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The Electrical Behavior of Charge-Transfer Salts Based on an Unsymmetrical Donor Bis(ethylenedithio)diselenadithiafulvalene (STF): Disorder Effect on the Transport Properties

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The hybrid donor between bis(ethylenedithio)tetrathiafulvalene and -tetraselenafulvalene (ET and BETS, respectively) has been synthesized and the electrical properties together with the crystal structures of its cation radical salts investigated. All of the crystals studied by X-ray structural analysis turned out to have an orientational disorder at the donor site. Although some of the charge-transfer salts were found to be isostructural with the corresponding ET and/or BETS salts, not all of their electrical properties are parallel to them; some are similar, others are significantly different from those of the parent donor salts. Such a trend indicates that the effect of the disorder on the electrical behavior might not be always equal, and should depend on some factor(s) yet to be clarified.

The research of the chemistry and physics of organic superconductors has made rapid progress recently.[1)] The major part of the accumulated data consists of those of the bis(ethylenedithio)tetrathiafulvalene (abbreviated as BEDT-TTF or simply "ET") system, mainly because this donor has proven to be a versatile building block for the design of an organic superconductor, sometimes with a transition temperature (T_c) higher than 10 K. Moreover, ET has provided many novel and unique electronic states which have not been realized in previous synthetic conductors. Such fascinating properties of ET also led to the advent of a variety of analogous donor molecules, including unsymmetrical ones, together with their radical cation salts or complexes, some of which have also been found to exhibit superconductivity.

Although bis(ethylenedithio)tetraselenafulvalene (BETS) is an analogous donor of ET, it was expected to form a more isotropic, and thus a more stable, molecular metal owing to its four selenium atoms incorporated in the TTF-skeleton.[2—6)] In fact, most of the charge-transfer salts of BETS turned out to be stable metals down to low temperature. Recently, a series of BETS salts has been reported to exhibit superconductivity at ambient pressure.[7,8)]

The title donor (abbreviated as STF) is a hybrid molecule of ET and BETS. One impetus for the investigation of STF salts comes from a prospect of discovering a new organic superconductor.

Another motive for this study lies in interest in the relation between the disorder and the electrical properties. Although there have been some previous studies concerning the effect of disorder on the transport properties of organic donor systems using alloy samples or X-ray, proton or neutron-irradiated samples or a theoretical approach,[1,9)] the net effect of the disorder is difficult to discuss, since there were some other lattice defects, like impurities or inhomogeniety, or due to the fact that the disorder lay in the anion site instead of directly in the electrical pathway. In the present system a randomness can be introduced in the conduction layer without any other perturbation. The STF salts will provide an unique approach for a systematic study of the metallic and superconducting mechanism of the ET and BETS salts.

Experimental

All of the chemicals were of reagent grade from Wako Chemical Co., and were used as received, unless noted otherwise. Triethyl phosphite was vacuum distilled, sealed under nitrogen and stored in a refrigerator until use. All of the solvents were degassed with high-purity dry nitrogen for at least a few minutes before use. 4,5-ethylenedithio-1,3-diselenol-2-one **1**,[2)] 4,5-ethylenedithio-1,3-dithiol-2-one **2**,[10)] and 4,5-ethylenedithio-1,3-dithiole-2-thione **3**[10)] were prepared by following the reported procedures.

Materials. Bis(ethylenedithio)diselenadithiafulvalene (2-(4,5-ethylenedithio-1,3-diselenol-2-ylidene)-4,5-ethylenedithio-1,3-dithiole, STF), **4** (Chart 1).

Method A. The intermediates **1** (0.483 g, 1.6 mmol) and **2** (0.333 g, 1.6 mmol) suspended in triethyl phosphite (100 ml) were slowly heated with stirring to a clear solution under a nitrogen atmosphere. Succesive heating to 110—120 °C turned the solution from yellow to scarlet within a few minutes and precipitation occurred.

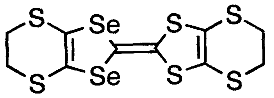

Chart 1.

The mixture was held in that temperature range with stirring for 30 min. After cooling to room temperature reddish-brown precipitates were filtered off, washed successively with acetone, methanol, ethanol, and hexane and dried in vacuo. The crude products were recrystallized from hot CS_2 (250ml×3) followed by column chromatography (silica gel, eluent CS_2), then HPLC (Kusano Kagakukikai Co., Si-10; eluent CS_2) gave analytically pure violet needles; yield: 50 mg (7%). Elemental analysis: Found: C, 25.13; H, 1.76; S, 39.86; Se, 32.25%. Calcd for $C_{10}H_8S_6Se_2$: C, 25.10; H, 1.69; S, 40.21; Se, 33.00%. MS(EI, 70 eV) *m*/*z*=480 (M+2; 100%), 478 (M^+; 83%). IR (KBr) 1407.8 (s), 1282.4 (s), 918.9 (s), 716.4 (s) cm^{-1}. For the crystal data, see Table 1 (later).

Method B. A similar procedure to method A was followed with **3** (0.359 g, 1.6 mmol) instead of **2**. This allowed a highly selective reaction, and only a trace amount of self-coupling products formed, which saved a tedious work-up for isolating the desired compound in method A; crude coupling products were filtered off from the phosphite, washed thoroughly with methanol, dried in vacuo and passed through a short column (silica gel, eluent CS_2), then recrystallized from hot CS_2; yield: 350 mg(46%).

