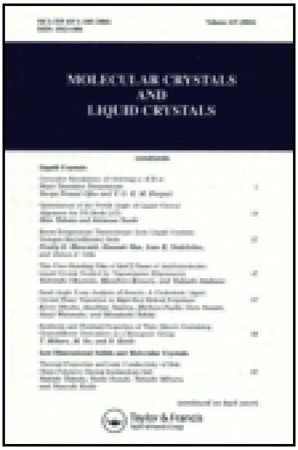

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New BETS Superconductors and Metals with Tetrahedral Non-Magnetic and Magnetic Anions (BETS = Bis(ethylenedithio)tetraselenafulvalene)

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NEW BETS SUPERCONDUCTORS AND METALS WITH TETRAHEDRAL NON-MAGNETIC AND MAGNETIC ANIONS

(BETS = Bis(ethylenedithio)tetraselenafulvalene)

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Abstract Two types of BETS conductors are reported. Needle crystals of λ-$BETS_2GaX_xY_{4-x}$ gave a series of new superconductors: λ-$BETS_2GaCl_4$ (T_c=7 K), λ-$BETS_2GaBrCl_3$ (8 K), λ-$BETS_2GaCl_3F$ (3.5 K), λ-$BETS_2GaBr_{0.5}Cl_{3.5}$ (6.5 K). λ-$BETS_2GaBr_{1.5}Cl_{2.5}$, which is a semiconductor at 1 bar, exhibited a superconducting transition at 8 K and *ca.* 1 kbar. Pressure and temperature dependencies of the resistivities of λ-$BETS_2GaX_xY_{4-x}$ closely resemble those of κ-type BEDT-TTF superconductors. Many BETS metals with magnetic ions (Fe^{3+}, Mn^{2+}, Co^{2+}, Cu^{2+}) were prepared. Among them, κ-type MX_4 (M=Fe, Co; X=Cl, Br) salts and θ-type Cu_2Cl_6 salts are metallic down to at least 4 K. The static susceptibility of λ-$BETS_2FeCl_4$ shows a characteristic magnetic field dependence below its metal-insulator transition temperature.

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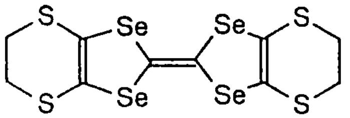
INTRODUCTION

Recent progress of solid state chemistry of the conducting molecular crystals is quite remarkable. Owing to the great improvement of the structure-chemical concept of molecular design achieved in 1980s, the development of stable two-dimensional (2D) metals becomes fairly easy. The intermolecular close contacts between peripheral chalcogen atoms of the planar π molecules and the suitable symmetries of the frontier molecular orbitals are of central importance to produce 2D metal bands. The development of 2D molecular π metals enabled the fundamental physical experiments on the metallic state of molecular crystals at low temperature and produced the increasing number of molecular superconductors. Nevertheless, the variety of their constituent molecules seems to be very limited. All the molecular superconductors hitherto reported are composed of π-donor molecules with TTF-like skeletons and/or π-acceptor molecules $M(dmit)_2$ (M=Ni, Pd) having similar molecular structures.[2] Needless to say, superconducting mechanism is far beyond the scope of the present molecular design because any conclusive theory or physical experiment to clarify the mechanism of the formation of Cooper pair has not been reported. Therefore the systematic approach to the development of new molecular superconductors with enhanced T_c is very difficult. At present, there might be two ways to explore new molecular conductors. One may be the design of new types of molecular metals with "multi-frontier electronic structures", where not only π molecular orbitals but also other orbitals are partially filled. As the partially occupied orbitals usually have electronic active nature, novel electronic properties will be realized by the cooperative interaction between these orbitals. The other will be to develop new molecular superconductors which can contribute to clarify the superconducting mechanism of molecular crystals. In this paper, a series of new λ-type BETS (=bis(ethylenedithio)tetraselenafulvalene) superconductors and BETS metals with magnetic anions will be reported.



