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New Organic Metals Based on BETS Compounds with MX_4^- Anions (BETS=bis(ethylenedithio)tetraselenafulvalene; M = Ga, Fe, In; X= Cl, Br)

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Crystal structures and electrical properties of BETS compounds with tetrahedral anions, MX_4^- (BETS= bis(ethylenedithio)tetraselenafulvalene; M = Ga, Fe, In; X= Cl, Br) were examined. Every κ-type salt is metallic below 50 K. λ-$(BETS)_2FeCl_4$, which is isomorphous to the superconductor $GaCl_4$ salt, undergoes a sharp metal-insulator transition at 8 K.

All the molecular superconductors ever discovered are composed of the π (or quasi-π) molecules such as TMTSF, BEDT-TTF, $M(dmit)_2$ and C_{60}. In the strategy of the design of a new organic superconductor developed in 1980s, the stabilization of the metallic state was an important guiding principle because the molecular metal was considered to have the inherent metal instability originated from the low dimensionality of the electronic structure. We have examined the crystal structures and electrical properties of a series of molecular conductors based on bis(ethylenedithio)tetraselenafulvalene (=BEDT-TSF or more simply BETS), since the introduction of Se atoms in the TTF-skeleton of the BEDT-TTF molecule was expected to increase the chance to give two-dimensional (2D) stable metallic state.1-3) In fact, many metallic compounds with 2D molecular arrangements such as "κ- and θ-type arrangements" were found out. In addition, we have recently found a new organic superconductor, λ-$(BETS)_2GaCl_4$ which has the highest transition temperature except for the BEDT-TTF compounds.4)

The strong metallic nature of BETS compounds will make it possible to prepare an organic conductor such as "organic Kondo system," where π-metal electrons interact with local magnetic moments of the anions at very low temperatures. In order to contribute to realize this new possibility, we examined as a first step the electrical and structural properties of BETS conductors with magnetic anions such as $FeCl_4^-$ and $FeBr_4^-$ and also isostructural nonmagnetic anions such as $GaCl_4^-$, $GaBr_4^-$,$InCl_4^-$ and $InBr_4^-$.

BETS was prepared according to the method developed by Kato.1) The $FeCl_4$ salt was obtained electrochemically from monochlorobenzene solution containing BETS and

Table 1. Crystal data of λ- and κ-$(BETS)_2MX_4$[a)]

	λ-$GaCl_4$	λ-$FeCl_4$	κ-$FeCl_4$	κ-$GaBr_4$	κ-$GaCl_4$	κ-$InCl_4$	κ-$FeBr_4$
a(Å)	16.141(3)	16.164(3)	11.663(8)	11.773(2)	11.665(5)	11.586(2)	11.754(5)
b(Å)	18.580(3)	18.538(3)	35.856(12)	36.635(7)	35.894(9)	36.492(2)	36.530(9)
c(Å)	6.594(1)	6.593(1)	8.456(4)	8.492(2)	8.464(3)	8.536(2)	8.482(2)
α(°)	98.37(1)	98.40(1)					
β(°)	96.77(1)	96.67(1)					
γ(°)	112.55(1)	112.52(1)					
V($Å^3$)	1774.0(5)	1773.0(5)	3536(3)	3663(1)	3544(2)	3609(1)	3642(2)
S.G.	$P\bar{1}$	$P\bar{1}$	Pnma	Pnma	Pnma	Pnma	Pnma

a) The structure of κ-$(BETS)_2GaCl_4$ has been already solved by Montogomery et al. independently.[5)]

(TEA)$FeCl_4$ (TEA=tetraethylammonium). The main products are plate crystals. Very thin needle crystals are minor products. The crystals of the other compounds were also prepared by similar procedure. X-ray studies have revealed that all the plate crystals of MX_4 (M=Fe, Ga, In; X=Cl, Br) are isostructural to each other and have κ-type structures. The thin needle crystal of the $FeCl_4$ salt belongs to triclinic system and is isostructural to the superconductor, λ-$(BETS)_2GaCl_4$.[4)] The lattice dimensions are listed in Table 1. The space group of κ-type salt is Pnma, which is the same as that of κ-$(BEDT\text{-}TTF)_2Cu(N(CN)_2)X$ (X=Cl, Br).[6)] The intensity data were collected by a Rigaku automated diffractometer with rotating anode X-ray generator. Monochromated Mo Kα radiation was used. The structures were solved by the direct method and refined by using full-matrix least-squares procedure.

