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k- and Modified k-Type Molecular Arrangements and Electrical Resistivities of $(BETS)_2InCl_4$, $(BETS)_2CLO_4(TCE)_{0.5}$, $(BETS)_2BF_4(TCE)_{0.5}$ and $(BETS)_2[(C_2H_5)_4N]_{0.7}InCl_5$

Akiko Kobayashi [a] & Hayao Kobayashi [b]

[a] Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113, Japan

[b] Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan

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κ- AND MODIFIED κ-TYPE MOLECULAR ARRANGEMENTS AND ELECTRICAL RESISTIVITIES OF $(BETS)_2InCl_4$, $(BETS)_2ClO_4 \cdot (TCE)_{0.5}$, $(BETS)_2BF_4(TCE)_{0.5}$ AND $(BETS)_2[(C_2H_5)_4N]_{0.7}InCl_5$

AKIKO KOBAYASHI
Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan
HAYAO KOBAYASHI
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

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Abstract $(BETS)_2ClO_4(TCE)_{0.5}$ and $(BETS)_2BF_4(TCE)_{0.5}$ have a unique molecular arrangement based on BETS tetrad, named κ(4x4) molecular arrangements, where BETS is bis(ethylenedithio)tetrathiafulvalene. $(BETS)_2(TEA)_{0.7}InCl_5$ has a new distorted tetrad structure. On the other hand, $(BETS)_2InCl_4$ has a κ(2x2) structure (more simply so-called κ-type structure). The temperature dependences of the resistivities of $(BETS)_2ClO_4(TCE)_{0.5}$ and $(BETS)_2BF_4(TCE)_{0.5}$ are metallic down to 4 K and that of $(BETS)_2(TEA)_{0.7}InCl_5$ is weakly metallic down to about 100 K and becomes semiconducting at low temperature. The temperature dependence of the electrical resistivity of κ-$(BETS)_2InCl_4$ has a characteristic flexion point at around 130 K.

Keywords: BETS, organic metal, band structure, semiconductor, Fermi surface

INTRODUCTION

One of the main motifs in the development of new crystalline organic conducting systems in 1980s was the design of two-dimensional (2D) superconducting systems based on multi-sulfur (or selenium) π molecules. The successive discoveries of $(BEDT\text{-}TTF)_2I_3$ superconductors (BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene) with β–,[1] θ-[2] and κ-type[3-4] molecular arrangements arround the middle of 1980s have revealed the existence of 2D molecular superconductors. Especially the characteristic 2D structures in κ-type BEDT-TTF superconductors have definitely demonstrated the importance of the network of chalcogen atoms in the design of molecular metals with ideally round 2D

Fermi surfaces. In order to obtain new organic metal systems with stronger 2D nature, we have tried to prepare various BETS (BETS= bis(ethylenedithio)tetraselenafulvalene) conductors. BETS is BEDT-TTF analogue with four Se atoms in the central TTF skeleton. We have obtained a variety of highly conducting cation radical salts with various counter anions,[5-6] TaF_6^-, SbF_6^-,[7] PF_6^-, AsF_6^-, divalent $HgBr_4^{2-}$,[8] linear I_3^-, ICl_2^- and tetrahedral MX_4 (M=Ga, Fe, In, Co, Zn, Mn, Ni, Al; X=Cl, Br,..) anions.[9-12] Among them, we have found a new organic superconductor λ-$(BETS)_2GaCl_4$.[9]

The remarkable feature of BETS compounds is the extraordinary variety of the structures and their strong metallic natures. The stability of metallic states of BETS compounds makes it easy to prepare the organic conductor with π-metal electrons interacting with local magnetic moments of the anions at very low temperatures. A good example can be seen in κ-$(BETS)_2FeCl_4$.[10-11] Another interesting BETS compound may be λ-$(BETS)_2FeCl_4$, which undergoes a sharp metal-insulator (MI) transition around 8 K, where an antiferromagnetic spin ordering of the $FeCl_4$ anion takes place cooperatively.[11]

In this paper we report a novel κ-type tetrad molecular arrangement κ(4x4) in $(BETS)_2ClO_4(TCE)_{0.5}$ and $(BETS)_2BF_4(TCE)_{0.5}$, a distorted tetrad structure in $(BETS)_2(TEA)_{0.7}InCl_5$, and a usual κ-type (or κ(2x2)) molecular arrangement in $(BETS)_2InCl_4$. Their electrical resistivities and band structure calculations are also reported.

EXPERIMENTAL

Synthesis

The synthesis of BETS was first reported by Schmaker et al. in 1983[13] and an improved synthetic method was reported by R. Kato.[5] The crystals of the BETS salts with ClO_4^-, BF_4^-, $InCl_4^-$ anions were prepared by electrochemical oxidation of BETS (5-10mg) in an appropriate solvent (20ml) (TCE=1,1,2-trichloroethane, monochlorobenzene, acetonitrile), with the corresponding $[(C_4H_9)_4N]ClO_4$, $[(C_4H_9)_4N]BF_4$ and $[(C_2H_5)_4N]InCl_4$ (20-50mg) as supporting electrolytes, under nitrogen atmosphere at 20°C. The constant current of 1 μA was used. The black pltate crystals of $(BETS)_2ClO_4(TCE)_{0.5}$, $(BETS)_2BF_4(TCE)_{0.5}$, κ-$(BETS)_2InCl_4$ and $(BETS)_2(TEA)_{0.7}InCl_5$ were obtained.