BETS

λ-TYPE BETS SUPERCONDUCTORS

We have recently prepared many BETS metals with tetrahalide anions MX_4^- (M=Ga, Fe,...; X=Cl, Br,...).[3] There are typically two types of crystals (κ and λ). As was reported, λ-$BETS_2GaCl_4$ is a superconductor.[4] Whereas isostructural λ-$BETS_2FeCl_4$

salt exhibits a sharp Metal-Insulator (MI) transition where a magnetic transition takes place cooperatively.[3,5] On the other hand, κ-type BETS conductors can be obtained with various anions such as $GaCl_4^-$, $GaBr_4^-$, $FeCl_4^-$, $FeBr_4^-$, $InCl_4^-$. All of them exhibit metallic behavior down to 4 K.[3] FIGURE 1 shows the crystal structure of λ-$BETS_2MCl_4$. At first sight, the BETS molecules are arranged along the *a* axis to take a quasi-stacking structure. The triclinic lattice and quasi-stacking structure resemble those of β-type ET superconductors (ET=bis(ethlenedithio)tetrathiafulvalene). But the periodicity of the donor stacks in the λ-type lattice is twice of β-type one. But the extended Huckel tight-binding band calculation gave 2D Fermi surface very similar to that of κ-type salt (FIG. 2). Compared with κ-type salts with small number of short Cl···S(or Se) contacts, the contacts between $FeCl_4^-$ anions and BETS layers in λ-type structure is fairly tight. As seen from FIG. 1, the terminal ethylene groups are bent to

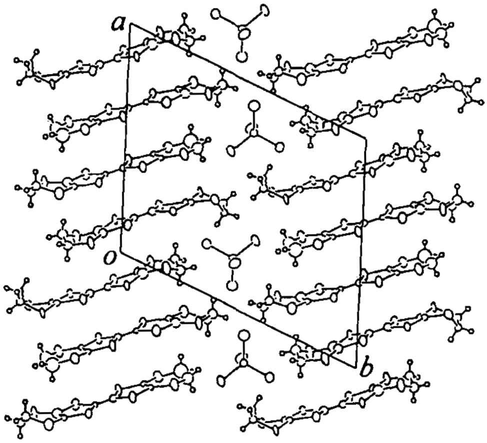


FIGURE 1
Crystal structure of λ-$BETS_2GaCl_4$.

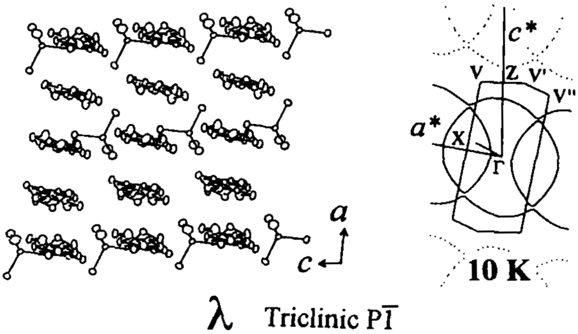


FIGURE 2 End-on projection of the structures and cross sections of 2D Fermi surfaces of λ-$BETS_2FeCl_4$.

accommodate the MCl_4^- anion. The molecular arrangement around anion seems to be fairly tight. Consequently, λ-type BETS salts are considered to be obtainable under very limited condition about anion size. FIGURE 3 shows the superconducting transitions of

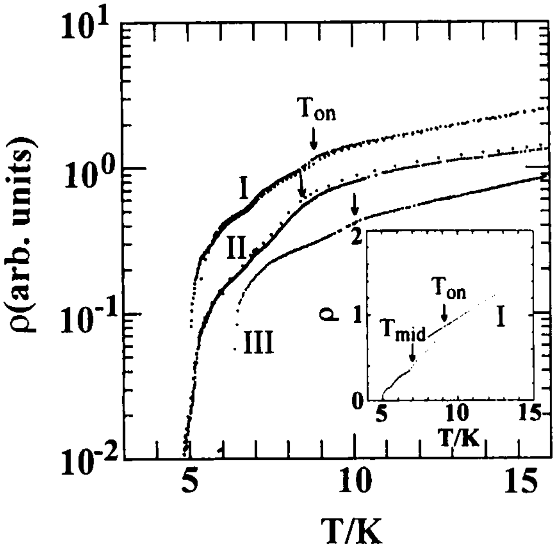


FIGURE 3 Superconducting transitions of three samples of λ-$BETS_2GaCl_4$.