Charge-Transfer Salts of STF. Single crystals of the charge-transfer salts of STF were prepared by the use of a standard electrocrystallization technique. All of the chemicals were purified prior to use and handled inside a drybox. The crystal growth was carried out in a standard H-cell (without glass-frit) using platinum electrodes of 1 mm in diameter under a nitrogen atmosphere. A typical procedure began with 7—12 mg of STF and 40—100 mg of the tetrabutylammonium salt of the desired anion as the supporting electrolyte in 20 ml of an appropriate solvent at a constant current at room temperature (19—21 °C) for several days. Sometimes a potentiostatic condition, a higher (lower) temperature and/or some other minor modification were applied. Each actual condition is

Table 1. Electrolytic Conditions for Preparation of STF Salts[a]

Counter ion[b] (X^{n-})	Crystal habit[c]	Current[d] μA	Voltage[e] V	$(C_4H_9)_4NX$ mg	STF mg	Solvent[f]	Time d
PF_6^-	Needles	1.2	—	38	8	CB	9
AsF_6^-	Needles	1.5	—	99	8	CB	9
SbF_6^-	Plates	0.5	—	90	10	CB	4
TaF_6^-	Needles	2.2	—	99	7	CB(Et)	9
BF_4^-	Plates	—	5.4	65	10	CB(31 °C)	4
ClO_4^-	Plates Needles	0.3	—	120	7	CB/THF	4
ReO_4^-	Plates(#1) Needles(#2)	—	3.2	56	9	CB(31 °C)	7
ReO_4^-	Plates(#3)	0.1	—	69	7	CB/THF	13
I_3^-	(α-)Plates	—	1.0	101	12	CB(43°C)	10
I_3^-	(α-)Plates	—	12.0	30	7	CB(43°C)	9
$AuCl_2^-$	Plates	0.3	—	37	7	CB/THF	10
$AuBr_2^-$	Plates	0.1	—	72	6	CB/THF[g]	9
AuI_2^-	Plates(#1)	1.0	—	88	11	CB	18
AuI_2^-	Plates(#2)	1.2	—	39	8	CB/THF[g]	7
AuI_2^-	Plates(#2)	1.2	—	44	7	CB(Et)	7
$Au(CN)_2^-$	Plates	0.3	—	56	7	CB/THF	10
$Ag(CN)_2^-$	Plates	0.3	—	75	8	CB/THF	16
$HgBr_4^{2-}$	Needles	0.2	—	109	8	CB/THF	7
TEA· $GaCl_4$	(κ-)Plates (λ-)Needles	1.3	—	60	10	CB(16 °C)	7
TEA· $FeCl_4$	Plates Needles	0.1	—	41	8	CB(16 °C)	8
$FeBr_4^-$	Plates	0.6	—	44	11	CB(16 °C)	4
	Needles	0.3	—	32	6	CB(16 °C)	4
TEA· $GaBr_4$	Plates Needles	0.1	—	54	8	CB(Et 5%)	5
TEA· $InCl_4$	Needles	1.2	—	42	7	CB(Et 5%)	16
TEA· $InBr_4$	Plates Needles	1.0	—	44	7	CB(Et 5%)	16
TEA· $TlCl_4$	Needles	1.1	—	52	8	CB(Et 5%)	16
TEA· $TlBr_4$	Needles	1.2	—	54	7	CB(Et 5%)	10
KNO_3 18-Crown-6	Plates	1.4	—	30 33	8	THF	5

a) All syntheses were carried out at (20±1) °C unless otherwise noted. b) In case the supproting electrolytes were provided with combination of some reagents or other than tetrabutylammonium salts, the chemical formulae or abbreviations are indicated. TBA =tetrabutylammonium ion, 18-crown-6= 1,4,7,10,13,16-hexaoxacyclooctadecane. c) All crystals are black. Plates are often elongated and appear needles at first sight. d) Galvanostatic condition. e) Potentiostatic condition. f) 20 ml unless otherwise noted. TCE = 1,1,2-trichloroethane, CB = chlorobenzene, (Et)=the solvent containing 10% ethanol (vol/vol) unless otherwise noted, THF = tetrahydrofuran, CB/THF = 1 : 1 (vol/vol) mixture of chlorobenzene and tetrahydrofuran otherwise noted. g) CB/THF = 9 : 1 (vol/vol) mixture of chlorobenzene and tetrahydrofuran.

tabulated in Table 2.

Electrical Resistivity Measurements. All of the electrical resistivity measurements were carried out by the usual four-probe method with a d.c. current. Over the range 4—293 K measurements were made using a ^{4}He insertable cryostat and a multichannel 4-terminal conductometer (HUSO Electrochemical System, HECS 994) controled by a personal computer (NEC PC-9801 Vm) through a GPIB. Contact to the crystals was made by gold wires (15 μmφ) attached with gold paste (Tokuriki Chemical, No. 8560) in a four-in-a-line configuration. The d.c. current was 0.1 μA.

Alternatively, over the 1.5—293 K range a similar ^{4}He insertable cryostat was used. The d.c. current from 5 μA to 5 mA was supplied from a Keithly 224 programmable current source. The current was dependent on the voltage between the two inner probe, which was monitored by a Keithly 181 nanovoltmeter or a Keithly 182 sensitive digital voltmeter. All of the procedures were controlled by a personal computer (NEC PC-9801 Vm) through a GPIB.

The pressure dependence of the conductivity was measured using the same equipment as that mentioned above (those of the range 1—4 K) and a hydrostatic method employing a clump cell made of Cu/Be alloy (Toshiba Tangalloy) and Daphne oil (No. 7373, Idemitsu Oil Co., Ltd.) as a pressure medium.

Results and Discussion

Electrical Properties of STF Salts. Octahedral Anion Salts. All of the octahedral anion salts make metal-insulator (MI) transitions in the range of 170—270 K; PF_6 (T_{MI} = 175 K), AsF_6 (T_{MI} = 180 K), SbF_6 (T_{MI} = 265 K) and TaF_6 (T_{MI} = 157 K) salts, respectively. As a typical example, the electrical behavior of the PF_6 salt is shown in Fig. 1.

