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CRYSTAL AND ELECTRONIC STRUCTURES OF (BEDSe-TSeF)$_2$AuBr$_2$

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The crystal structure of (BEDSe-TSeF)$_2$AuBr$_2$ is very similar to that of the superconducting β-type BEDT-TTF system. Unlike the β-type salt with 2-dimensional(2D) closed Fermi surface, however, (BEDSe-TSeF)$_2$AuBr$_2$ has a 1D plane-like Fermi surface, as a result of strong dimerization and weak transverse interaction.

The concept that in the molecular metal the dimensionality of the electronic structure is closely related to the stability of the metallic state and would be controlled by the molecular design is the fruit of the recent chemical and physical studies of the cation radical salts based on the organic donor BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) and related compounds. The selenium analogue of BEDT-TTF, BEDSe-TSeF (bis(ethylenediseleno)tetraselenafulvalene), was synthesized by Lee et al.$^{1)}$ and has potentiality to construct the multi-dimensional electronic system with broader energy band. We have pointed out that the molecular packings of BEDSe-TSeF cations would be very similar to those in the BEDT-TTF salts in the same oxidation state.$^{2)}$ In this paper, the crystal and electronic structures of the first 2:1 salt of BEDSe-TSeF, (BEDSe-TSeF)$_2$AuBr$_2$, are reported and compared with those of β-(BEDT-TTF)$_2$X (X=I$_3$, AuI$_2$•••) system.

The electrochemical oxidation (at a constant current of 1 μA) of a solution containing BEDSe-TSeF and n-Bu$_4$NAuBr$_2$ in 1:1 mixture of 1,1,2-trichloroethane and carbon disulfide under N$_2$ gave black elongated plates of (BEDSe-TSeF)$_2$AuBr$_2$. The crystal data are: C$_{20}$H$_{16}$Se$_{16}$AuBr$_2$, triclinic, space group P$\bar{1}$. a=17.210(10), b=8.101 (3), c=6.815 Å, α=106.39(3), β=95.78(5), γ=103.02 (4)°, V=874.3 Å^3, Z=1. Intensities were measured on a Rigaku automated diffractometer with Mo Kα radiation. Independent 1700 reflections ($2\theta \leq 60°$, $|Fo| > 3\sigma(|Fo|)$) were used in the calculations. The final R value was 0.089. Final positional parameters are given in Table 1.

As shown in Fig. 1, the crystal of (BEDSe-TSeF)$_2$AuBr$_2$ has a modified structure of the organic superconductor β-(BEDT-TTF)$_2$X (X=I$_3$, IBr$_2$, and AuI$_2$). Dimerized BEDSe-TSeF molecules (A and B in Fig. 1) align along the b axis. Interplanar distances are 3.646 Å (A•••B) and 4.180 Å (A•••C), respectively. Short intradimer Se•••Se distaces (3.882 and 3.919 Å) are observed. The mode of intradimer overlapping is of the type described as "double bond over the ring",

Table 1. Fractional atomic coordinates (x 10^4) with their estimated standard deviations

Atom	x	y	z
Au	0	0	0
Br	743(4)	-2154(8)	53(10)
Se(1)	5552(4)	7716(8)	8799(8)
Se(2)	5008((3)	7763(8)	13106(8)
Se(3)	3643(4)	5379(7)	6312(8)
Se(4)	3102(3)	5491(7)	10637(7)
Se(5)	7347(4)	10042(8)	10782(9)
Se(6)	6681(4)	10019(8)	15794(8)
Se(7)	1861(4)	3162(8)	3785(8)
Se(8)	1291(4)	3330(8)	8688(9)
C(1)	4659(30)	6942(65)	10113(73)
C(2)	4005(25)	6098(54)	9296(60)
C(3)	6315(27)	8970(59)	11271(66)
C(4)	6071(26)	8900(58)	13138(65)
C(5)	2553(26)	4263(57)	6337(65)
C(6)	2332(29)	4314(63)	8244(71)
C(7)	7952(33)	10533(70)	13529(79)
C(8)	7652(36)	11501(77)	15393(87)
C(9)	969(42)	4133(88)	4812(100)
C(10)	594(35)	3226(75)	6155(85)

