Organic Antiferromagnetic Metals Exhibiting Superconducting Transitions κ-(BETS)$_2$FeX_4 (X = Cl, Br): Drastic Effect of Halogen Substitution on the Successive Phase Transitions

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IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

The magnetic and thermal properties of an organic conductor incorporating localized magnetic moments, κ-(BETS)$_2$FeCl$_4$, were investigated down to 60–70 mK. Similar to the Br analogue, κ-(BETS)$_2$FeBr$_4$, κ-(BETS)$_2$FeCl$_4$ exhibited successive antiferromagnetic and superconducting transitions with lowering temperature (T_N = 0.45 K, T_C = 0.1 K). That is, κ-(BETS)$_2$FeCl$_4$ is the second antiferromagnetic organic metal that exhibits a superconducting transition at ambient pressure. It became clear that the halogen exchange (Br → Cl) in the anions results in the strong reduction of both magnetic and superconducting transition temperatures. Resistivities showed a small drop at 0.45 K ($= T_N$), which gave a direct evidence of the existence of π–d interaction between π metal electrons and localized magnetic moments of Fe atoms. In contrast to κ-(BETS)$_2$FeBr$_4$ exhibiting a three-dimensional nature of the magnetic transition, the specific heat of κ-(BETS)$_2$FeCl$_4$ indicates the low dimensionality of the spin system.   © 2001 Academic Press

INTRODUCTION

Electronic properties of molecular materials have long been a subject of continual interest in the field of solid state science. In particular, since the first discovery of an organic superconductor in 1980 (1), various types of molecular conductors including a number of two-dimensional organic superconductors (2) and even a three-dimensional molecular metal composed of single-component planar molecules (3) have been developed. Although most of the molecular conductors ever developed are π conductors where only π electrons are responsible for the solid state properties, molecular metals incorporating localized magnetic mo-

ments have recently attracted an increasing interest (4, 5). With the aim of the systematic studies on the role of the localized magnetic moments in π molecular conductors, we have prepared a series of BETS salts (BETS = bis(ethylenedithio)tetraselenafulvalene) with magnetic and non-magnetic tetrahalogenometalate anions, MX_4 (M = Ga, In, Fe; X = Cl, Br) (6). There are two main modifications in these systems, λ- and κ-(BETS)$_2$$MCl_4$. Recent studies on λ- and κ-(BETS)$_2$FeX_4 have disclosed a new class of organic solids, that is, magnetic organic superconductors, that has contributed to opening a new area between the fields of molecular conductors and molecule-based magnets.

