. The C_p/T versus T^2 plots for these salts and their brother materials are shown in Fig. B.1[45] and Fig. B.2[46]. Remarkably, the electronic specific heat coefficient γ in spin-liquid materials shows the non-zero value at low temperature region in contrast to the other insulating brother materials. The obtained γ values are 19.9 and 12.6 ($\text{mJK}^{-2}\text{mol}^{-1}$) for $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ and $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$, respectively. This behavior is generally seen in the metallic phase. These non-zero values of γ suggest the gapless state in the spin excitation like a metallic phase, although they show the insulating property in the transport measurements. This behavior characterizes the spin-liquid phase of these salts.

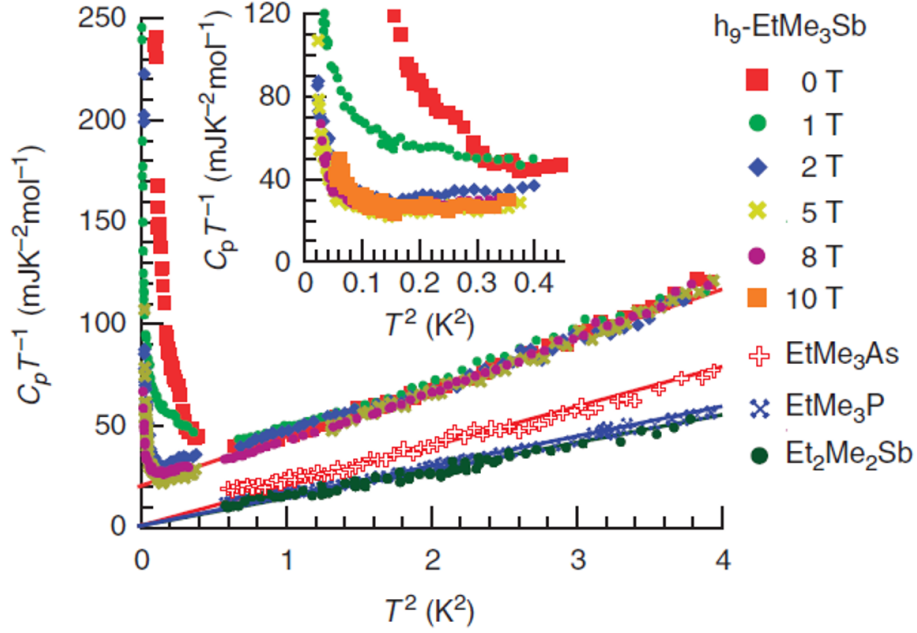


Figure B.1: Low temperature heat capacities of $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ below 2K for various magnetic field[45].

¹H-NMR

¹H-NMR spectrum of $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$ is shown in Fig. B.3(a). Remarkably, the shape of spectrum does not change at the whole temperature range. On the contrary, that of the $\text{Cu}_2[\text{N}(\text{CN})_2]\text{Cl}$ salt shows the obvious splitting due to the AF ordering below 27 K. From this fact, it is expected that there is no magnetic ordering in $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$ down to 32 mK although it is expected to have a strong AF exchange interaction $J \sim 250$ K from susceptibility measurement [47]. As shown in Fig. B.4, $1/T_1$ of $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$ decreases with decreasing temperature dramatically below 50 K and it means that the AF spin fluctuation is suppressed at low temperature region. Below 0.5 K, the relaxation curve is not given by the single exponential curve. In this case, the two kinds of proton sites are separated by the macroscopic different