Structure Determination

Crystallographic data are listed in Table I. X-Ray intensity data were collected at room temperature on a Rigaku AFC-5R automatic four-circle diffractometer with

TABLE I Crystal data and experimental details for BETS compounds

	$(BETS)_2ClO_4(TCE)_{0.5}$	$(BETS)_2BF_4(TCE)_{0.5}$	$(BETS)_2InCl_4$	$(BETS)_2(TEA)_{0.7}InCl_5$
chemical formula	$Se_8S_8C_{21}H_{17.5}Cl_{2.5}O_4$	$Se_8S_8C_{21}BF_4Cl_{1.5}H_{17.5}$	$InSe_8S_8Cl_4C_{20}H_{16}$	$InSe_8S_8Cl_5C_{25.7}N_{0.7}H_{30}$
formula weight	1310.66	1298.01	1401.14	1527.77
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
crystal color	black	black	black	black
crystal habit	plate	plate	plate	plate
crystal dimension (mm)	0.3x0.3x0.1	0.25x0.35x0.1	0.15x0.30x0.05	0.2x0.25x0.1
a Å	19.251(3)	19.114(5)	11.586(2)	20.469(4)
b	8.569(2)	8.561(1)	36.492(2)	9.670(1)
c	22.556(2)	22.550(3)	8.536(2)	23.444(2)
β °	109.09(1)	109.17(1)		96.64(1)
V $Å^3$	3516(1)	3485(1)	3609(1)	4609(1)
space group	$P2_1/c$	$P2_1/c$	Pnma	$P2_1/a$
Z	4	4	4	4
dcalc(g/cm^3)	2.480	2.470	2.578	2.200
μ(MoKα) cm^{-1}	90.12	90.24	95.0	75.05
absorption range	0.225-1.0	0.549-1.0	0.632-1.0	0.410-1.0
diffractometer	Rigaku AFC5R	Rigaku AFC5R	Rigaku AFC5R	Rigaku AFC5R
radiation	MoKα	MoKα	MoKα	MoKα
scan rate(2θ °)	16	16	8	16
2θmax °	55.0	55.0	55.0	50.0
no. of ref. measured	8915	8835	4726	8971
no. of reflection	2221	2273	1971	4028
no. of variable	406	386	190	415
R, Rw	0.056,0.041	0.06,0.35	0.040,0.040	0.051,0.038
g.o.f.	1.73	1.93	1.18	1.72
max. peak in final diff. map. e/A^3	0.82	1.36	0.82	0.77
min. peak	-0.78	-0.74	-0.84	-0.69

monochromated Mo-Kα radiation. Empirical absorption corrections were made. The crystal structure were solved by the direct method and refined by the full-matrix least-squares method. The calculations were performed by using the teXsan crystallographic software package of Molecular Structure Corporation.[14] The content of TCE in $(BETS)_2ClO_4(TCE)_{0.5}$ was determined as 0.5 by electron probe microanalysis (EPMA) and a population refinement in the X-ray structure analysis. The stoichiometry of $(BETS)_2(TEA)_{0.7}InCl_5$ was determined by X-ray structure studies on the same needle crystal used for the conductivity measurements. The content of tetramethylammonium cation was determined by population analysis of the crystal structure determination and the elemental analysis by EPMA.

The simple tight-binding band structure was calculated on the basis of the extended Hückel approximation, using the highest occupied molecular orbitals of BETS.

Resistivity Measurements

The resistivities were measured by the conventional four-probe method in the 300-2 K temperature range. Four 15 μm diameter gold wires bonded to the crystals with gold conducting paint were used as current and voltage terminals.

RESULTS AND DISCUSSIONS

$(BETS)_2ClO_4(TCE)_{0.5}$ and $(BETS)_2BF_4(TCE)_{0.5}$

The crystal structure of $(BETS)_2ClO_4(TCE)_{0.5}$ is shown in Figure. 1. The cation layers of BETS molecules and layers of ClO_4 anions and TCE are arranged alternately along the direction of the a axis. The metal plane is composed of two types of BETS tetramers, which are nearly perpendicular to each other in the bc plane. The mode of BETS arrangement shown in Figure 2 reveals a novel type of molecular arrangement, which follows the well known κ-type molecular arrangement composed of two types of dimers with almost rectangular orientations. This molecular arrangement was named κ(4x4) structure. Each tetramer has an inversion symmetry and two BETS molecules A and B are crystallographically independent. Dihedral angles of A, B" molecules is 82.9° and B, B" is 80.2°. BETS molecules form a dimer with a "ring over double bond" arrangement (Figure 3). The intradimer spacing is 3.622 Å and the interdimer spacing between A and A' molecules which is related by an inversion center is 4.219 Å. The average bond length of the central C-C double bond of BETS molecules is 1.29 Å. The conformation of all the ethylene groups is staggered. The average C-C bond length of ethylene groups of two BETS molecules is 1.46 Å. The ClO_4 anions are located between the cation layers