Although determining the role of the π–d interaction between π metal electrons and localized magnetic moments is a central problem in the studies on magnetic molecular conductors, there have been almost no organic metal systems exhibiting clear evidence of the π–d interaction until recently. Despite that λ-(BETS)$_2$GaCl$_4$ without magnetic anions is a superconductor under ambient pressure, the isostructural crystal of λ-(BETS)$_2$FeCl$_4$ undergoes a metal–insulator transition around 8 K below which a unique π–d coupled antiferromagnetic insulating state develops (7, 8). The mixed anion system, λ-(BETS)$_2$Fe$_{1-x}$Ga$_x$Cl$_4$, shows an unprecedented superconductor-to-insulator transition (9, 10). Furthermore, λ-(BETS)$_2$FeCl$_4$ exhibits a superconducting transition at high pressure (11). These facts show a crucial role of π–d interaction in the stabilization of the low-temperature metallic state of λ-type BETS conductors containing Fe^{3+} ions. On the other hand, κ-(BETS)$_2$$MX_4$ with a two-dimensional arrangement of BETS molecules has a much stabler metallic state (Fig. 1). Recently we have discovered the successive phase transitions of κ-(BETS)$_2$FeBr$_4$ from paramagnetic metal to anitiferromagnetic metal (T_N = 2.5 K) and to superconductor (T_C = 1.1 K) with lowering temperature
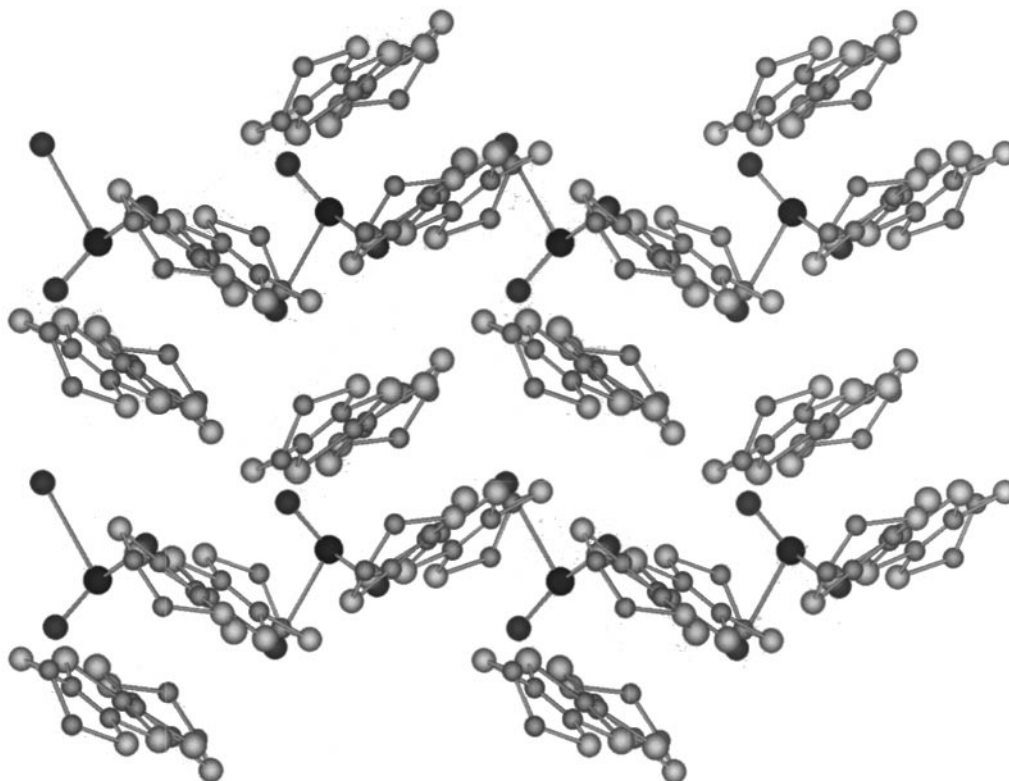
FIG. 1. Crystal structure of κ-(BETS)$_2$FeCl$_4$.

(12). The antiferromagnetic phase showed a metamagnetic behavior and the system becomes a ferromagnetic metal above approx. 2 T (13). The specific heat shows a large λ-type peak at T_N but no anomaly at T_C (13). This specific heat behavior and the anisotropy of the resistivity under a magnetic field below T_C indicate the coexistence of the magnetic order and superconductivity below T_C (13). On the other hand, the Cl analogue, κ-(BETS)$_2$FeCl$_4$, exhibits no transition down to 2 K (6). In order to illuminate the origin of the difference between the electronic properties of FeBr$_4^-$ and FeCl$_4^-$ salts, we measured magnetic susceptibilities of κ-(BETS)$_2$FeX_4 (X = Cl, Br) and the specific heat of κ-(BETS)$_2$FeCl$_4$ down to 60–70 mK and discovered the successive magnetic and electric phase transitions.

EXPERIMENTAL

Synthesis

Black plate crystals of κ-(BETS)$_2$FeX_4 (X = Cl, Br) were prepared electrochemically from the 5–10% ethanol/chlorobenzene solution containing BETS and [(C$_2$H$_5$)$_4$N][FeX_4] under nitrogen. The solvents were reagent grade and freshly distilled. The electrocrystallization was made under a constant current (0.7 μA: κ-(BETS)$_2$FeBr$_4$) or a constant voltage condition (4.0 V: κ-(BETS)$_2$FeCl$_4$).