As shown in Fig. 1, the BETS molecules of λ-type structure are apparently arranged along [100] with fourfold "quasi-stacking structure". However, there are Se...Se, Se...S and S...S contacts shorter than the van der Waals distances along [001]. The tight-binding band calculation suggested the 2D metallic nature of the system. Tetraselenafulvalene ring in BETS molecule forms a good plane. Although the S atoms of the outer six-membered rings are almost on this plane, bis(ethylene) groups are deviated

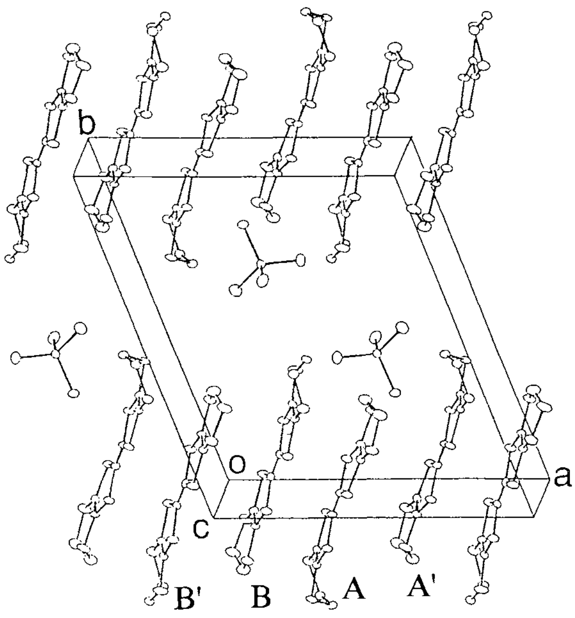

Fig. 1. Crystal structure of λ-$BETS_2FeCl_4$.

from the plane by 0.3-1.5 Å. The mode of the intermolecular overlapping between A and B (see Fig. 1) and that between A and A', which are related by the inversion symmetry, are so-called "ring over double bond type". However, in the overlapping between the molecules B and B', the double bond does not overlap on a five-membered ring but rather on a six-membered ring. One end ethylene group of each molecle is concaved from the BETS plane to accommodate an anion.

In every κ-type salt, two BETS molecules form a pair with a ring over double bond arrangement (Fig. 2). The dihedral angle of each pair is about 77°. Similar to the cases of λ-type salts, the tetrahedral anions are all ordered. The M-X bond lengths (M=Fe, Ga, In; X=Cl, Br) are: 2.324 Å (Fe-Br), 2.332(In-Cl), 2.184(Fe-Cl), 2.296(Ga-Br), 2.151 (Ga-Cl). The shortest M...M distance in κ-(BETS)$_2$MCl$_4$ salt is smaller than that of λ-(BETS)$_2$MCl$_4$ salt: R(Fe...Fe)=R(Ga...Ga)=5.88 Å(κ) and 6.59 (λ). The simple tight-binding band structure calculations of κ-type salts gave nearly isotropic 2D Fermi surfaces. The details will be reported separately.7)

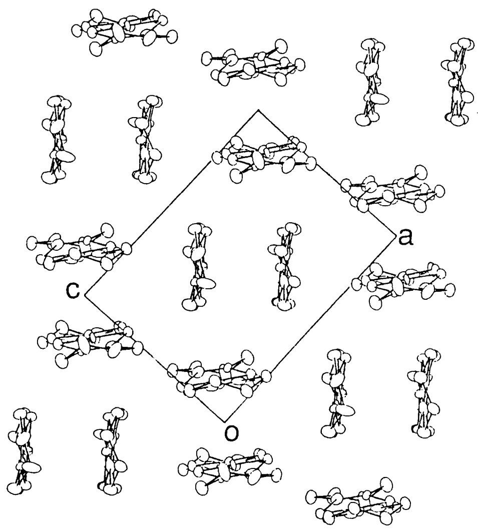

Fig. 2. Molecular arrangement in κ-(BETS)$_2$FeCl$_4$.