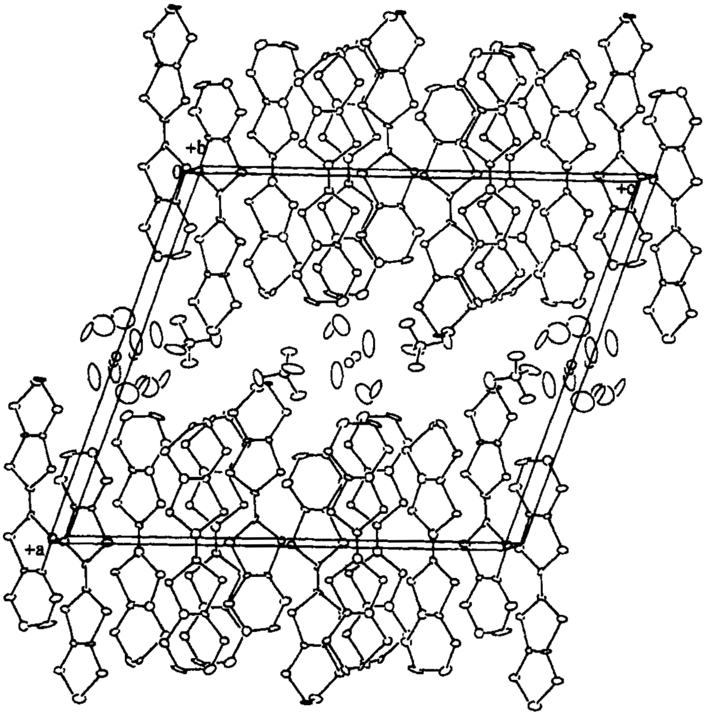

FIGURE 1 The crystal structure of $(BETS)_2ClO_4(TCE)_{0.5}$.

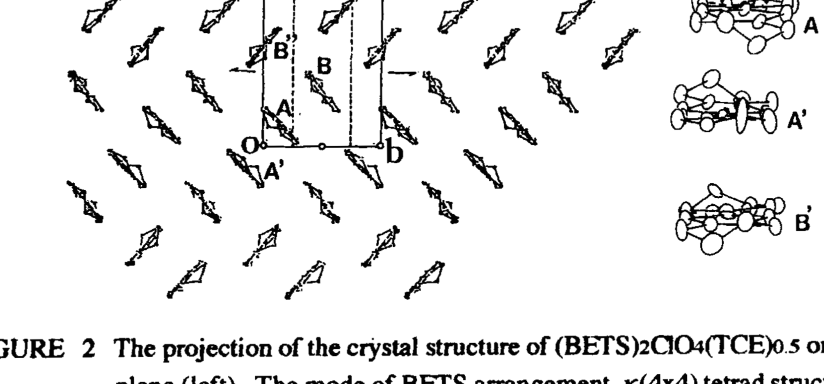

FIGURE 2 The projection of the crystal structure of $(BETS)_2ClO_4(TCE)_{0.5}$ on the bc plane (left). The mode of BETS arrangement, κ(4x4) tetrad structure in $(BETS)_2ClO_4(TCE)_{0.5}$ (right).

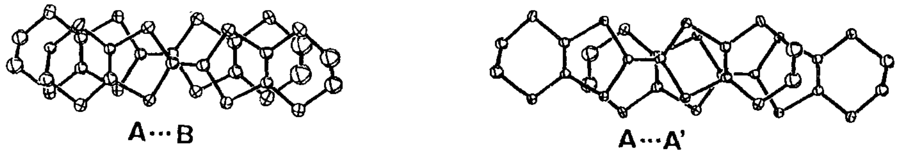

FIGURE 3 Molecular overlaps in κ(4x4) tetrad in $(BETS)_2ClO_4(TCE)_{0.5}$.

with solvent molecules. The average Cl-O distance is 1.365 Å. Many intermolecular chalcogen...chalcogen distances less than the sum of the van der Waals radii were observed. The shortest Se···S , S···S, Se···Se distances are 3.487(7), 3.455(8) and 3.787(3) Å, respectively. There are strong two dimensional chalcogen···chalcogen transverse interactions in the bc plane. The solvent molecules (TCE) are heavily disordered. The crystal of $(BETS)_2BF_4(TCE)_{0.5}$ is isostructural to the ClO_4 salt, however the disorder of the solvent molecule is heavier than that in the ClO_4 salt .