Physical Properties

The *ac* magnetic susceptibilities χ_{ac} were measured in the temperature range of 60 mK–7 K by using a homemade dilution refrigerator and a homemade ac susceptometer system based on the *dc* SQUID magnetometer (Conductus Inc.). The oscillating field of about 1–10 mOe and the frequency 175 Hz are charged to the sample for the measurement. The geomagnetic field of approx. 300 mOe is reduced by about 1/100 using a μ metal shield so that the measurements were done at a field less than 10 mOe. The isotropic susceptibility, χ_{ac}, was measured using a polycrystalline sample of about 6 mg. For the anisotropy measurements, about 10 to 20 crystals were stuck to the sample space using apiezon N grease, where their crystallographical axes *a*, *b*, and *c* were oriented parallel to the external field altogether. The typical mass of the sample was approx. 3 mg. The absolute value of χ_{ac} was calibrated so that the temperature dependence at 2 K $< T <$ 7 K agrees with the χ_p value obtained by the high-temperature measurements using the SQUID magnetometer (MPMS-2, MPMS-7) (13, 14). As reported before, the χ_p value suggests the high spin states ($S = \frac{5}{2}$) of Fe^{3+} (14).

The heat capacity C_p was measured in the temperature range of 70 mK–1.5 K using a homemade dilution refrigerator and a homemade calorimeter. The adiabatic

method was adopted. A polycrystalline sample of 5.80 mg was used.

RESULTS

Magnetic Susceptibilities of κ-$(BETS)_2FeX_4$ $(X = Cl, Br)$

The temperature dependencies of the magnetic susceptibilities of κ-$(BETS)_2FeBr_4$ and κ-$(BETS)_2FeCl_4$ are shown in Fig. 2. The susceptibilities of κ-$(BETS)_2FeBr_4$ were obtained using oriented crystals, while the randomly oriented polycrystalline sample was used for κ-$(BETS)_2FeCl_4$. As was reported briefly (13, 15), κ-$(BETS)_2FeBr_4$ undergoes a magnetic phase transition and become a metallic antiferromagnet below 2.5 K $(= T_N)$ (12, 13). The cusp around T_N and the branches below T_N clearly show the existence of long-range order as shown in Fig. 2a, where the measurements were made by applying the field parallel to the easy axis $(H//a)$ or perpendicular to it $(H \perp ac)$. The second drop at 1 K corresponds to the superconducting transition. As seen from Fig. 2b, a similar susceptibility anomaly was observed at 0.65 K in κ-$(BETS)_2FeCl_4$ (see Fig. 2b), which is considered to be a transition from the paramagnetic metal phase to the antiferromagnetic metal phase on the analogy of the transitions in κ-$(BETS)_2FeBr_4$. However, the transition temperature was reduced strongly. The second sharp drop at 0.1 K was assigned to the Meissner signal because the χ_{ac} value decreased very sharply to minus. Compared with the T_C of κ-$(BETS)_2FeBr_4$, the T_C of κ-$(BETS)_2FeCl_4$ was also depressed. It should be noted that the antiferromagnetic transition of κ-$(BETS)_2FeCl_4$ was found independently by Zhang et al. and Uozaki et al. (16, 17).

Specific Heat of κ-$(BETS)_2FeCl_4$

As mentioned above, the magnetic transition of κ-$(BETS)_2FeCl_4$ was observed around 0.65 K. In order to examine whether the bulk magnetic long-range order really exists, we performed specific heat measurements down to 70 mK. Figure 3 shows the temperature dependence of the specific heat for κ-$(BETS)_2FeCl_4$. A sharp peak was observed at 0.45 K, which suggests the development of antiferromagnetic long-range order with the Néel temperature (T_N) of 0.45 K. However, no anomaly was detected around T_C $(\approx 0.1$ K), indicating that the magnetic order is not destroyed by the onset of superconductivity. It is worth noting that the temperature where χ_{ac} took a cusp (approx. 0.65 K) was 0.2 K higher than T_N. This kind of deviation was not observed in κ-$(BETS)_2FeBr_4$ (13). Furthermore, the peaks of specific heat of κ-$(BETS)_2FeCl_4$ trail a significant tail at a temperature region higher than T_N. In fact, the entropy $S(T)$ around the T_N calculated by neglecting small contributions from the lattice and the conduction electrons shows a gradual increase at $T > T_N$ but reaches no more than approx. 86% of the expected total magnetic entropy $S(\infty) = R\ln(2S + 1)$ $(= 14.9$ J/mol K for $S = \frac{5}{2})$: at $T = 3T_N (\approx 13.5$ K) S is $0.81 \times S(\infty)$, and at $T \approx 1.5\,T_N$ S is
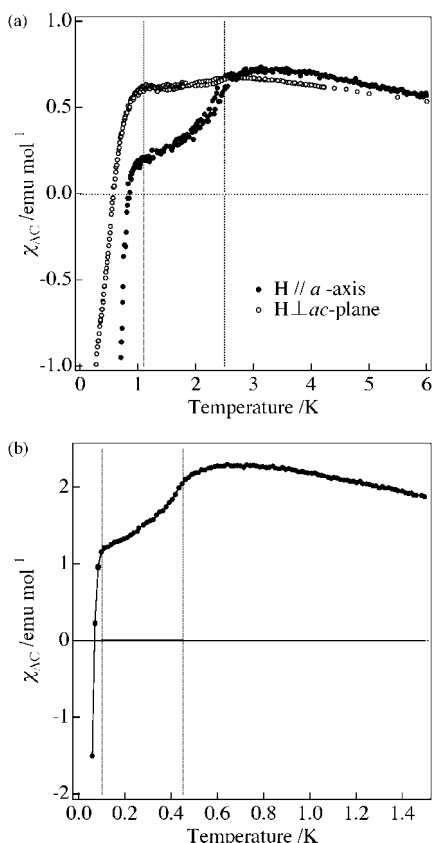