Tetrahedral Anion Salts. BF_4 salt is a semiconductor with an activation energy of 0.06 eV.

The ClO_4 salt exhibited an MI transition at 80 K at ambient pressure (Fig. 2). This salt has turned out to be isomorphous with $(ET)_3(ClO_4)_2$[11] (see Table 2) and the qualitative electrical behavior is similar to the ET salt. However, the STF salt keeps decreasing the resitivity down to a lower temperature than the ET salt. The room-temperature conductivities and MI transition temperatures are 50 S cm^{-1}, 170 K for $(ET)_3(ClO_4)_2$[11] and 6 S cm^{-1}, 80 K for $(STF)_3(ClO_4)_2$. The insulating phase of $(STF)_3(ClO_4)_2$ was completely suppressed under a pressure higher than 9 kbar.

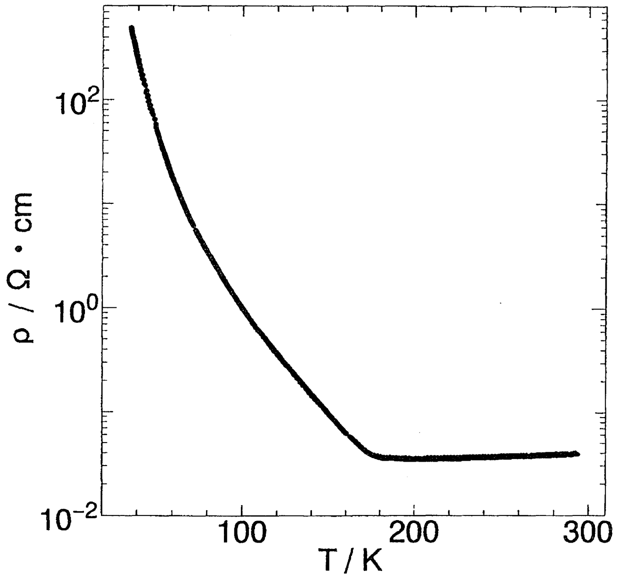

Fig. 1. Electrical resistivity of the PF_6 (T_{MI} = 175 K) salt as function of temperature.

The ReO_4 salt has two metallic phases (Fig. 3 (a) with

Table 2. Crystal Data of STF, Its Charge-Transfer Salts and Related Isostructural Compounds

	ET[a]	STF	BETS[b]	α-ET_2I_3[c]	α-STF_2I_3	α-$BEST_2I_3$[b]	$ET_3(ClO_4)_2$[d]
	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	6.614(11)	6.644(3)	6.662	9.211(2)	9.198(2)	9.209	16.463(2)
b/Å	13.985(2)	14.148(4)	14.227	10.850(4)	10.802(3)	10.816	9.498(2)
c/Å	16.646(3)	16.998(7)	16.216	17.488(5)	17.607(5)	17.777	7.613(2)
α/°				96.95(2)	96.86(2)	96.63	95.91(2)
β/°	109.55(2)	109.67(3)	92.97	97.97(2)	97.88(2)	97.87	87.17(1)
γ/°				90.75(2)	90.75(2)	90.69	90.84(1)
V/Å^3	1449.6	1504.6	1534.9	1717	1719.7		1182
Z	4	4	4	2	2	2	1

	$STF_3(ClO_4)_2$	STF_2AuCl_2	θ-STF_2AuI_2[e]	λ-STF_2GaCl_4	λ-$BETS_2GaCl_4$[f]	κ-STF_2GaCl_4	κ-$BETS_2GaCl_4$[f]
	Triclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic	Orthorhombic	Orthorhombic
	$P\bar{1}$	$P2/c$		$P\bar{1}$	$P\bar{1}$	$Pnma$	$Pnma$
a/Å	16.702(6)	16.371(4)	34.094(24)	16.244	16.141(3)	11.587	11.665(5)
b/Å	9.522(3)	6.718(1)	20.268(19)	18.355	18.580(3)	35.696	35.894(9)
c/Å	7.634(2)	15.395(4)	9.928(9)	6.581	6.594(1)	8.493	8.464(3)
α/°	95.65(3)			98.46	98.37(1)		
β/°	87.17(3)	105.72(2)		96.90	96.77(1)		
γ/°	91.16(3)			112.46	112.55(1)		
V/Å^3	1206.6	1629.8(6)	6860	1759.9	1774.0(5)	3512.8	3544(2)
Z	1	2	8	2	2	4	4

a) From Ref. 15. b) From Ref. 2. Both cell volume and standard deviations are not available in the reference. c) From Ref. 12. d) From Ref. 11. e) Metallic phase (#1 in Table 1). X-Ray structural analysis was not completed due to the poor quality of the crystal. f) From Ref. 5.

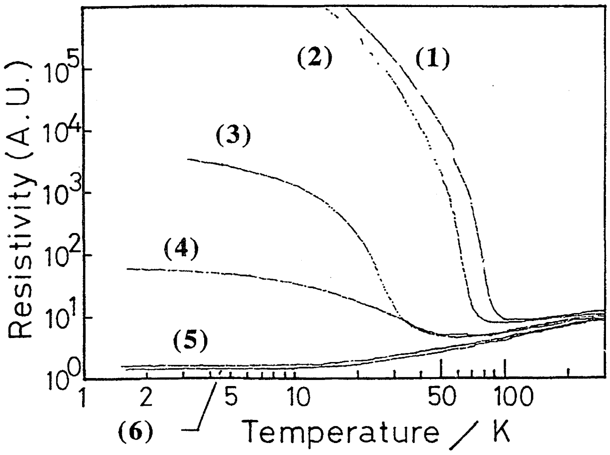

Fig. 2. Electrical resistivity of the ClO$_4$ salt as function of temperature: (1) 0 kbar, (2) 2.6 kbar, (3) 6.0 kbar, (4) 7.0 kbar, (5) 9.1 kbar, and (6) 11.4 kbar, respectively.

preparation condition (#1) in Table 1 and Fig. 3 (b), (#3) and one insulating phase (#2), and both metallic phases are stable down to 4 K.