The resistivity measurements were made within the temperature range of 2-300 K by using the conventional four-probe method. The room-temperature conductivity is about 50 S cm^{-1} for every salt. All the κ-type salts retain metallic conductivity down to 4 K (Fig. 3). The residual resistance ratio ρ(300 K)/ρ(4 K) was larger than 300 in GaCl$_4$ and FeCl$_4$ salts. The GaBr$_4$ and FeBr$_4$ salts exhibit resistivity maxima around 80-100 K. In κ-(BETS)$_2$InCl$_4$, the resistivity is almost constant from room temperature to 130 K. Abnormal resistivity maximum was found around 130 K, below which resistivity decreases rapidly down to 4 K.

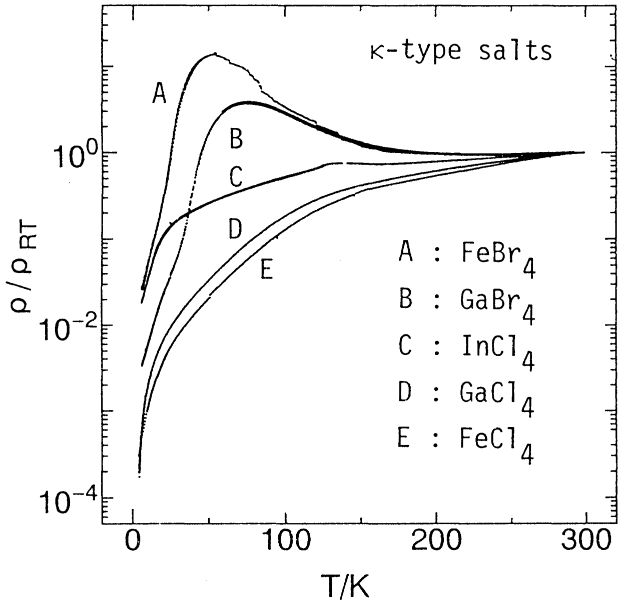

Fig. 3. Resistivities of κ-(BETS)$_2$MX$_4$.

The resistivity behavior of λ-(BETS)$_2$FeCl$_4$ is quite different from that of λ-(BETS)$_2$GaCl$_4$ (Fig. 4). The latter shows a superconducting transition at 8 K4) and the former transforms to insulating state around the same temperature. The resistivities of both salts have maxima around 90 K. As seen in Fig. 3, similar resistivity maximum has been often observed in the κ-type conductors.

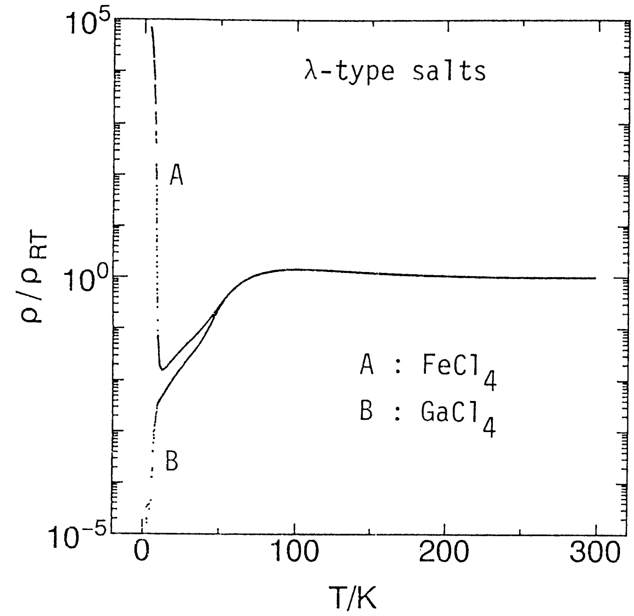

Fig. 4. Resistivities of λ-(BETS)$_2$MCl$_4$.

Recent ESR measurements showed the antiferromagnetic interaction between Fe^{3+} ions and that the metal-insulator (MI) transition is accompanied by the transition of the magnetic state of anions. This seems to indicate the interaction between π-metal electrons and the localized magnetic moments of Fe^{3+} plays an essential role in the low-temperature properties of the system. The details of the MI transition will be reported in near future.8)

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