FIG. 2. (a) The ac susceptibility of κ-$(BETS)_2FeBr_4$ (oriented crystals). (b) The ac susceptibility of κ-$(BETS)_2FeCl_4$ (polycrystalline sample).
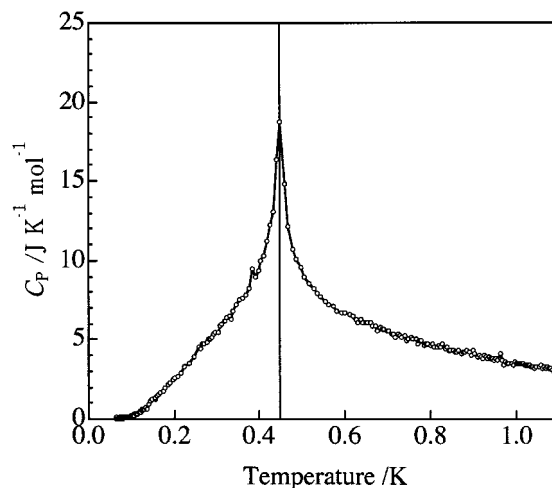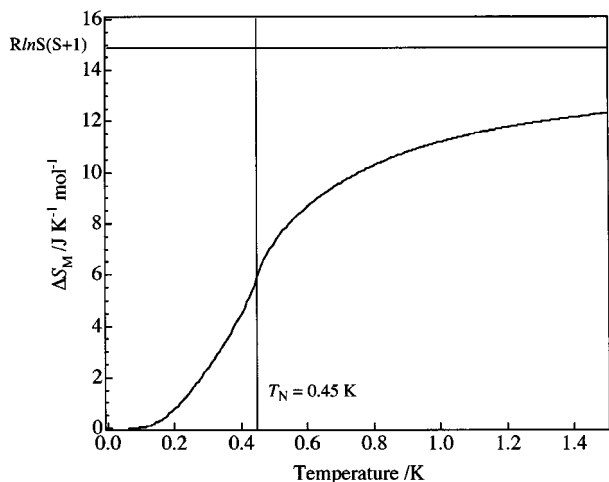

FIG. 3. The specific heat of κ-$(BETS)_2FeCl_4$.

FIG. 4. The calculated entropy of the magnetic transition of κ-$(BETS)_2FeCl_4$.

$0.68 \times S(\infty)$ (Fig. 4). The critical magnetic entropy of κ-$(BETS)_2FeCl_4$ is $S(T_N) = 0.40S(\infty)$, which is considerably smaller than the entropy of κ-$(BETS)_2FeBr_4$: $S = 0.64S(\infty)$ at T_N and $1.0\ S(\infty)$ at 3.6 K ($\approx 1.5\ T_N$) (13).