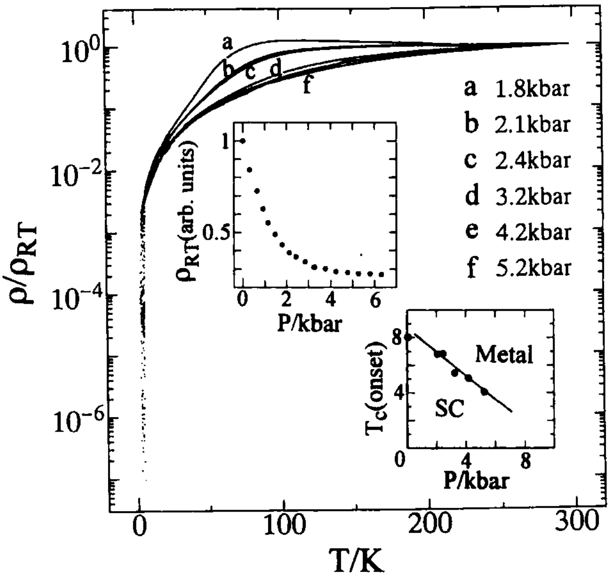


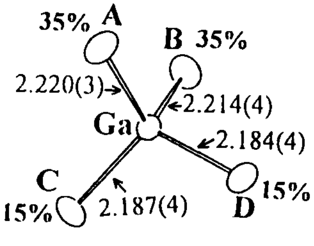
FIGURE 4 Pressure dependences of resistivity and T_c of λ-$BETS_2GaCl_4$.

three samples of λ-BETS$_2$GaCl$_4$. The average T_c (midpoint) is 7 K. As shown in FIG. 4, the room-temperature resistivity decreases with increasing pressure and tends to saturate above 3 kbar. At the same time, the characteristic resistivity maximum around 100 K is suppressed and T_c decreases with increasing pressure. This pressure dependence of T_c suggests that T_c would be enhanced if "negative pressure" could be applied. Therefore we tried to prepare similar λ-BETS salt with larger anions.

Recently, we have prepared the needle crystals of λ-BETS$_2$GaBrCl$_3$.[6] According to B. R. McGarvey et al., the halogen ions of mixed-halide gallium anions tend to be easily substituted by another halogen ions in solution.[7] It means that the description like "GaBrCl$_3^-$" does not represent just one species of GaBrCl$_3^-$, but the mixtures of GaCl$_4^-$, GaBrCl$_3^-$, GaBr$_2$Cl$_2^-$, GaBr$_3$Cl$^-$ and GaBr$_4^-$, which was confirmed by our recent ^{71}Ga NMR measurement on the [Et$_4$N]GaBrCl$_3$, which was a supporting electrolyte used in the electrocrystallization.[8] Thus, the description of "GaX$_x$Y$_{4-x}$" means the average stoichiometry of the mixture of mixed-halide anions. Temperature dependence of the resistivity was dependent on the cooling rate, which will be related to the positional disorder of the mixed halide anion GaBrCl$_3^-$. The X-ray crystal structure refinement showed the existence of two preferred positions for Br atoms (FIG. 5). The occupancy probabilities are 35 % for positions A and B and 15% for C and D. In order to avoid the freezing of the positional disorder as much as possible, the resistivity measurement was performed with extremely slow cooling rate. It took 80 h to decrease from 300 K to 4.2 K. This cooling rate is about 20 times smaller than the average cooling rate of the other resistivity measurements in this study. The resistivity exhibited a round maximum around 50 K then decreased very rapidly . After reaching minimum around 15 K, the resistivity began to drop at 10 K. T_c(midpoint) was 8 K (FIG. 6). In usual cooling rate the superconducting transition took place at 7 K (FIG. 7). Under the magnetic field of 1T, T_c was depressed and large resistivity increase was observed at low temperature region.

In the case of λ-BETS$_2$GaCl$_3$F with relatively small anion GaCl$_3$F$^-$, the resistivity decrease slowly to 100K, then decreased rapidly with lowering temperature,

FIGURE 5 Bond lengths (Å) and occupancy probabilities of Br of GaBrCl$_3^-$.