The room temperature conductivities of $(BETS)_2ClO_4(TCE)_{0.5}$ and $(BETS)_2BF_4(TCE)_{0.5}$ were 5-30 Scm^{-1}. The temperature dependences of the resistivities are shown in Figures 4 and 5. They are metallic down to low temperature. The resistivity ratio of ρ(300 K)/ρ(4 K) of the ClO4 salt was 20. The small temperature dependence of the resistivities seems to be related to the lattice defects due to the solvent molecules involved in the crystal. Similar to $(BETS)_2ClO_4(TCE)_{0.5}$, the resistivity of κ-$(BETS)_2GaCl_4$ decreases monotonously down to 4 K,[10] but the resistivity ratio ρ(300 K)/ρ(4 K) of κ-$(BETS)_2GaCl_4$ is more than 1000. The increace of the resistivities below 20 K and relatively small ratio of ρ(300 K)/ρ(4 K) (~10) in $(BETS)_2BF_4(TCE)_{0.5}$ seems to be ascribed also to the lattice defects in the crystal.

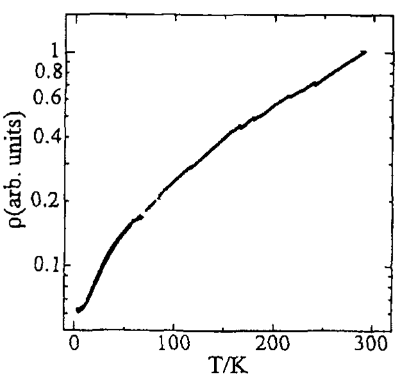

FIGURE 4 The temperature dependence of the resistivities of $(BETS)_2ClO_4(TCE)_{0.5}$. The solid line shows the cooling process and the dotted line the heating process.

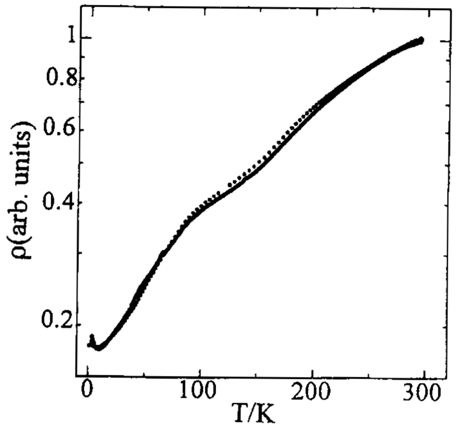

FIGURE 5 The temperature dependence of the resistivities of $(BETS)_2BF_4(TCE)_{0.5}$. The solid line shows the cooling process and the dotted line the heating process.

The intermolecular overlap integrals of HOMO of the $(BETS)_2ClO_4(TCE)_{0.5}$ were calculated using Slater-type atomic orbitals, which is shown in Figure 6. The strong transfer integrals form a zigzag chain along the b axis (b, d, b, d). The adopted semi-empirical parameters are listed in Table II. The simple tight-binding band structure was

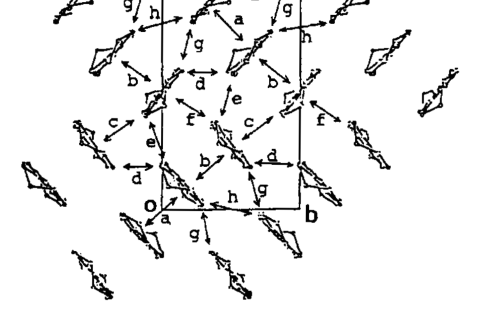

FIGURE 6 Intermolecular overlap integrals of $(BETS)_2ClO_4(TCE)_{0.5}$. Overlap integrals ($\times 10^3$) are : a=16.74, b=70.07, c=14.85, d=46.83, e=23.56, f=14.85, g=2.41, h=20.62.

calculated on the basis of the extended Hückel approximation, and the frontier molecular orbitals of BETS. The band structure calculation gave eight energy branches and demonstrated that $(BETS)_2ClO_4(TCE)_{0.5}$ has a closed small 2D Fermi surface around Z and three corrugated extended Fermi surfaces (Figure 7). It may be of interest that 1D and 2D Fermi surfaces coexist in this compound.

TABLE II The exponents ζ and the ionization potentials (eV) for atomic orbitals.