Electrical Conductivity of κ-$(BETS)_2FeCl_4$

Electric resistivity measurements of κ-$(BETS)_2FeCl_4$ crystal were carried out down to approx. 0.1 K (Fig. 5a). The temperature dependencies of the resistivities of κ-$(BETS)_2FeCl_4$ and κ-$(BETS)_2FeBr_4$ at $T > 2$ K are also shown in Fig. 5b (6). Similar to κ-$(BETS)_2FeBr_4$, κ-$(BETS)_2FeCl_4$ showed a resistivity drop at T_N irrespective of the direction of the current. This means the decrease of conduction electron scattering due to the onset of magnetic

order therefore gave direct evidence of π–d interaction between π metal electrons and localized magnetic moments of Fe^{3+} ions (Fig. 5a). The resistivities at $T < T_N$ clearly show κ-$(BETS)_2FeCl_4$ to be the second example of an organic antiferromagnetic metal at ambient pressure. The resistivity along the direction perpendicular to the conduction plane exhibited a relatively large temperature dependence below T_N, but no clear indication of the onset of a resistivity drop suggesting superconducting transition was observed down to 0.1 K.

Anisotropy of Magnetic Susceptibilities of κ-$(BETS)_2FeCl_4$

The magnetic susceptibilities of κ-$(BETS)_2FeCl_4$ measured for the field applied along the a, b, and c axes using oriented crystals ($\chi_{//a}$, $\chi_{//b}$ and $\chi_{//c}$) are shown in Figs. 6a, 6b, and 6c. The susceptibilities increased with decreasing temperature at $T > 0.65$ K. Below 0.65 K, the susceptibilities became anisotropic. The $\chi_{//a}$ value decreased asymptotically to approximate zero down to T_C (≈ 0.1 K). The temperature dependence of $\chi_{//a}$ was steepest around the peak temperature of specific heat (0.45 K). While $\chi_{//b}$ was approximately constant at $T_C < T < 0.65$ K. The variation of $\chi_{//c}$ below 0.65 K was also small except for the temperature range of 0.45 K $< T < 0.65$ K. The anisotropic magnetic susceptibility at $T_C < T < T_N$ is typical of the antiferromagnet with uniaxial magnetic anisotropy where the easy axis is parallel to the a axis. The susceptibility drop indicating superconducting transition was observed for every direction. The susceptibility drop was largest for the field along the direction perpendicular to the conduction plane, that is, the b direction, which is consistent with the two-dimensional character of the tight-binding band structure (18, 19).
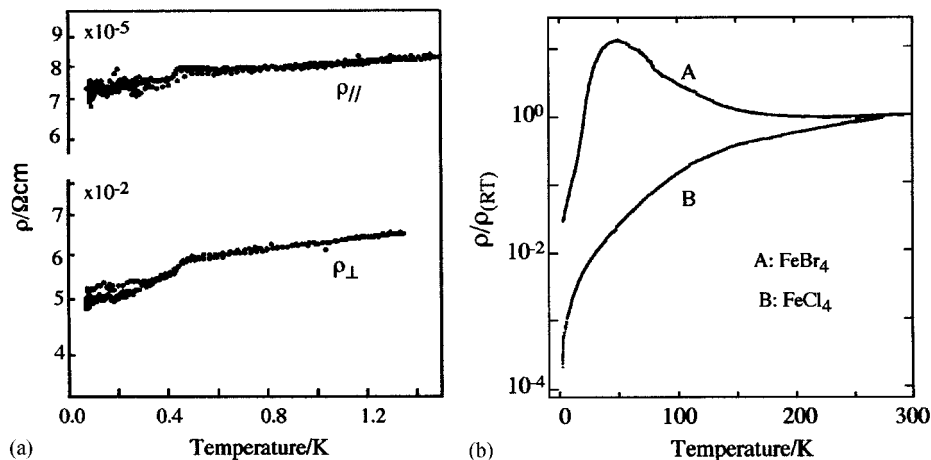