The [HgBr$_4$]$^{2-}$ salt is a semiconductor. The [MX$_4$]$^-$ (M = Fe, Ga, In, Tl; X = Cl, Br) salts are all semiconductors. The electrical behavior of the GaCl$_4^-$ salts, λ-(STF)$_2$GaCl$_4$ and κ-(STF)$_2$GaCl$_4$, are shown in Fig. 4. λ-(STF)$_2$GaCl$_4$ is isostructural with λ-(BETS)$_2$GaCl$_4$,[4,5,7] and κ-(STF)$_2$GaCl$_4$ with κ-(BETS)$_2$GaCl$_4$;[4,5] κ-(BETS)$_2$GaCl$_4$ remains metallic down to 4 K and λ-(BETS)$_2$GaCl$_4$ undergoes a superconducting transition at 8 K, whilst the potential metallic nature of both STF salts have collapsed completely. In the meantime, κ-(STF)$_2$GaCl$_4$ retains a hump at around 100 K in the temperature dependence of the resistivity, which seems to be much alike what is observed in κ-(BETS)$_2$GaCl$_4$ as well as among many κ-type organic superconductors.[1]

Linear Anion Salts. The linear anion yielded the widest variety of salts. The I$_3$ salt showed a gentle MI transition at 65—80 K. An X-ray study revealed that it is isomorphous with α-(ET)$_2$I$_3$[12] and α-(BETS)$_2$I$_3$[2] (see Table 2), and that their qualitative behavior is similar to each other (Fig. 5). Interestingly, the critical temperature and sharpness of the MI transition in α-(STF)$_2$I$_3$ fall into the middle of the same salts of ET and BETS. A similar result, except for the T_{MI}'s, was observed in the DSeDTF-TCNQ complex (DSeDTF = diselenadithiafulvalene),[9(a),9(b)] where the donor molecule DSeDTF is actually a mixture of the cis- and trans-isomers, and both of them are different from the fulvalene part of the STF molecule studied here.

The AuCl$_2$ salts showed two different types of behavior: one kept decreasing its electrical resistivity down to 1 K (Fig. 6(a)), #1 in Table 1); the other exhibited an M-I transition at ca. 70 K (Fig. 6(b), #2 in Table 1). As shown in Fig. 7, although the latter (#2) phase has a four-fold stacking structure similar to (PT)$_2$AuCl$_2$ (PT =bis(pripylenedithio)-tetrathiafulvalene), the PT salt remains a semiconductor over the entire temperature region of the measurement, even under a high pressure of 14 kbar.[13] The stacking mode of the donor molecules and an overall arrangement of the donor in the sheet are much the same as the PT salt, but the STF salt has a larger number of intermolecular short contacts (< 3.7 Å) between the chalcogen atoms in the donor sheet (Fig. 7(c)), whereas the PT salt has only a few of them. The consequent two-dimensional network based on short chalogen–chalcogen contacts can be thought to make the electronic structure of the STF salt more two-dimensional (2D), and to make metallic behavior emerge.

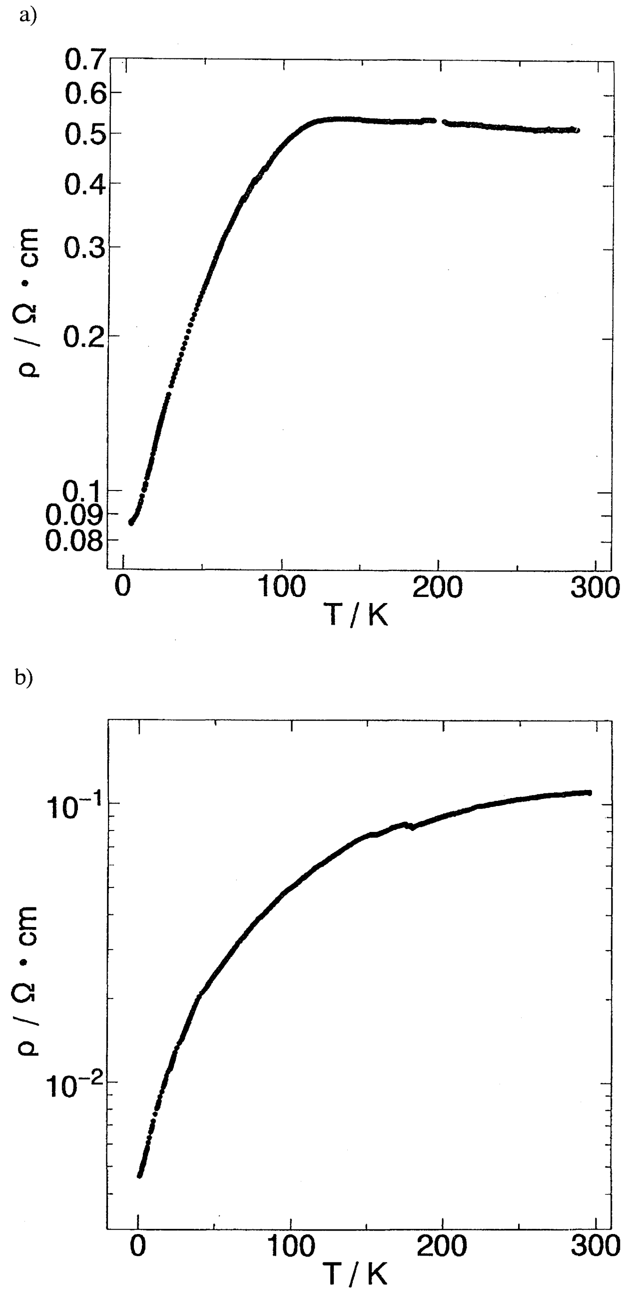

Fig. 3. Electrical resistivity of the metallic ReO$_4$ salts as function of temperature; Their synthetic conditions are (a) #1 and (b) #3 in Table 1, respectively.