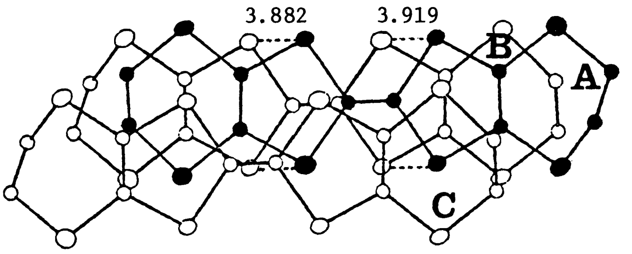


Fig. 2. Mode of intermolecular overlapping.

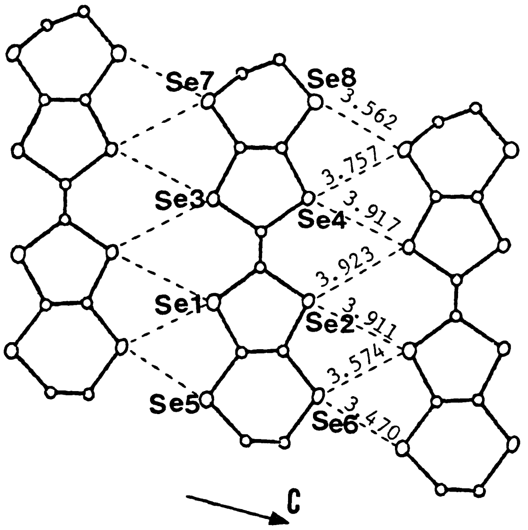


Fig. 3. Side-by-side arrangement of BEDSe-TSeF molecules.

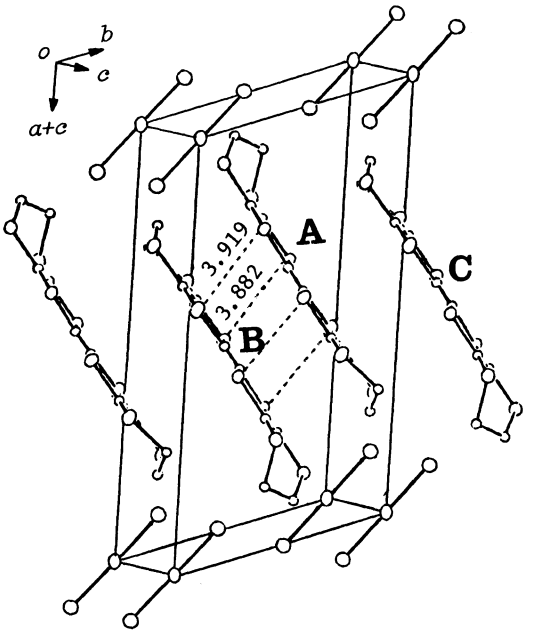
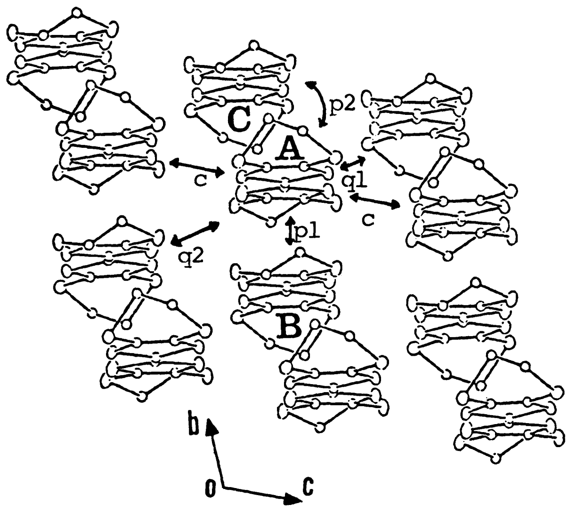


Fig. 1. Crystal structure of $(\mathrm{BEDSe\text{-}TSeF})_2\mathrm{AuBr}_2$.