FIG. 5. (a) The resistivities of κ-$(BETS)_2FeCl_4$ along the directions parallel ($\rho_{//}$) and perpendicular ($\rho_\perp$) to the ac plane. (b) The resistivities of κ-$(BETS)_2FeCl_4$ and κ-$(BETS)_2FeBr_4$ at $T > 2$ K, reproduced from the data reported in Ref. (6).
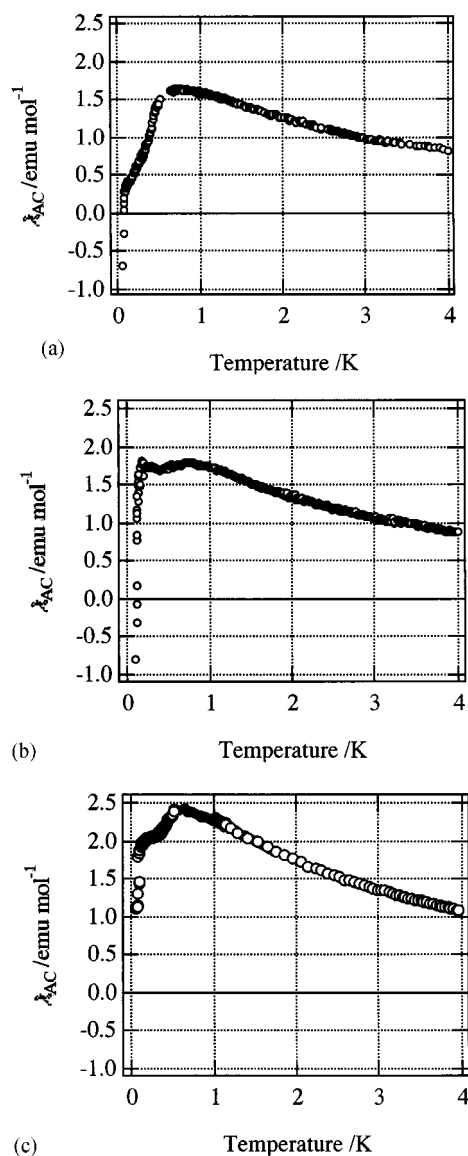
FIG. 6. The *ac* susceptibility of oriented crystals of κ-(BETS)$_2$FeCl$_4$ for the magnetic field parallel to the directions of the *a*, *b* and *c* axes.

TABLE 1
The Unit Cell Dimensions for κ-(BETS)$_2$FeX$_4$

	a (Å)	b (Å)	c (Å)	V (Å)
κ-(BETS)$_2$FeBr$_4$	11.787(6)	36.607(9)	8.504(5)	3669(2)
κ-(BETS)$_2$FeCl$_4$	11.678(8)	35.925(7)	8.481(8)	3557(3)

between the Fe^{3+} seems to indicate that κ-(BETS)$_2$FeCl$_4$ salt has a somewhat advantage in acquiring stronger interaction, but this is in striking contrast to the strongly depressed magnetic transition temperature of FeCl$_4$ salt. Then the superexchange interactions through BETS molecules are considered to be crucial. As seen from Table 2, the shortest distances of the halogen–S contact ($d_{S \cdots X}$) is 3.693 Å for κ-(BETS)$_2$FeBr$_4$ and 3.547 Å for κ-(BETS)$_2$FeCl$_4$. These distances are 0.06 and 0.11 Å shorter than the sum of the van der Waals radii of X and S, respectively. Therefore the lowering of T_N in FeCl$_4$ salt is hardly to be explained on the basis of interatomic distances.

The halogen atoms of FeX$_4^-$ anions are considered to play an important role in the superexchange interaction, and the energy level of the *p* orbital of the halogen atom will be critical. Since the energy level of the 4*p* orbital of the Br atom is higher than that of the 3*p* orbital of the Cl atom, the stronger *d*–π mixing will be expected in the "*d*-like orbital" of FeBr$_4^-$. Furthermore, the electron cloud of Br is much more expanded than that of Cl. Therefore, stronger π–*d* interaction between the *d*-like orbital of FeX$_4^-$ and the π molecular orbital of BETS is expected in FeBr$_4^-$, which will lead to a stronger antiferromagnetic interaction between Fe^{3+} ions. Thus, it may be imagined that the antiferromagnetic interaction will be much enhanced if we can obtain an isostructural κ-type crystal with FeI$_4^-$ anions. However, the trial to prepare BETS conductors with FeI$_4^-$ anions was not made because the synthesis of [(C$_4$H$_9$)$_4$N][FeI$_4$] was not successful.