		ζ	eV			ζ	eV
S	3s	2.122	-20.0	C	2s	1.625	-21.4
	3p	1.825	-11.0		2p	1.625	-11.4
	3d	1.5	-5.44				
Se	4s	2.112	-20.0	H	1s	1.0	-13.6
	4p	1.827	-11.0				
	4d	1.5	-6.8				

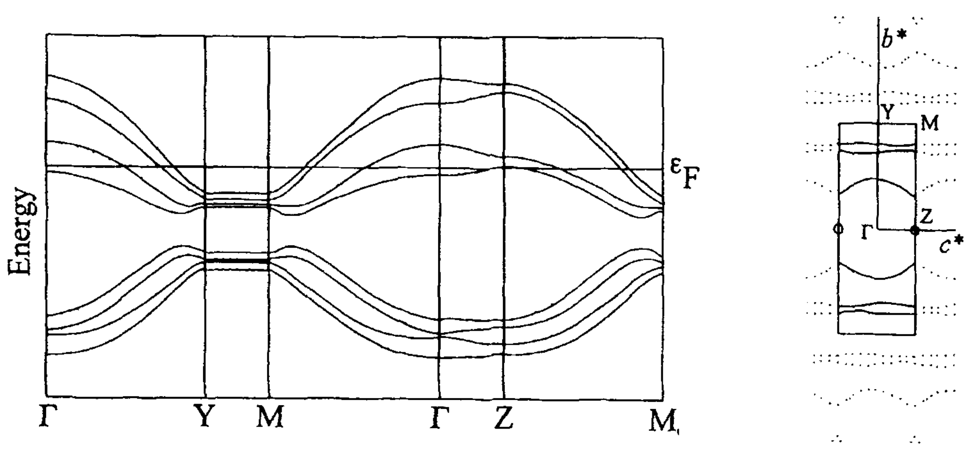

FIGURE 7 Fermi surface (right) and energy diagram (left) of $(BETS)_2ClO_4(TCE)_{0.5}$.

κ-$(BETS)_2InCl_4$

The crystal of κ-$(BETS)_2InCl_4$ (Figure 8) is isostructural to κ-$(BETS)_2GaCl_4$.[10,15] Following the naming of κ(4x4) structure, the conventional κ-type molecular arrangement can be also called as κ(2x2) arrangement. Two BETS molecules form a dimer with a ring over double bond arrangement. The dihedral angle of neighbouring dimer molecules is 79.3° and the intradimer distance is 3.478Å. The bond length of the central C-C double bond of BETS is 1.34(1) Å. The C-C bond lengths of two ethylene groups are 1.31(3) and 1.45(2) Å and the conformations are staggered. Tetrahedral

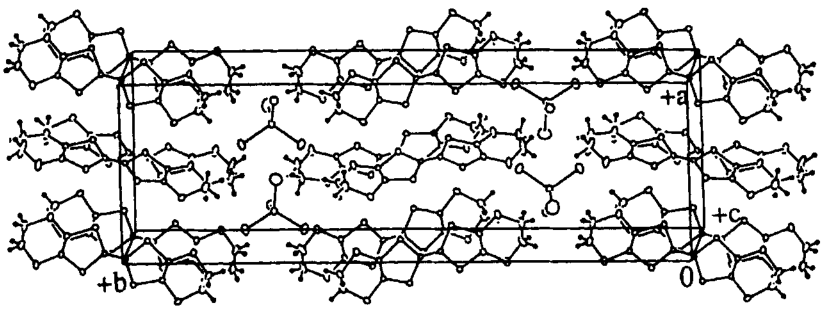

FIGURE 8 The crystal structure of κ-$(BETS)_2InCl_4$.

$InCl_4$ anion is ordered with the average In-Cl distance of 2.332 Å. The shortest In...In and In...Cl distances are 5.83 Å and 4.78 Å, respectively. The BETS cation sheets and $InCl_4$ anion sheets are arranged alternately along the b axis. The shortest Se···Se non-bonded contact is 3.744 (2) Å, Se···S is 3.578(3) Å, S···S is 3.366(5) Å and S···Cl is 3.560(4) Å.

The resistivity behavior of κ-$(BETS)_2InCl_4$ is shown in Figure 9 together with those of κ-$(BETS)_2GaBr_4$ and κ-$(BETS)_2GaCl_4$. The temperature dependence of the resistivity of the $InCl_4$ salt is an intermediate of those of κ-$(BETS)_2GaBr_4$ and κ-$(BETS)_2GaCl_4$, which seems to be related to the fact that κ-$(BETS)_2InCl_4$ has an intermediate cell volume of those of κ-$(BETS)_2GaBr_4$ and κ-$(BETS)_2GaCl_4$. The resistivity of κ-$(BETS)_2InCl_4$ is weakly temperature-dependent from room temperature to 130 K. The flexion of the resistivity curve was observed at around 130 K in all the samples examined.

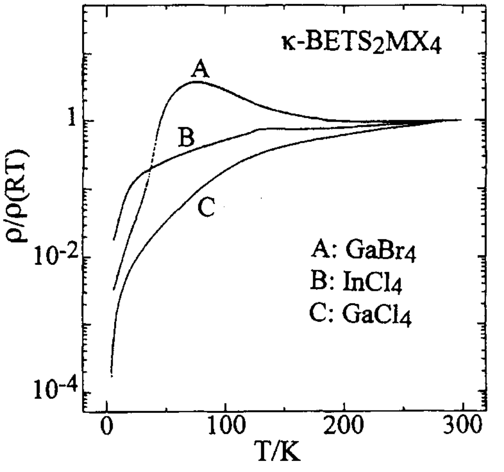

FIGURE 9 The temperature dependences of the resistivities in κ-$(BETS)_2GaBr_4$ (A), κ-$(BETS)_2InCl_4$ (B) and κ-$(BETS)_2GaCl_4$ (C).