The AuBr$_2$ salt behaved like a semiconductor with an activation energy of 0.16 eV at all temperatures of the measurement, but with a peculiar hump at around 120 K.

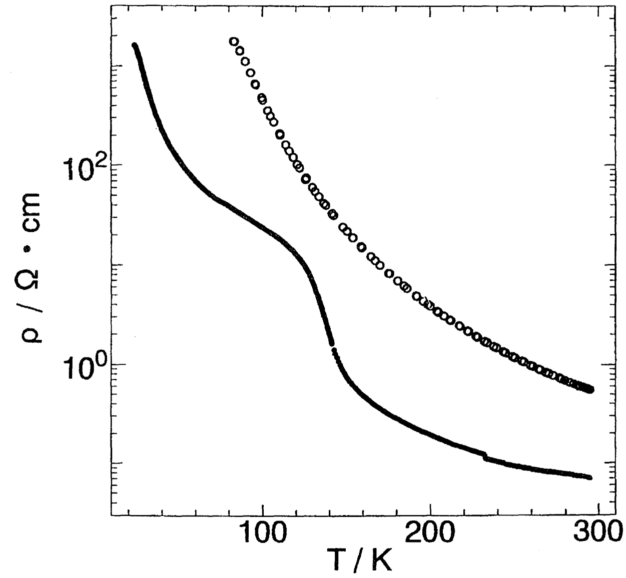

Fig. 4. Electrical resistivity of the $GaCl_4$ salts (filled, $\varkappa$-; empty, λ-) as function of temperature.

One of the AuI_2 salts (#1 in Table 1) kept decreasing monotonously in electrical resistivity down to 4 K (see Fig. 8(a)). This crystal has a θ-type structure with the lattice constants summarized in Table 2. The θ-type donor arrangement is a typical 2D crystal structure, which often leads to a 2D electronic structure and a stable metallic or superconducting state.[1—3] The other AuI_2 salt (#2 in Table 1) exhibited a clear anomaly at around 190 K like the $AuBr_2$ salt mentioned above. Below 150 K the resistivity increased steeply (Fig. 8(b)). Although a similar anomalous behavior was observed in common in the semiconducting $Ag(CN)_2$ salts, the cause(s) is/are not yet known.

The $Au(CN)_2$ salt is a semiconductor with an activation energy of 0.14 eV.

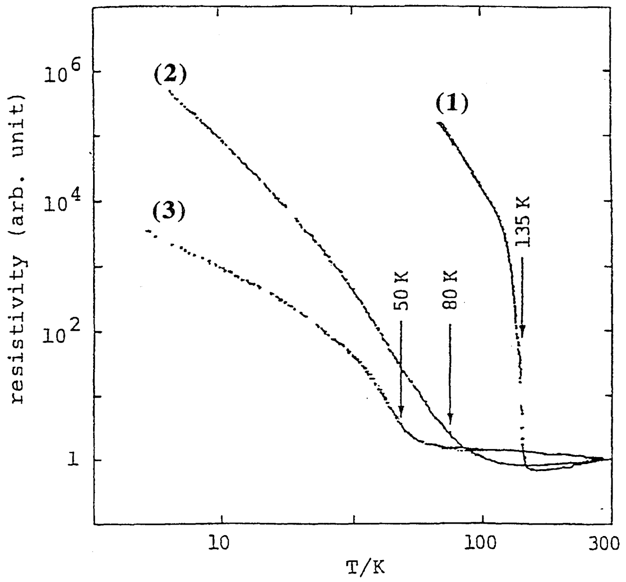

Fig. 5. Electrical resistivity of the α-type I_3 salts of (1) ET, (2) STF, and (3) BETS as function of temperature. The arrows with temperatures indicate each metal-insulator (MI) transition.

The $Ag(CN)_2$ salt crystallized in two different phases (metallic and semiconducting, respectively) from the same batch, and the metallic phase kept decreasing in electrical resistivity down to 4 K (Fig. 9).

Other Salt. The NO_3 salt behaved narrowly metallic above ca. 200 K with a feature at around 230 K, and gradually increased in resistivity at a lower temperature (Fig. 10).