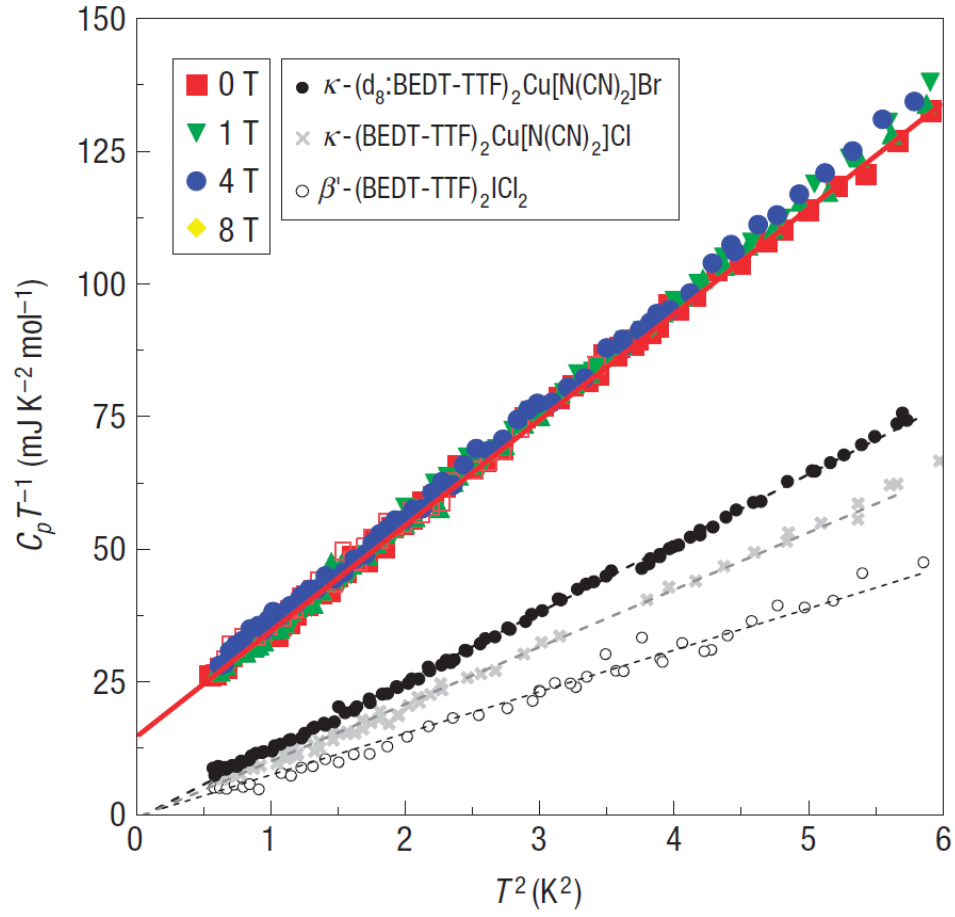


Figure B.2: Low temperature heat capacities of $\kappa\text{-(ET)}_2\text{Cu}_2\text{(CN)}_3$ for 0 T (red square), 1 T (green triangle) and 4 T (blue circle)[46].

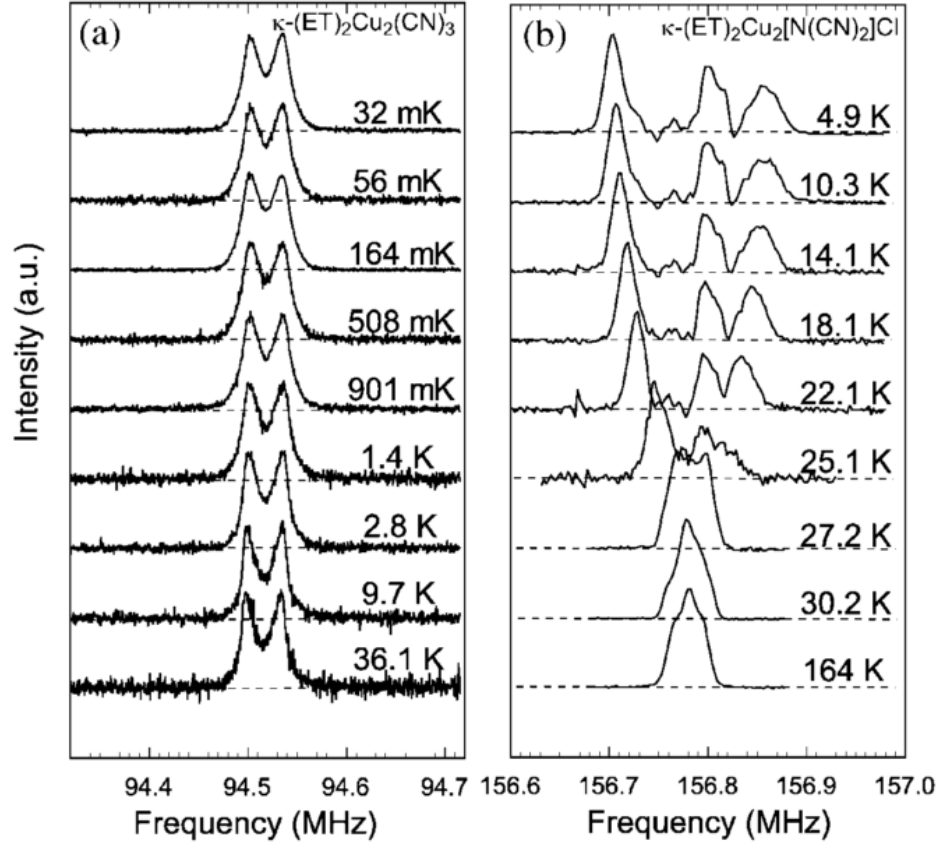


Figure B.3: ^1H -NMR spectrum of (a) $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$ and (b) $\kappa\text{-(ET)}_2\text{Cu}_2[\text{N}(\text{CN})_2]\text{Cl}$ for various temperature[47].