Roughly speaking, there are two types of temperature dependence of resistivities in κ-(BETS)$_2$MX$_4$ (M=Ga, In; X=Cl or Br) compounds. In κ-(BETS)$_2$GaBr$_4$ the resistivity increases slowly down to about 70 K, where the resistivity takes a maximum (Figure 9 (A)). Then the resistivity decreases rapidly with lowering temperature. The resistivity ratio $\rho(70\ K)/\rho(4\ K)$ is about 10^3. This behavior resembles well to those of so-called 10 K class BEDT-TTF superconductors. However, any sign of the superconducting transition has not been observed down to at least 2 K in κ-(BETS)$_2$GaBr$_4$.

On the other hand, κ-(BETS)$_2$GaCl$_4$ exhibits normal metallic behavior down to 2 K. Considering that κ-(BETS)$_2$GaCl$_4$ has a smaller unit cell volume than that of κ-(BETS)$_2$GaBr$_4$ ($\Delta V = 100\ Å^3$), it may be imagined that the ambient pressure state of κ-(BETS)$_2$GaCl$_4$ corresponds to the high pressure state of κ-(BETS)$_2$GaBr$_4$. Similar change of resistivity behavior can be seen by applying pressure in some organic superconductors, such as κ-(BEDT-TTF)$_2$Cu(NCS)$_2$,[16] κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X (X=Br,Cl),[17] λ-(BETS)$_2$GaCl$_4$, λ-(BETS)$_2$GaBrCl$_3$,[18] which have comparatively high superconducting temperatures. They have resistivity maxima at the temperature range 50K-100K. These resistivity maxima disappear and the systems tend to exhibit normal metallic behaviors at high pressure. These resistivity behaviors seem to suggest the similarity in the electronic states of κ-(BETS)$_2$MX$_4$ (M=Ga, In; X=Cl, or Br) and κ-type BEDT-TTF superconductors. In this connection, the origin of the flexion of the resistivity curve of κ-(BETS)$_2$InCl$_4$ may be interesting. The tight-binding band structure calculation of κ-(BETS)$_2$InCl$_4$ gave 2D Fermi surface similar to those of the κ-(BETS)$_2$GaCl$_4$ [10,15] and κ-(BETS)$_2$FeCl$_4$.[11]

(BETS)$_2$(TEA)$_{0.7}$InCl$_5$

The crystal structure of new BETS compound prepared by electrocrystallization of BETS and $(C_2H_5)_4NInCl_4$ in TCE has revealed that the crystal contains BETS, $InCl_5^{2-}$ and the tetraethylammonium cation. As mensioned before, the chemical formula was determined to be (BETS)$_2$(TEA)$_{0.7}$InCl$_5$. The crystal structure of (BETS)$_2$(TEA)$_{0.7}$InCl$_5$ is shown in Figure 10. The BETS cation sheets and the $TEA_{0.7}^{+}InCl_5^{2-}$ sheets are arranged alternately along the c axis. The $InCl_5^{2-}$ forms a distorted trigonal bipyramid. The In-Cl bond distances are in the range from 2.385Å to 2.494Å, which are longer than the In-Cl distance (2.332Å) in $InCl_4^-$ anion. The remarkable feature of this compound is a novel $TEA_{0.7}^{+}InCl_5^{2-}$ sheet. BETS molecules form a distorted tetrad in the ab plane. There are many transverse Se···Se (3.782(2) Å), Se···S (3.496(4) Å) and S···S (3.450(5) Å) interactions among the tetrads. There are two independent BETS molecules A and B. The distorted tetrad is composed from A, B, B' and A' molecules, which is shown in Figure 11. The intermolecular distance of A···B is 3.661Å and the

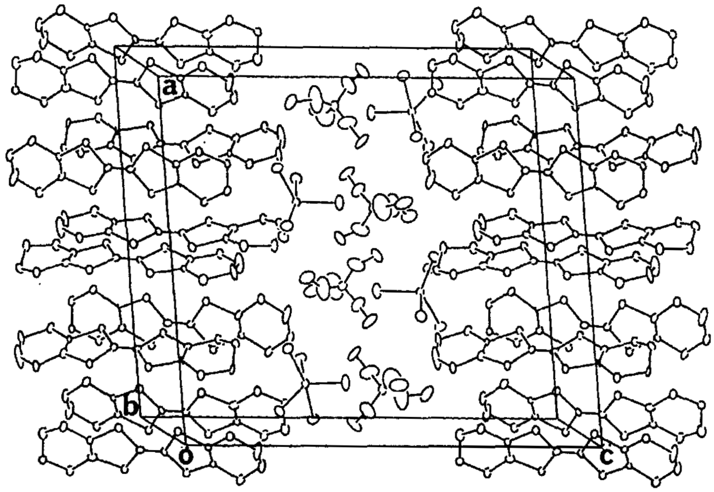

FIGURE 10 The crystal structure of $(BETS)_2(TEA)_{0.7}InCl_5$.