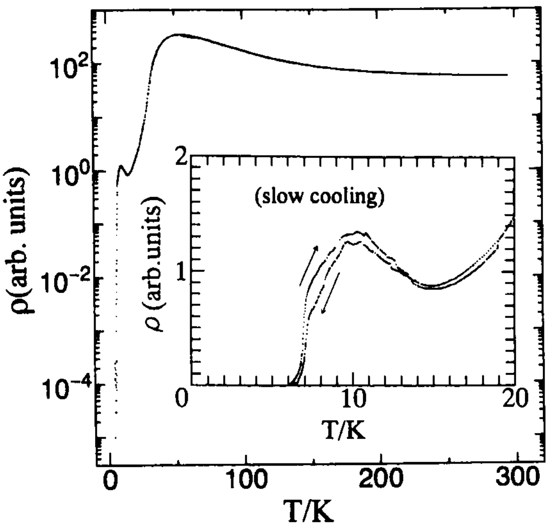


FIGURE 6 Temperature dependence of the resistivity and superconducting transition of λ-$BETS_2GaBrCl_3$.

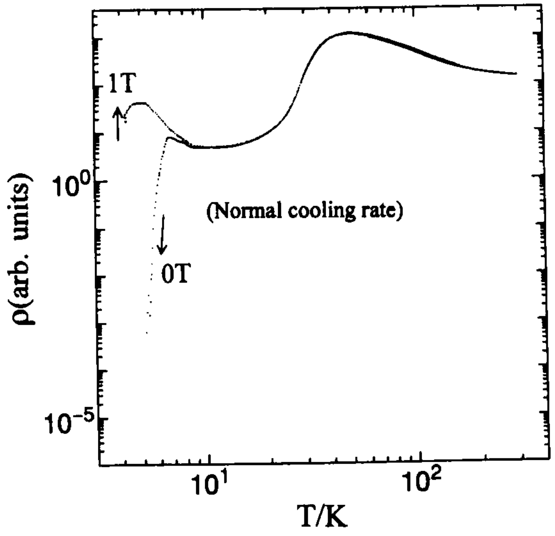


FIGURE 7 Superconducting transition of λ-$BETS_2GaBrCl_3$ and the suppression of T_c by magnetic field (1T).

and the superconducting transition occurred at about 3.5K (FIG. 8).[8] The normal metallic behavior and the reduced T_c closely resemble those of λ-$BETS_2GaCl_4$ and λ-$BETS_2GaBrCl_3$ salts at high pressure, which is consistent with the idea that the small

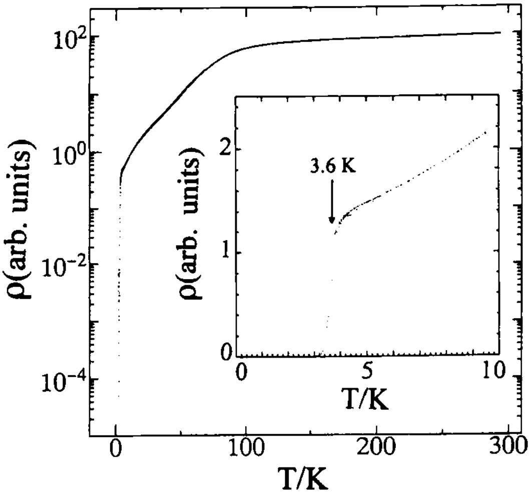


FIGURE 8
Temperature dependence of the resistivity of λ-$BETS_2GaCl_3F$.

size anion produces "effective pressure". In contrast to λ-$BETS_2GaBrCl_3$, λ-$BETS_2GaCl_3F$ exhibited no resistivity increase below 15 K. On the other hand, similar to $GaBrCl_3^-$ anion, X-ray structure analysis gave two preferred positions of F atoms of $GaCl_3F^-$. If the resistivity increase observed in λ-$BETS_2GaBrCl_3$ is originated from the electron localization effect due to the positional disorder of tetrahalide gallium anions, the resistivity increase should be observed also in λ-$BETS_2GaCl_3F$. The smooth resistivity decrease above T_c strongly suggests that the disorder effect is not so important in the λ-type salt. There seems to be an insulating state bordering on the superconducting state.