Grouping of the Salts: Group I and Group II. All of the STF salts examined by the X-ray study were found to have an orientational disorder at the STF site. Some of the salts are isostructural with the corresponding ET and/or BETS salts, and their electrical behavior can be divided into

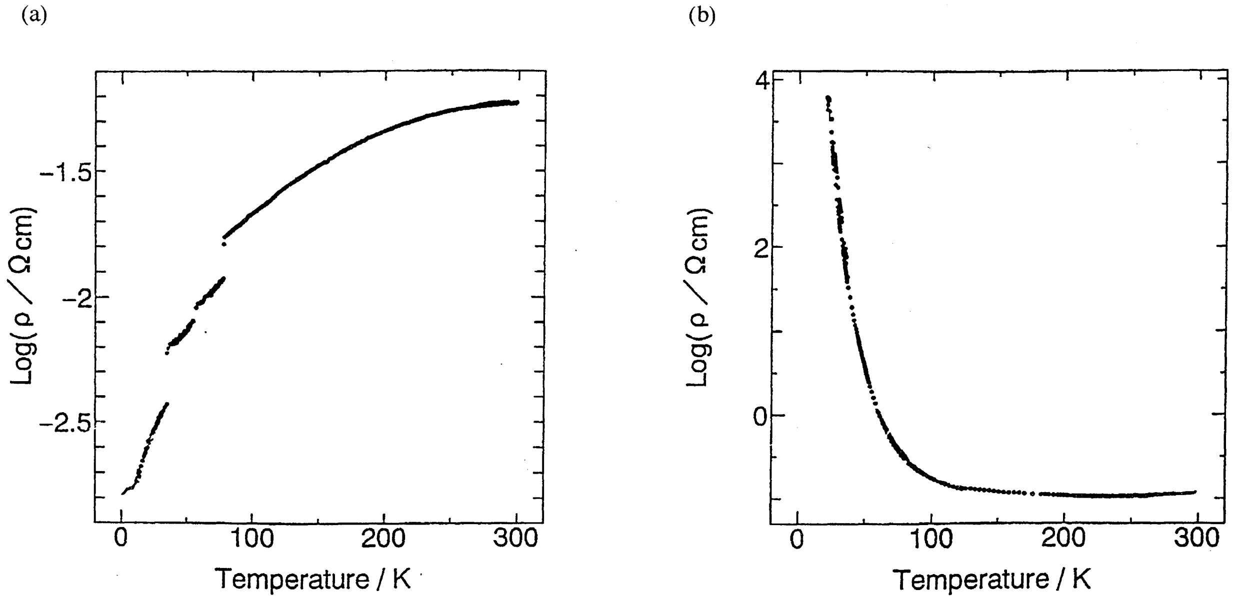

Fig. 6. Electrical resistivity of the metallic $AuCl_2$ salts of STF as function of temperature: (a) #1, (b) #2 in Table 1, respectively.

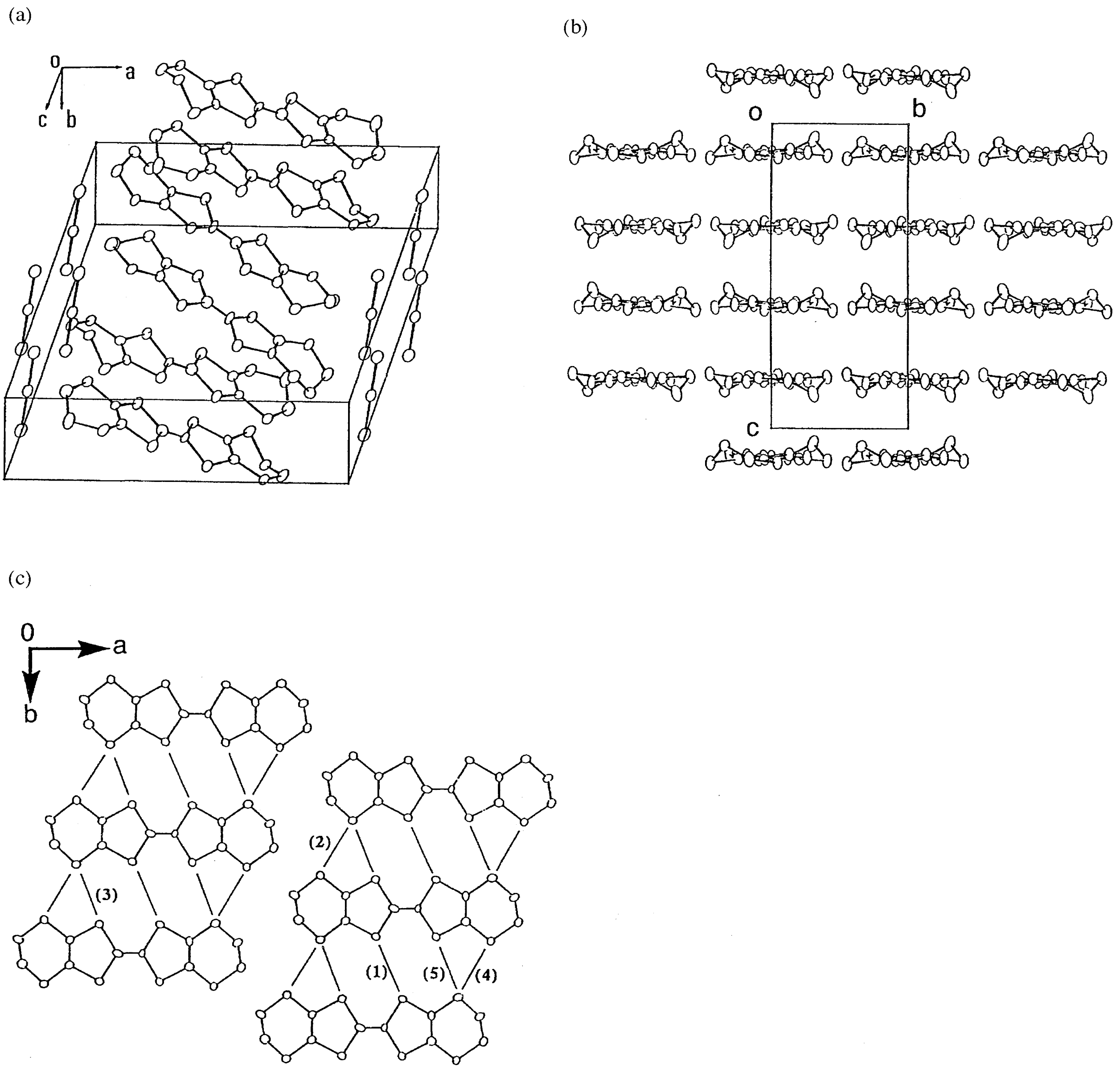

Fig. 7. Crystal structure of the $AuCl_2$ salt with MI transition; (a) unit cell, (b) donor arrangement. The thin lines indicate chalcogen–chalcogen short contacts: (1) 3.678, (2) 3.486, (3) 3.427, (4) 3.501 and (5) 3.520 Å, respectively.

two classes according to the effect of disorder on the electrical properties.