corresponding intermolecular overlap is a direct overlap (Figure 11(a)). Dihedral angle of A and B molecules is 9.3 °. The average intermolecular distance between A and B molecules is 3.636 Å . One of the conformations of the ethylene groups of BETS (B) is eclipsed and the others are staggard. The average bond length of the central C-C double bond of BETS is 1.33 Å and the average C-C bond lengths of two ethylene groups of staggered form is 1.42 Å and the eclipsed form is 1.21 Å. All the non-hydrogen atoms of the tetraethylammonium cation are ordered. The shortest intermolecular contact between chalcogen and Cl distance is 3.554 Å.

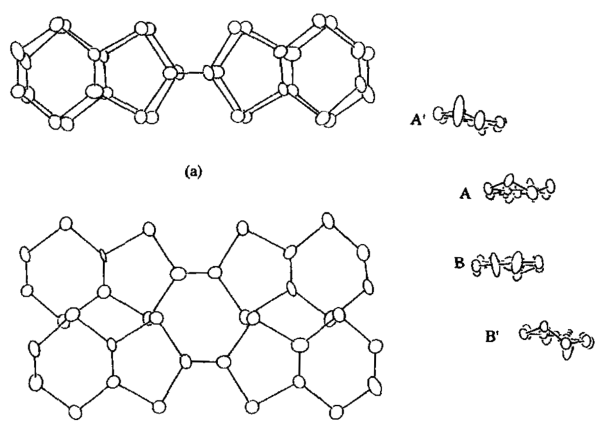

FIGURE 11 The mode of overlaps (left) in the distorted tetrad structure (right) of $(BETS)_2(TEA)_{0.7}InCl_5$.

The resistivity of $(BETS)_2(TEA)_{0.7}InCl_5$ is shown in Figure 12. The room temperature resistivity of $(BETS)_2(TEA)_{0.7}InCl_5$ is about 5 Scm^{-1}. The temperature dependence of the resistivity of $(BETS)_2(TEA)_{0.7}InCl_5$ is weakly metallic and is almost the same with that of κ-$(BETS)_2InCl_4$ within the temperature range 300 K-130 K. $(BETS)_2(TEA)_{0.7}InCl_5$ becomes a semiconductor at low temperature. Below 55 K, the resistivity increases according to the activation process $\rho=\rho_0\exp(\Delta/kT)$ (Δ = 0.0076eV) .

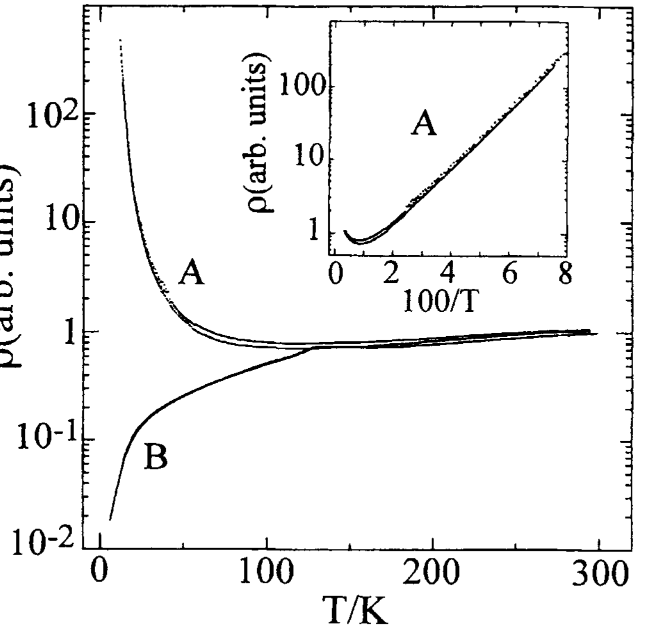

FIGURE 12 The resistivity of $(BETS)_2(TEA)_{0.7}InCl_5$.

The overlap integrals of $(BETS)_2(TEA)_{0.7}InCl_5$ are calculated and are shown in Figure 13. The strongest interaction was obtained between the molecules (A···B) with direct overlap. There are strong intermolecular interactions between the neighbouring BETS tetrads. The tight-binding band structure calculation gave nearly isotropic 2D round Fermi surface (Figure 14). As easily imagined, if TEA were not included, the average charge of BETS would be +1 and Fermi surfaces would be vanished. And if the TEA cation were fully occupied, there would be no Fermi surface and $(BETS)_2(TEA)_{0.7}InCl_5$ would be a semiconductor. Therefore, the metallic nature above 100 K is ascribed to the partial occupation of TEA cation.