The resistivity behavior of λ-$BETS_2GaBr_{0.5}Cl_{3.5}$ closely resembles that of λ-$BETS_2GaBrCl_3$. A round resistivity maximum appears around 60 K and a superconducting transition occurs at 6.5 K. It may be of special interest that the λ-$BETS_2GaBr_{1.5}Cl_{2.5}$ with the largest unit cell volume showed semiconducting behavior

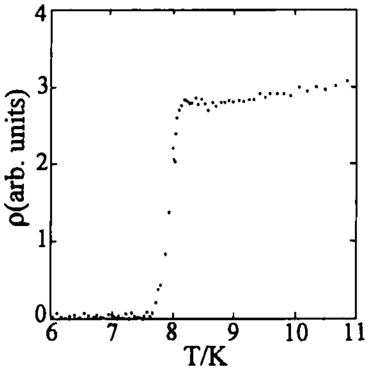


FIGURE 9.
Superconducting transition of
λ-$BETS_2GaBr_{1.5}Cl_{2.5}$ (at *ca.* 1 kbar).

from room temperature down to 4K. But at *ca.* 1 kbar, a very sharp superconducting transition was observed (T_c= 8 K) (FIG. 9). It will be noteworthy that needle crystal of $BETS_2GaBr_4$ has not λ-type structure but modified λ(or λ')-type structure, which has an insulating ground state at ambient pressure.[8]

The unit cell volumes determined by four circle diffractometer (Rigaku RASA7R) and/or Weissenberg type imaging plate X-ray system (MAC DIP320S) have a strong correlation with the magnitude of T_c's in λ-$BETS_2GaX_xY_{4-x}$. The systematic change of T_c's and metallic properties remind us the electrical behavior of a series of κ-type ET superconductors: κ-$ET_2Cu[N(CN)_2]Cl$ (smiconducting behavior) → $ET_2Cu(NCS)_2$ and κ-$ET_2Cu[N(CN)_2]Br$ (round resistivity maximum followed by superconducting transition around 10 K)→ κ-ET_2I_3 (normal-metallic state and superconducting transition at 4.2 K).[1,9,10] That is, κ-type ET superconductors and λ-type BETS superconductors seem to share a common phase diagram, which strongly suggested the existence of the general phase diagram in the organic superconductors. Comparison of these two series of superconductors with different constituent molecules and different crystal structures will provide a good hint to make clear the superconducting mechanism in organic conductors.

BETS CONDUCTORS WITH MAGNETIC ANIONS

In contrast to the large activity of the field of molecular conductors, the variety of molecular metals currently studied appear to be rather monotonous because almost all of the molecular conductors ever prepared are essentially π electron systems. In order to design "multicolored stage" of crystalline molecular metals, the entry of new types of "active electrons" will be needed. Since the open-shell electron orbital usually has its own character, it would be of great interest to design molecular metals having two types of open-shell orbitals. Needless to say, one type of orbitals may still consists of π orbitals, whose intermolecular interaction will produce the metallic properties. The other type could consist of localized *d* orbitals of a magnetic transition metal complex anion, which will act as a magnetic center.

A prototypical good example of electrically and magnetically active molecular compounds may be the DCNQI-Cu system reported a decade ago.[11] It has been pointed out that the mixed valency of Cu ($Cu^{1.3+}$) provides a π-d mixing band.[12] However, the coexistence of the π conduction electrons and the localized magnetic moments could not be achieved in this system. The magnetic moments of Cu^{2+} appear only in the insulating state. To our knowledge, the first example of stable molecular π metals incorporating magnetic anions is (BEDT-TTF)$_3$CuCl$_4$·H$_2$O reported by Day *et al.*[13] It retains a metallic state down to 0.2 K. κ-BETS$_2$FeCl$_4$ may be the second moleular metals where π metal electrons and magnetic moments coexist down to at least 2 K. We have recently reported the preparation, crystal structures, and electric and magnetic properties of (BETS)$_2$MX$_4$ molecular conductors (M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}; X = Cl, Br, CN).[14] The crystals were prepared by electrochemical oxidation of BETS (4-8 mg) in an appropriate solvent (20 ml), with the corresponding tetraethylammonium salt of MX$_4^{n-}$ (20-50 mg) as supporting electrolyte, under nitrogen atmosphere at 20 °C (see TABLE I).