—The Group I salts (the PF_6, AsF_6, SbF_6, TaF_6, ClO_4, ReO_4 (#1 and #3), I_3, $AuCl_2$ (#1 and #2), AuI_2 (#1) and $Ag(CN)_2$ salts) exhibit clear metallic properties. Some kept their metallic states down to 4 K, and others exhibited sharp MI transitions. Such behavior indicates that the conduction electrons should hardly suffer from the random potential caused by disorder. Such a trend reminds us of a previous study of TTF-TCNQ, DSeDTF-TCNQ and TSeF-TCNQ.[9]

—The Group II STF salts (λ-$(STF)_2GaCl_4$ and $\varkappa$-$(STF)_2GaCl_4$) exhibited totally different electrical properties from the corresponding symmetrical donor salts: a semiconducting behavior from room temperature. Such a behavior suggests that the disorder seriously perturbs the electronic motion; otherwise, they might have showed metallic properties judging from the isostructural BETS salts.

The STF's unique position between BETS and ET is most evidently manifested in the electrical behavior of the charge-transfer salts of Group I. All of their behavior suggests that the substitution of selenium for the sulfur atoms makes intermolecular interactions closer, and, thus, the metallic phase stabler, even if it introduces disorder in the electrical pathway. In other words, the STF salts of Group I behave as if they consist of "BEDT-TXF", where X is an imaginary atom that has an average radius between sulfur and selenium atoms, though the electrical behavior is sometimes a slightly more obscure than the counterpart systems without disorder. This trend may enable a delicate tune of the intermolecular interactions in the solid state.

Metallic Behavior and Disorder. With respect to the relation between the electrical behavior and x in $\varkappa$-

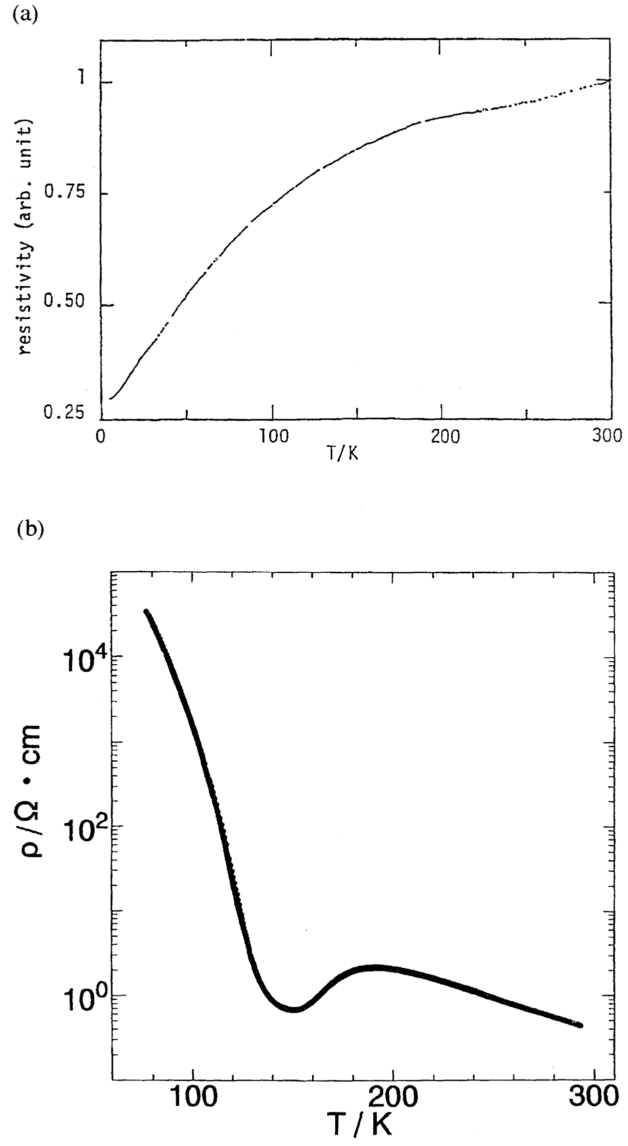

Fig. 8. Electrical resistivity of the AuI_2 salts as function of temperature; (a) #1 in Table 1 and (b) #2 in Table 1, respectively.

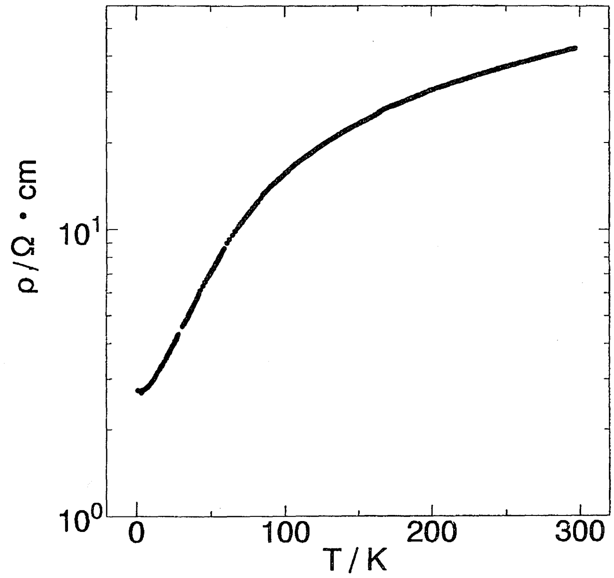

Fig. 9. Electrical resistivity of the metallic $Ag(CN)_2$ salt as function of temperature.