Table 2. Overlap integrals (x 10^3) of the HOMO in $(\mathrm{BEDSe\text{-}TSeF})_2\mathrm{AuBr}_2$.



S_{p1}	20.3	S_{q1}	14.36	S_c	0.86
S_{p2}	4.95	S_{q2}	1.81		

and adjacent dimers are "slipped" along the c axis (Fig. 2). Along the c axis, there exists the side-by-side arrangement of BEDSe-TSeF molecules (Fig. 3). This side-by-side arrangement is the most characteristic feature of the cation radical salts of BEDT-TTF. Compared to the BEDT-TTF compound, in which the transverse interaction is based on the outer sulfur atoms, the replacement of the chalcogen atom has added short intermolecular chalcogen-chalcogen distances based on the inner selenium atoms. The centrosymmetric $AuBr_2^-$ anion tilts with respect to the b axis and short Se•••Br distances (3.528 and 3.669 Å) and large interanion Br•••Br distance (4.719 Å) are observed.

In the conducting cation radical salts, the conduction band is largely composed of the HOMO (highest occupied molecular orbital). Table 2 shows the intermolecular overlap integrals (S) of the HOMO of BEDSe-TSeF.[3)] The alternate S values along the b axis (S_{p1} and S_{p2}) show the dimerization of the BEDSe-TSeF molecules and the large S_{q1} value indicates that the main conduction path is along the [011] direction. The energy dispersion relation derived from the simple tight-binding approximation is,

$$E(\mathbf{k})=2t_c\cos(\mathbf{kc})\pm D^{1/2},\quad D=\{(t_{p1}+t_{p2})\cos(\mathbf{kb}/2)+(t_{q1}+t_{q2})\cos(\mathbf{kb}/2+\mathbf{kc})\}^2$$
$$+\{(t_{p1}-t_{p2})\sin(\mathbf{kb}/2)-(t_{q1}-t_{q2})\sin(\mathbf{kb}/2+\mathbf{kc})\}^2.$$

On the basis of the approximation that the transfer integral (t) is proportional to the overlap integral ($t \simeq ES$; E is a constant of the order of the energy of HOMO ($\simeq -10$ eV)), the band structure and the shape of the Fermi surface were calculated (Fig. 4). The HOMO energy bands are separated into the upper and lower bands and there exists an energy gap (ΔE). This is the result of the strong dimerization. The upper band is half-filled and the Fermi surface is open perpendicular to the (b^*+c^*) axis.

Fig. 5 shows that $(BEDSe\text{-}TSeF)_2AuBr_2$ is a semiconductor. This is very similar to the case of β'-$(BEDT\text{-}TTF)_2ICl_2$, where we cannot neglect the electron-electron interaction.[4)] However, it is instructive to consider the dimensionality