Resistivity measurements revealed the coexistence of the π metal electrons of BETS molecules and the localized magnetic moments of the anions (Fe^{3+}, Co^{2+}) in the κ-(BETS)$_2$FeCl$_4$, (BETS)$_2$FeBr$_4$ and κ-(BETS)$_4$(CoCl$_4$)(C$_2$H$_3$Cl$_3$) salts at 4 K.[3,14] Another FeCl$_4$ phase, λ-(BETS)$_2$FeCl$_4$, undergoes a sharp metal-insulator (MI) transition around 8 K (FIG. 10).[3] At the same temperature, a magnetic transition takes place cooperatively.[14] ESR intensities of κ-(BETS)$_2$FeCl$_4$ and λ-(BETS)$_2$FeCl$_4$ showed the high-spin states of Fe^{3+} ions. The Curie-Weiss temperature dependencies of the ESR intensities indicate the antiferromagnetic interaction between Fe^{3+} ions (θ=15 K(λ), 8.5 K(κ)) (FIG. 11). The large paramagnetism is mainly originated from the high-spin Fe^{3+} ions. Below T_{MI}, ESR intensities drops sharply.[14] Static susceptibility measurement on the fairly oriented needle crystals of λ-(BETS)$_2$FeCl$_4$ by

TABLE I Electrocrystallization conditions for some BETS salts, crystal habit, room-temperature conductivity, and electrical behavior.

compound	solvent	crystal habit	σ(RT) (Scm^{-1})	electrical behavior
BETS$_2$FeCl$_4$	CB(Et)[a]	plate (κ)[b]	100	metallic (> 2 K)
		needle (λ)	20	MI transition (8.5 K)
BETS$_2$FeBr$_4$	CB	plate (κ)	60	metallic (> 4 K)
BETS$_4$CoCl$_4$(TCE)	TCE	plate (κ)	20	metallic (>2 K)
BETS$_n$MnCl$_4$	TCE	plate	40	MI transition (~40 K)
BETS$_n$NiBr$_4$	CB(Et)	plate	50	weakly metallic(> 4 K)
BETS$_4$Cu$_2$Cl$_6$	THF	needle (θ)	100	metallic (> 4 K)

[a] CB = chlorobenzene, (Et) = the solvent contains 10 % ethanol, TCE = 1,1,2-trichloroethane, THF = tetrahydrofurane.

[b] κ, λ and θ correspond to the κ-, λ- and θ-type structures.

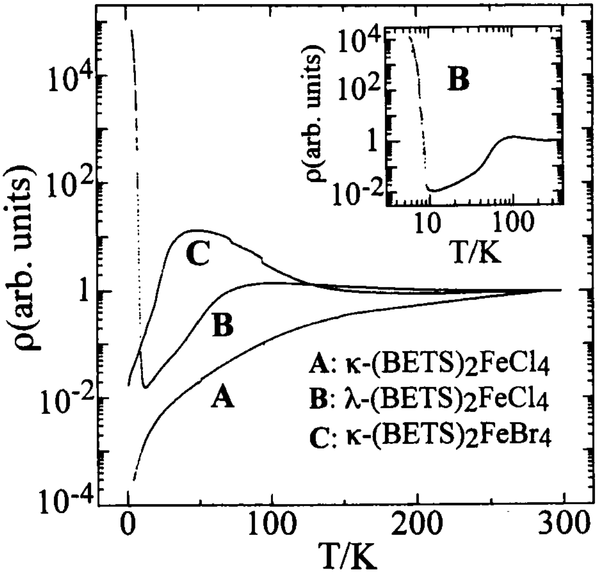


FIGURE 10 Resistivities of BETS$_2$FeX$_4$ (X=Cl, Br).