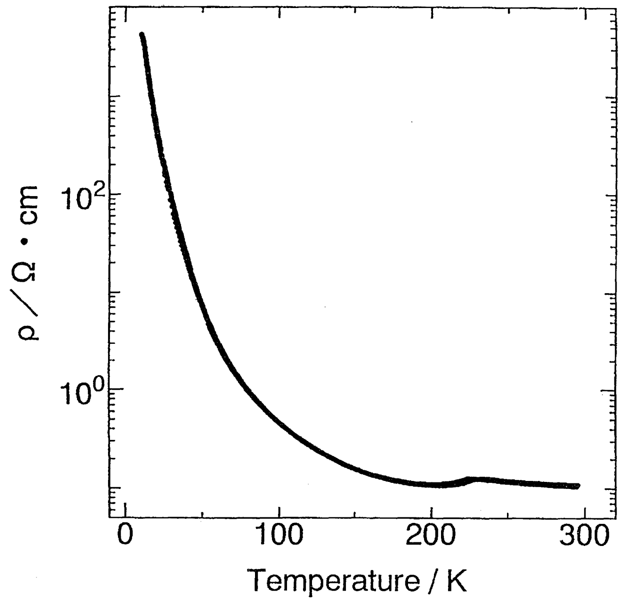

Fig. 10. Electrical resistivity of the NO_3 salt as function of temperature.

$[(ET)_{1-x}(STF)_x]_2Cu[N(CN)_2]Br$, it was found[14] that: (1) the small expansion of the b lattice parameter and small reduction of the a and c lattice parameters suggested an enhanced donor overlap in the donor sheets and a reduction of the intersheet interaction on STF incorporation; (2) the conductivity measurements yielded a gentle decline in the room-temperature conductivity and a rapid decrease in the superconducting transition temperature, but, at the same time, an increasing stability of the metallic phases of the alloys with increasing x.

These results indicate that the organic metals should prefer metallic states to superconducting states under perturbations like disorder. An excessively high pressure is also well-known to stabilize a metallic state rather than a superconducting state.[1] On the other hand the electrical behavior of the Group II salts, i.e complete disruption of the metallic conductivity in spite of the identical crystal structures to the stable metallic BETS salts, have not been found among the known organic conductors. Unless intermolecular donor interactions are extremely sensitive to a subtle difference in the crystal structure, and rapidly decrease in going from the BETS salts to the STF salts, it remains to be clarified what makes such a significant difference in effect of disorder on the electrical properties.

References

1) For example see: a) J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M-H. Whangbo, "Organic Superconductors (Including Fullerenes)," Prentice Hall, New Jersey (1992); b) "The Physics

and Chemistry of Organic Superconductors," ed by G. Saito and S. Kagoshima, Springer Proceedings in Physics, Springer, Berlin (1990), Vol. 51; c) T. Ishiguro and K. Yamaji, "Organic Superconductors," Springer-Verlag, Berlin (1989).

2) R. Kato, H. Kobayashi, and A. Kobayashi, *Synth. Met.*, **41-43**, 2093 (1991).

3) T. Naito, A. Miyamoto, H. Kobayashi, R. Kato, and A. Kobayashi, *Chem. Lett.*, **1991**, 1945.

4) A. Kobayashi, R. Kato, T. Naito, and H. Kobayashi, *Synth. Met.*, **55-57**, 2078 (1993).

5) A. Kobayashi, T. Udagawa, H. Tomita, T. Naito, and H. Kobayashi, *Chem. Lett.*, **1993**, 2179.

6) H. Kobayashi, H. Tomita, T. Udagawa, T. Naito, and A. Kobayashi, *Synth. Met.*, **70**, 867 (1995).

7) H. Kobayashi, T. Udagawa, H. Tomita, K. Bun, T. Naito, and A. Kobayashi, *Chem. Lett.*, **1993**, 1559.

8) H. Kobayashi, H. Tomita, T.Naito, H. Tanaka, A. Kobayashi, and T. Saito, *J. Chem. Soc., Chem. Commun.*, **1995**, 1225.

9) For example see: a) E. M. Engler and V. V. Patel, *J. Chem. Soc., Chem. Commun.*, **1975**, 671; b) H. K. Spencer, M. V. Lakshmikantham, M. P. Cava, and A. F. Garito, *J. Chem. Soc., Chem. Commun.*, **1975**, 867; c) S. Etemad, T. Penney, E. M. Engler, B. A. Scott, and P. E. Seiden, *Phys. Rev. Lett.*, **34**, 741 (1975), and references cited therein.

10) K. S. Varma, A. Bury, N. J. Harris, and A. E. Underhill, *Synthesis*, **1987**, 837.

11) H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, *Chem. Lett.*, **1984**, 179.

12) K. Bender, I. Hennig, D. Schweitzer, K. Dietz, H. Endres, and H. J. Keller, *Mol. Cryst. Liq. Cryst.*, **108**, 359 (1984).

13) A. Kobayashi et al., unpublished results.

14) T. Naito, A. Miyamoto, H. Kobayashi, R. Kato, and A. Kobayashi, *Chem. Lett.*, **1992**, 119.

15) H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **59**, 301 (1986).