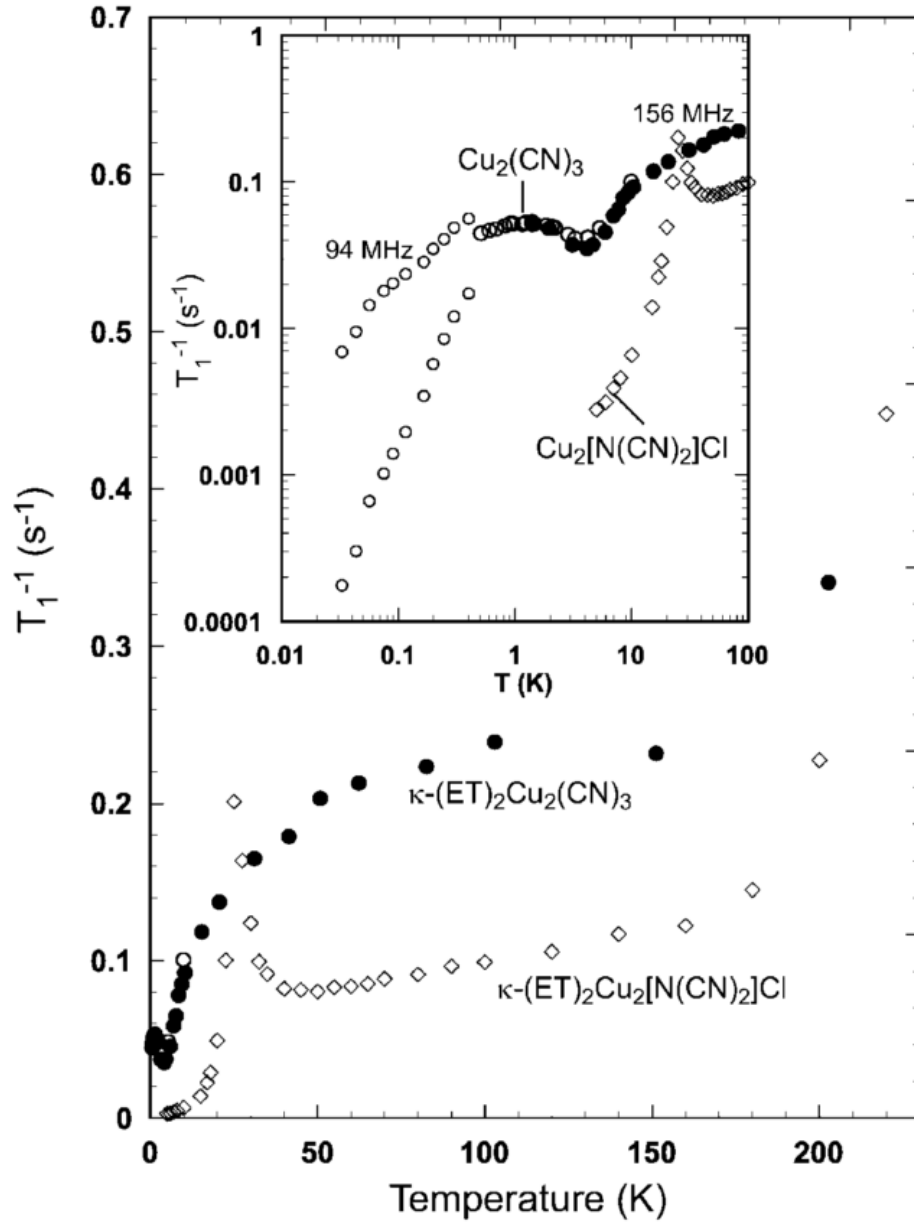


Figure B.4: Temperature dependence of the $1/T_1$ obtained by the ^1H -NMR measurement for κ -(ET)₂Cu₂(CN)₃[47].

spin state, which is induced by some impurity or another cause. This $1/T_1$ behavior is different to the present result for λ -(STF)₂GaCl₄. We need more sensitive investigation at low temperature to clarify the difference in the spin state between these salts.