DISCUSSION

Small T_N of κ-(BETS)$_2$FeCl$_4$

As mentioned above, both T_N and T_C of κ-(BETS)$_2$FeX$_4$ were decreased strongly by the halogen exchange (Br → Cl). Table 1 shows the lattice parameters of κ-(BETS)$_2$FeBr$_4$ and κ-(BETS)$_2$FeCl$_4$. The lattice constants of κ-(BETS)$_2$FeCl$_4$ are contracted by 1–3% from those of κ-(BETS)$_2$FeBr$_4$. Consequently, the distances between the Fe^{3+} spins are shortened. Table 2 summarizes the important intermolecular contacts. The shortest distance between Fe atoms (d(Fe $\cdots$ Fe)) is 5.920 Å for κ-(BETS)$_2$FeBr$_4$ and 5.879 Å for κ-(BETS)$_2$FeCl$_4$. At first sight, the distances

TABLE 2
Selected Bond Lengths (Å) of κ-(BETS)$_2$FeBr$_4$ (a) and κ-(BETS)$_2$FeCl$_4$ (b)

(a)	
Fe1–Fe1	5.920
Br1–S3	3.707
Br1–S1	3.776
Br1–S2	3.905
Br3–S2	3.693
(b)	
Fe1–Fe1	5.879
Cl1–S3	3.592
Cl1–S1	3.780
Cl1–S2	3.800
Cl3–S2	3.547

The effect of halogen exchange can be also found in the electrical behavior. As reported in λ-type BETS conductors, the decrease of unit cell volume induced by the Br $\to$ Cl exchange in MX_4 anions produces "chemical pressure" in the crystal lattice (20, 21). Similar to the real pressure, the chemical pressure enhances the metallic nature of the system. Similar to the round resistivity maximum characteristic to the highly correlated π metal systems such as κ-type BEDT-TTF superconductors (2), which is suppressed by applying real pressure, the round resistivity maximum observed in κ-(BETS)$_2$FeBr$_4$ with large anions disappears in κ-(BETS)$_2$FeCl$_4$ (Fig. 5b). A very low T_C of κ-(BETS)$_2$FeCl$_4$ can also be considered to be consistent with the chemical pressure effect because the T_C of an organic superconductor is usually lowered by pressure.

Anisotropy of Antiferromagnetic State

The anisotropic magnetic susceptibility of κ-(BETS)$_2$FeCl$_4$ revealed the easy axis to be parallel to the a axis. At first glance, the magnetic anisotropy of κ-(BETS)$_2$FeX_4 ($X =$ Cl, Br) seems to be independent of halogen atoms because this orientation of the easy axis coincides with that of κ-(BETS)$_2$FeBr$_4$ (11). However, recent magnetic studies on the oriented polycrystals of mixed halogen systems κ-(BETS)$_2$FeCl$_x$Br$_{4-x}$ indicate the situation to be not so simple (22). The main results are as follows: (1) T_N and T_C get smaller with decreasing x ($T_N \approx 2.0$ K and T_C (onset) ≈ 0.8 K at $x = 0.5$). (2) The direction of easy axis changes with changing x. It is parallel to the ac plane for $x < 0.5$ but perpendicular to it for $x > 1.2$. It was very difficult to determine the anisotropy of susceptibility by SQUID magnetometer at $x > 3.0$ because T_N is strongly lowered. At $x = 4.0$, as mentioned before, the easy axis becomes parallel to the a axis again.

CONCLUSION

The magnetic and thermal properties of the d–π system κ-(BETS)$_2$FeCl$_4$ were investigated down to very low temperature. Similar to the Br analogue, κ-(BETS)$_2$FeBr$_4$, the crystal exhibited successive magnetic and electric transitions with lowering temperature. Thus the κ-(BETS)$_2$FeCl$_4$ is found to be the second antiferromagnetic organic metal that exhibits a superconducting transition at ambient pressure. A small resistivity drop observed around 0.45 K ($= T_N$) clearly shows the existence of π–d interaction between π metal electrons and localized magnetic moments of Fe^{3+} ions. The temperatures of magnetic and superconducting transitions of κ-(BETS)$_2$FeCl$_4$ are much lower than those of κ-(BETS)$_2$FeBr$_4$. Unlike κ-(BETS)$_2$FeBr$_4$ exhibiting a three-dimensional magnetic transition, the specific heat of

κ-(BETS)$_2$FeCl$_4$ indicates the low dimensionality of the spin system.

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