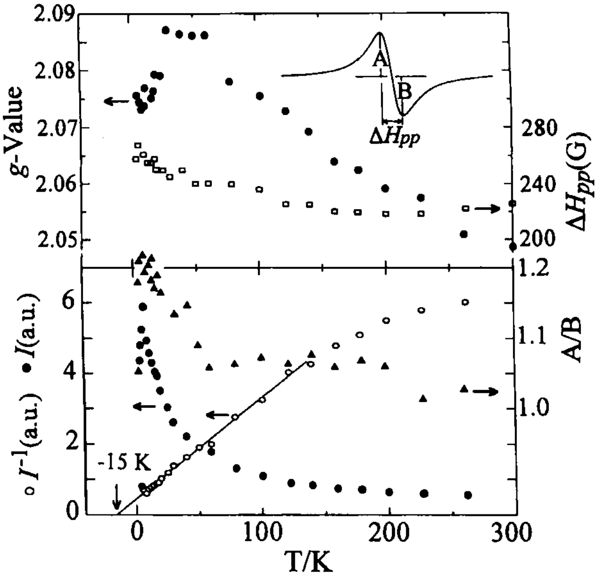


FIGURE 11 The g-value and peak-to-peak line width, and intensity of the ESR signal of λ-(BETS)$_2$FeCl$_4$.

Tokumoto et al. gave characteristic temperature and field dependencies (FIG. 12). At low magnetic field, M/H tends to become very small at low temperature, which seems to be consistent with the results of ESR experiments. Almost discontinuous susceptibility drop appeared at T_{MI}, which was suppressed at higher magnetic field. The most prominent feature of λ-(BETS)$_2$FeCl$_4$ is "field-restored highly conducting state(FRHCS)" discovered recently.[15] T_{MI} decreases with increasing magnetic field. The metallic state is completely stabilized above 10 T. The crystal structure analyses of κ- and λ-(BETS)$_2$FeCl$_4$ have been carried out at 298 K and 10 K. Closer BETS···FeCl$_4$ contacts in λ-(BETS)$_2$FeCl$_4$ are consistent with the relatively large

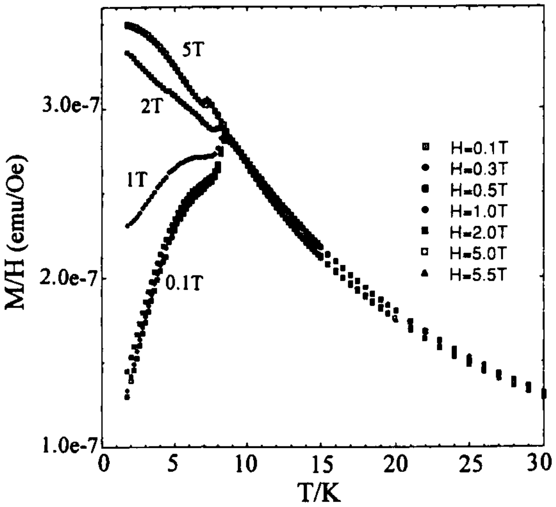


FIGURE 12
Temperature and field(H) dependence of magnetization (M) of λ-(BETS)$_2$FeCl$_4$.

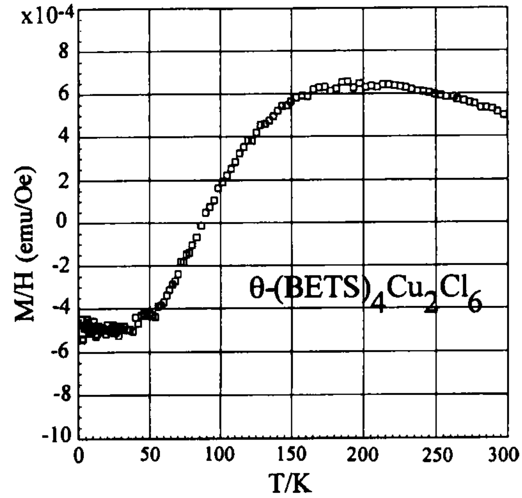


FIGURE 13
Static magnetic susceptibility of θ-BETS$_4$(Cu$_2$Cl$_6$).

Weiss temperature of this compound.

The θ-(BETS)$_4$(Cu$_2$Cl$_6$) salt remains metallic down to 4.2 K. Susceptibility measurements showed a broad maximum around 200 K, indicating that two Cu^{2+} ions in Cu$_2$Cl$_6$$^{2-}$ are coupled antiferromagnetically to give the susceptibility explained by "singlet-triplet model" (J=150 K) (FIG. 13).[16] Pauli paramagnetic contribution of π metal electrons will be derived by estimating the diamagnetic susceptibility.

In this paper, a series of λ-type new organic superconductors were presented. Stable 2D BETS metals incorporating magnetic ions were also reported. Further details will be reported elsewhere in near future.

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