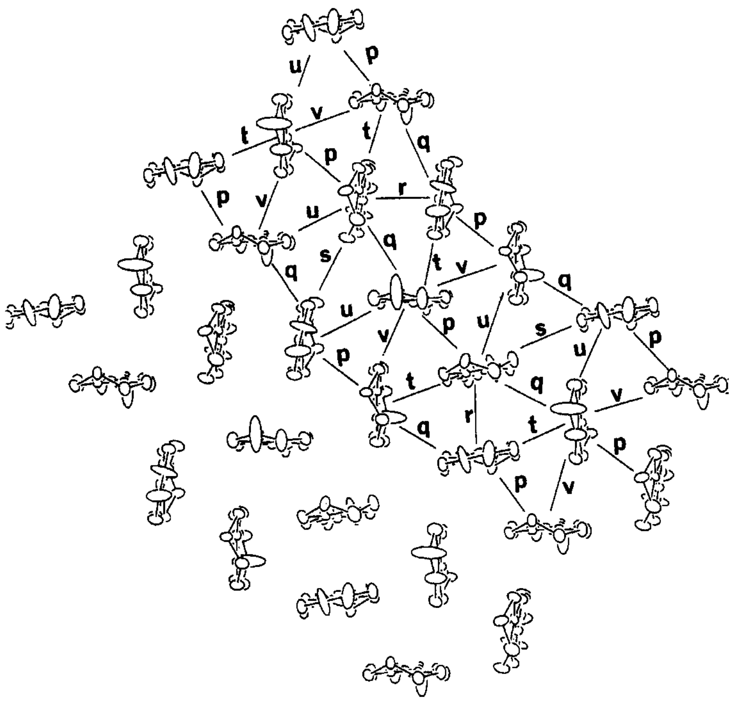

FIGURE 13 The overlap integrals of $(BETS)_2(TEA)_{0.7}InCl_5$. Overlap integrals ($\times 10^3$) are : p=-4.51, q=25.28, r=79.71, s=1.75, t=-40.0, u= -8.24, v=24.73.

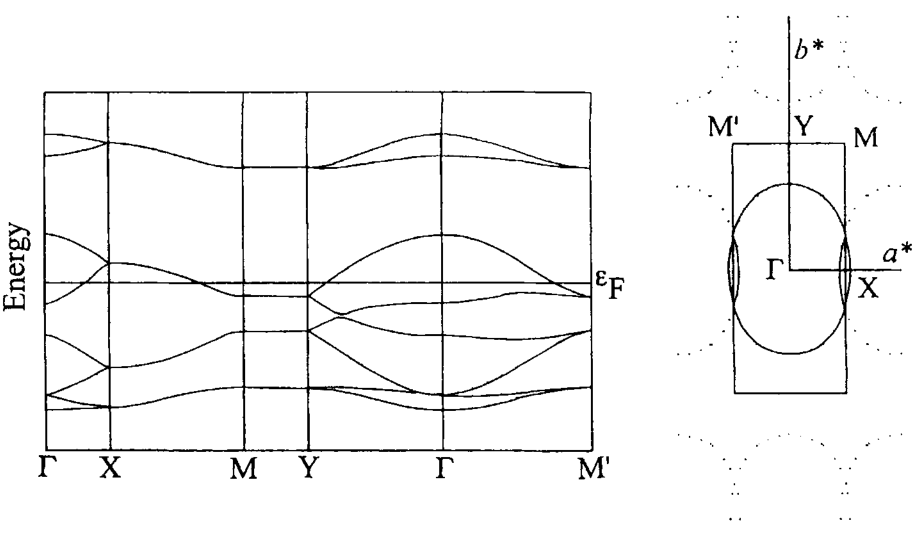

FIGURE 14 Fermi surface (right) and energy diagram (left) of $(BETS)_2(TEA)_{0.7}InCl_5$.

CONCLUSIONS

$(BETS)_2ClO_4(TCE)_{0.5}$ and $(BETS)_2BF_4(TCE)_{0.5}$ have a unique BETS tetrad, named κ(4x4) molecular arrangements. $(BETS)_2(TEA)_{0.7}InCl_5$ has a new distorted tetrad structure. $(BETS)_2InCl_4$ has a κ(2x2) structure or so-called κ-type structure. The temperature dependences of the resistivities of $(BETS)_2ClO_4(TCE)_{0.5}$ and $(BETS)_2BF_4(TCE)_{0.5}$ are metallic down to 4 K and that of $(BETS)_2(TEA)_{0.7}InCl_5$ is weakly metallic down to about 100 K and becomes semiconducting at low temperature. The temperature dependence of the electrical resistivity of κ-$(BETS)_2InCl_4$ has a characteristic flexion point around 130 K, which has not been observed in other κ-$(BETS)_2MX_4$ (M= Ga; X= Cl, Br) compounds. Simple tight-binding electronic band structure calculations of $(BETS)_2ClO_4(TCE)_{0.5}$ and $(BETS)_2(TEA)_{0.7}InCl_5$ gave two-dimensional Fermi surfaces.

DEDICATION.

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