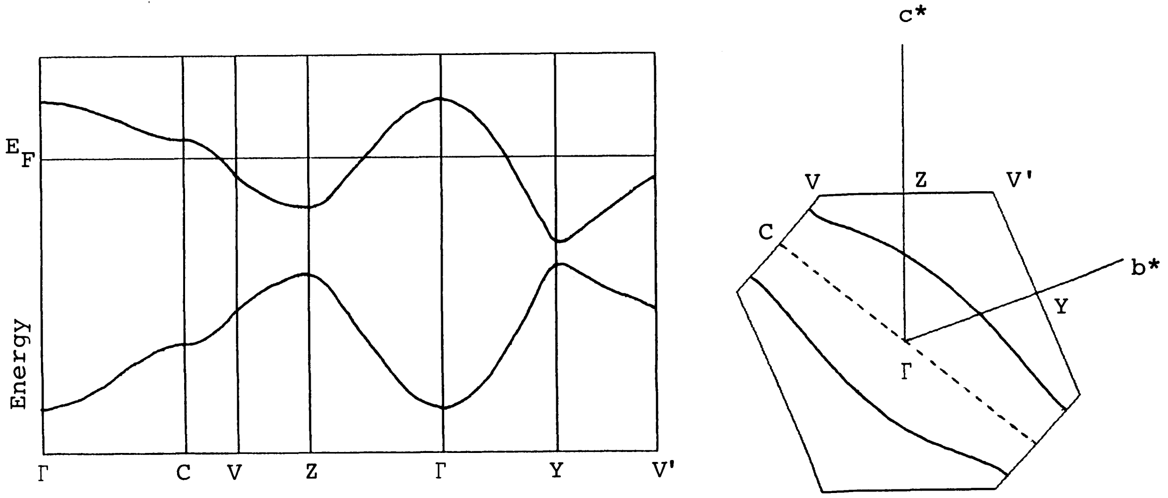


Fig. 4. Energy band and Fermi surface of $(BEDSe\text{-}TSeF)_2AuBr_2$.

of the system based on the above simple approximation. In $(BEDSe\text{-}TSeF)_2AuBr_2$, the dimerized BEDSe-TSeF units with one hole are linked along the [011] direction, forming the one-dimensional conduction path. The dimensionality of the system is very sensitive to a slight variation of S_c. Decrease of the S_c value distorts the Fermi surface and we obtain a two-dimensional closed Fermi surface and a smaller ΔE value when $S_c \simeq -2.5 \times 10^{-3}$. We must notice that in spite of the close transverse Se•••Se contacts (Fig. 3) the $|S_c|$ value is very small. This is an accident of the anisotropy of the $p\pi$ orbital. As indicated by Mori et al., the sign and absolute value of the intermolecular overlap integral of HOMO change drastically with the relative angle ϕ (defined in Ref. 5), in TTF-type compounds. While the ϕ value between molecules interrelated by a unit cell translation along the c axis is 14° in the β-$(BEDT\text{-}TTF)_2I_3$, that in $(BEDSe\text{-}TSeF)_2AuBr_2$ is 9.7°. This indicates that if we make a slight modification of the crystal structure by the choice of anion or application of a high pressure, we will meet a β-type electronic structure. In this sense, $(BEDSe\text{-}TSeF)_2AuBr_2$ is situated in close vicinity to the organic superconductor.

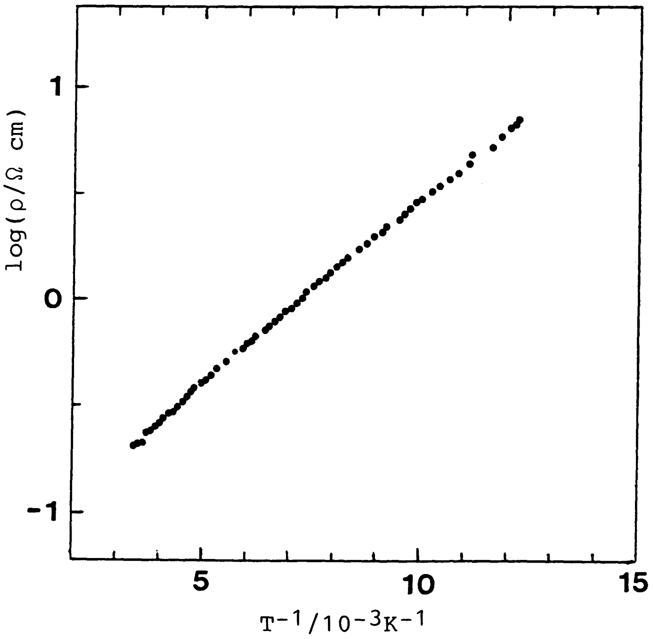


Fig. 5. Electrical resistivity of $(BEDSe\text{-}TSeF)_2AuBr_2$ along the c axis.

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